A Frequency Based Theory of Catalysts

"Much of chemistry involves energy. In the right place, right time, and right amount, energy drives the reactions, separations and other functions of the chemical universe. In the wrong place, wrong time, or wrong amount, energy can ruin a batch, create unwanted by-products, or otherwise interfere with the desired outcome. Thus, chemical research is intimately involved with the control of the type, amount, and timing of energy introduction into a system." Microwave-Enhanced Chemistry: Eds. HM Kingston & SJ Haswell.1997.
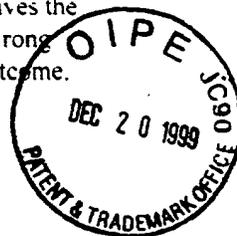
Background

Chemical reactions are driven by energy. The energy comes in many different forms - chemical, thermal, mechanical, acoustic, and electromagnetic. Various features of each type of energy are thought to contribute in different ways to the driving of chemical reactions. Irrespective of the type of energy involved, chemical reactions are undeniably and inextricably intertwined with the transfer and combination of energy. An understanding of energy is, therefore, vital to an understanding of chemical reactions.

Chemical energy drives a reaction by catalyzing it. Catalysts are chemicals that speed the rate of a reaction, but are neither used nor consumed in the reaction. Many reactions are said to be catalyzed. That is, the addition of a small amount of a chemical substance (the catalyst) can greatly speed the rate of the reaction. How did this definition evolve?

In 1770, only 15 elements were known. After Boyle's recognition that chemistry was properly the study of matter[1], catalytic action was noted for the first time. In 1835, Berzelius proposed a theory of "catalysis". He believed that since the catalyst was unchanged by the reaction, a catalytic "force" must be involved. By the turn of the century the kinetic theory of chemistry had been developed. In 1911, Ostwald proposed the modern theory of catalysis, which has stood unchallenged for nearly one hundred years. This theory abandons Berzelius' catalytic force, and states there are five essential steps in catalysis:

1. Diffusion of the reactant to the catalyst site;
2. Bond formation between reactant and catalyst;
3. Reaction of the catalyst-reactant complex;
4. Bond rupture at the catalytic site to produce product;
5. Diffusion of product away from the catalyst.

Thus, catalysts are thought to speed reactions by bonding with chemicals.

Catalysis and Chemical processes: Eds. Pearce R & Patterson WR. Wiley & Sons.1981.

Thermal energy is used to drive chemical reactions by applying heat and increasing the temperature. The addition of heat increases the kinetic (motion) energy of the chemical reactants. A reactant with more kinetic energy moves faster and farther, and is more likely to take part in a chemical reaction. Mechanical energy likewise, by stirring and moving the chemicals, increases their kinetic energy and thus their reactivity. The addition of mechanical energy often increases temperature, by increasing kinetic energy.

Acoustic energy is applied to chemical reactions as orderly mechanical waves. Because it is mechanical, acoustic energy increases kinetic energy of chemical reactants, and can also elevate temperature. Electromagnetic (EM) energy consists of waves of electric and magnetic fields. EM energy increases kinetic energy and heat in reaction systems. It also energizes electronic orbitals in some reactions.

Both acoustic and electromagnetic energy consist of waves. The number of waves in a period of time can be counted. Waves are often drawn, as in Figure 1., below. Usually, time is placed on the horizontal X-axis. The vertical Y-axis shows the strength or intensity of the wave. This is also called the amplitude. A weak wave will be of weak intensity and will have low amplitude (Figure 2.a., below.) A strong wave will have high amplitude (Figure 2.b.)

Amplitude ↑

Time →
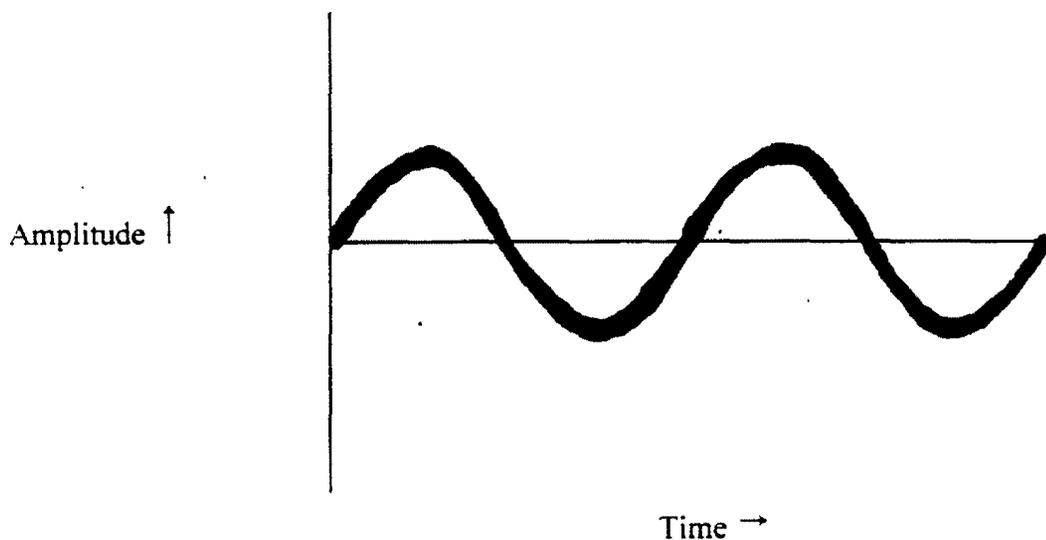
Figure 1. - Wave representation (acoustic or electromagnetic)
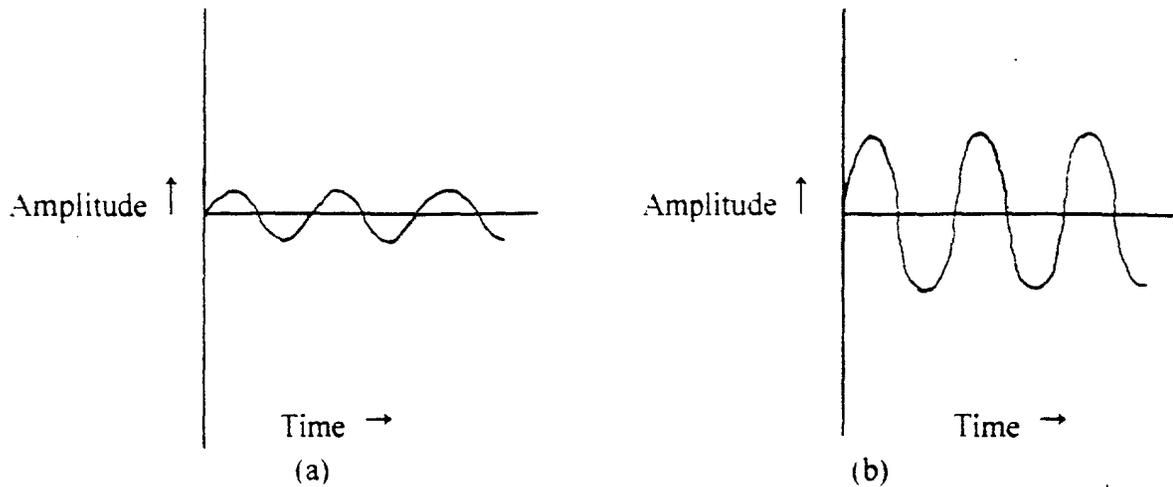
Figure 2. - Waves of different amplitudes but the same frequency. (a) Low intensity wave with low amplitude. (b) High intensity wave with high amplitude.

Traditionally, the number of waves per second is counted, to give the frequency.

Frequency = Number of waves / time = Waves/second = Hz.

Another name for "waves per second", is "hertz" (abbreviated as Hz) so named for Heinrich Hertz who did much of the early research in defining electromagnetic waves. Frequency is drawn on wave diagrams by showing different numbers of waves in a period of time (Figure 3. (a) below.) It is also drawn by placing frequency itself, rather than time, on the X-axis (Figure 3. (b).).
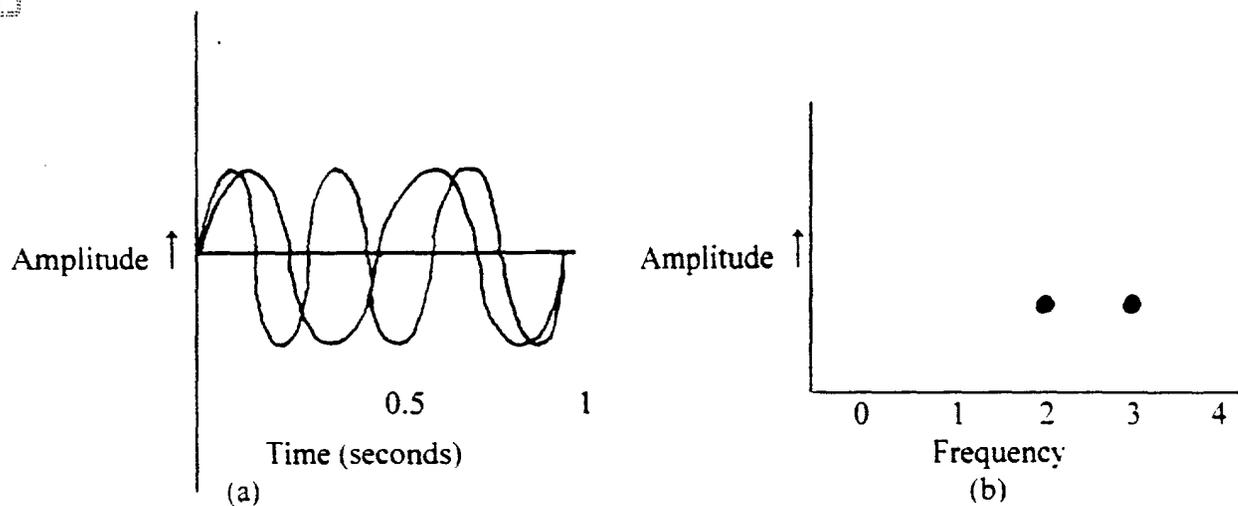
Figure 3. Frequency diagrams. (a) Time on the X-axis. 2 and 3 Hz frequency waves. (b) Frequency on the X-axis. 2 and 3 Hz waves.

Energy waves and frequency have some interesting properties, and combine in interesting ways. The manner in which wave energy transfers and combines, depends largely on the frequency. Say, for instance, that we combine two waves of energy, each of the same amplitude, but one at a frequency of 400 Hz (waves per second) and the other at 100 Hz. The waves will combine and add their frequencies, to produce a new frequency of 500 Hz, the *sum* frequency. They will also subtract when they combine, to produce a *difference* frequency of 300 Hz. All wave energies add and subtract this way, and it is called heterodyning. The results of heterodyning are probably familiar to most people as the harmonies in music.

There is a mathematical, as well as musical basis, to the harmonics produced by heterodyning. Consider a continuous progression of heterodyned frequencies. Using our example above, beginning with 400 Hz and 100 Hz, we get 500 Hz and 300 Hz. If we heterodyne (add and subtract) these new frequencies, we get 800 (500 + 300) and 200 (500 - 300). Heterodyning 800 and 200, gives us 1,000 and 600 (see Figure 4. below).

Soon a mathematical pattern begins to emerge. Both the addition and the subtraction columns contain alternating series of numbers that double with each set of heterodynes. In the additive column, 400 Hz, 800 Hz, and 1,600 Hz, alternates with 500 Hz, 1000 Hz, and 2000 Hz. The same sort of doubling phenomenon occurs in the subtraction column.

FIGURE 4. - Heterodyne Progression
Initial Frequencies (Hz)

400	And	100
400 + 100 = 500	and	400 - 100 = 300
500 + 300 = 800	and	500 - 300 = 200
800 + 200 = 1000	and	800 - 200 = 600
1000 + 600 = 1600	and	1000 - 600 = 400

Sum (Added) Frequencies (Hz)	Difference (Subtracted) Frequencies (Hz)
400	100
500	300
800	200
1000	600
1600	400
2000	1200
3,200	800

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Heterodyning of frequencies is the natural process that occurs whenever waveform energies combine. It results in patterns of increasing numbers that are mathematically derived. The number patterns are multiples of the original frequencies. These multiples are called harmonics. For instance, 800 Hz and 1600 Hz are harmonics of 400 Hz. In musical terms, 800 Hz is one octave above 400 Hz, and 1600 Hz is two octaves higher. Most of us have an intuitive understanding of harmonics through our exposure to music. Few understand the mathematical heterodyne basis for harmonics, which occurs in all waveform energies, and thus in all of nature.

The mathematics of frequencies can take us to even more interesting places than the concert hall. Frequency heterodynes increase mathematically in visual patterns (see figure 5. below).
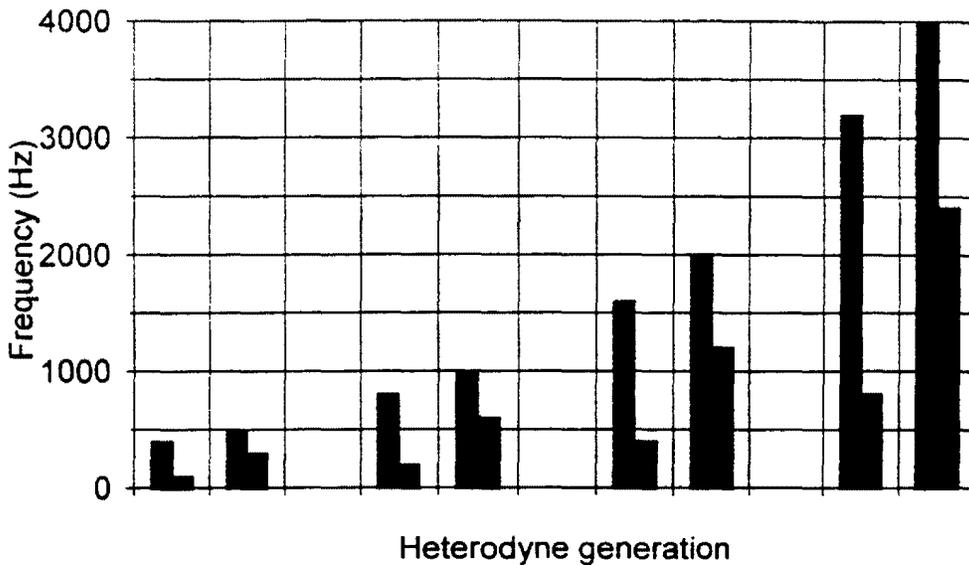
Figure 5. - Visual pattern created by heterodyned series from Figure 4.

Mathematics has a name for this - it is called a fractal. A fractal is defined as a mathematical function which produces a series of self-similar patterns or numbers. Fractal patterns have spurred a great deal of interest because they are found everywhere around us in nature. They can be found in the patterning of large expanses of coastline, all the way down to micro-organisms. They are found in the behavior of organized insects and in the behavior of fluids. The visual patterns produced by fractals are very characteristic (see Figure 6.[2])

[2] Encyclopedia of Physics: Eds. Lerner RG & Trigg GL. VCH Publ. Inc.. 1991.

A heterodyne is a mathematical function. governed by mathematical equations, just like a fractal. A heterodyne also produces self-similar patterns of numbers, like a fractal. If graphed, a heterodyne series produces the same familiar visual shape and form which is so characteristic of fractals. Compare the heterodyne series in Figure 5. with the fractal series in Figure 6.
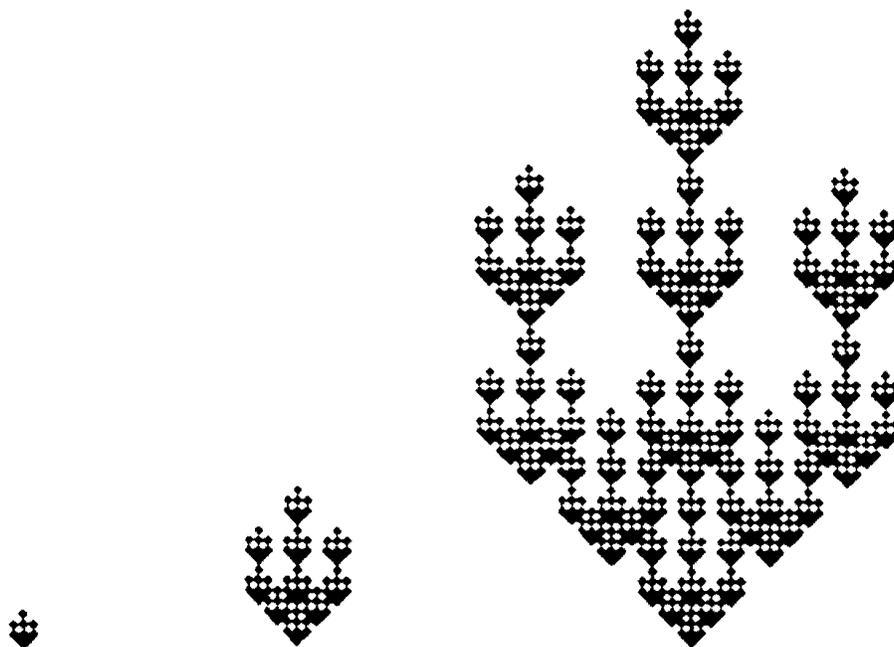
Figure 6. - Fractal diagram

Heterodynes are fractals - the conclusion is inescapable. Heterodynes and fractals are both mathematical functions which produce a series of self-similar patterns or numbers. All wave energies combine in heterodyne patterns. Thus, all wave energies actually combine in fractal patterns. Once you understand that the fundamental process of combining energies is itself a fractal process, it becomes easier to understand why so many creatures and systems in nature also exhibit fractal patterns. The fractal processes and patterns of nature are built in at a fundamentally basic level. As the scorpion said to the frog, "It's in my nature."[3]

Well, you say, nature is made up of more than just energy. There is quite a bit of matter out there also. What about matter? Good question. After all, if energy can transfer and combine by heterodyning, what about

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The scorpion asked the frog to give him a ride across a stream. He promised not to sting the frog. Just as the frog carried the scorpion to the other side of the stream. the scorpion stung him anyway. When the frog asked why. the scorpion replied. "It's in my nature."

matter? Chemical reactions occur between atoms and molecules, not just between little bits of energy. The answer is, matter interacts by heterodyning also. All matter, whether large or small, has what is called a natural oscillatory frequency. The natural oscillatory frequency (NOF) of an object, be it atom or elephant, is the frequency at which the object prefers to vibrate, once set in motion. The NOF of an object is related to many factors such as size, dimensions, and composition. Basically, the smaller an object is, the smaller the distance it has to cover when it wriggles back and forth. The smaller the distance, the faster it can wriggle back and forth, and the higher its NOF.

Consider a wire composed of metal atoms. The wire has a natural oscillatory frequency. The individual metal atoms also have unique oscillatory frequencies. The NOF of the atoms and the NOF of the wire heterodyne by adding and subtracting, just the way energy heterodynes,

$$NOF_{atom} + NOF_{wire} = \text{Added Frequency}_{atom-wire},$$

$$\text{and}$$

$$NOF_{atom} - NOF_{wire} = \text{Subtracted Frequency}_{atom-wire}.$$

If you stimulate an atom on the wire with the Subtracted Frequency$_{atom-wire}$, (this experiment was actually done using a laser to generate the subtracted frequency[4]) it will heterodyne (add) with the NOF_{wire} to produce NOF_{atom}, the natural oscillatory frequency of the atom,

$$\text{Subtracted Frequency}_{atom-wire} + NOF_{wire} = NOF_{atom}.$$

Matter heterodynes with matter the same way that wave energy does. This means that matter combines in fractal processes also. It now becomes doubly easy to understand why so many creatures and systems in nature exhibit fractal processes and patterns. Matter, as well as energy, combines by the mathematical equations of heterodynes, to produce harmonics and fractal patterns. That is why we see fractals everywhere we turn.

There is a third leg to this stool. We already know that energy heterodynes with energy, and matter heterodynes with matter. Can matter

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[4] Cirac & Zoller. *Science*. July. 1995.

heterodyne with energy? The answer is yes. Remember our metal wire and atoms? The Subtracted Frequency$_{atom-wire}$ in the experiment was provided by a laser, using electromagnetic wave energy at a frequency equal to the Subtracted Frequency$_{atom-wire}$. The matter in the wire via its' natural oscillatory frequency, heterodyned with the laser's wave energy frequency, to produce the frequency of an individual atom of matter. So, energy and matter *do* heterodyne with each other.

This of course leads to the interesting curiosity of just how matter and energy interact. It helps in understanding chemical reactions, to understand energy and matter interactions. When energy encounters matter, one of three things generally happens. The energy either bounces off the matter (reflected energy), passes through the matter (transmitted energy), or combines with the matter (heterodyning). The crucial factor which determines which of these three things will happen is - you guessed it - the frequency of the energy compared to the frequency of the matter. If the frequencies do not match, the energy will either be reflected, or will pass on through as transmitted energy. If the frequencies match either exactly or as harmonics (heterodynes), then the energy combines with the matter.

Think of matter as a glass of water. When energy heterodynes and combines with the matter, it is just like adding another spoonful of matching water to the glass of water. It all mixes and combines together until you cannot tell what was in the glass and what was from the spoon. Add a spoonful of oil to the glass of water however, and things will be quite different. The oil and water don't match, so they will not mix. The oil will float to the top of the glass, like reflected energy. So when the frequencies of matter and energy match, they will combine by heterodyning. When the frequencies do not match, they will not combine, and the energy will either be reflected or transmitted.

There is another term often used for matching of frequencies. That term is resonance. A lot is written about resonance, much of it erroneous. It all boils down to one simple concept. Resonance means the frequencies match. If the frequency of energy and the frequency of matter match, they are in resonance and the energy combines with the matter. Resonance, or frequency matching, is merely an aspect of heterodyning that enables the coherent transfer and combination of energy with matter.

So in our example above with the wire and atoms, we could have created resonance with the atom, and transferred energy to it directly, by stimulating it with a laser exactly matching its NOF. We would be

energizing it with its' resonant frequency. Or, as the clever scientists did who performed the experiment, we could take advantage of the heterodyning that naturally occurs between frequencies of energy and matter. We can produce the resonant frequency of the atom (NOF_{atom}) indirectly, as an additive (or subtractive) heterodyned frequency, between the resonant frequency of the wire (NOF_{wire}) and the frequency of the laser. Either direct resonance, or indirect resonance through heterodyned frequency matching produces resonance and combining of the matter and energy.

Another indirect form of resonance not used by the scientists in that experiment is quite familiar to music lovers in the form of harmonics. A harmonic is a frequency that is an integer multiple of the resonant (NOF) frequency. For instance, we can play the note "A" at 440 Hz. If we double that frequency to 880 Hz, we will play "A" an octave higher. This first octave is called the first harmonic. Doubling our note or frequency again, from 880 Hz to 1760 Hz (four times the frequency of the original note) gives us another "A", two octaves above the original note. This is called the third harmonic. Every time you double the frequency you get another octave, so these are the even integer multiples of the resonant frequency.

In between the first and third harmonic is the second harmonic, which is three times the original note. This is not an octave like the first and third harmonics. It is an octave and a fifth, equal to the second "E" above our original "A". All of the odd integer multiples are fifths, rather than octaves. Because harmonics are simply multiples of the fundamental natural oscillatory frequency, they stimulate the NOF or resonant frequency indirectly. Play the high "A" at 880 Hz on a piano, and the string for middle "A" at 440 Hz will also begin to vibrate.

Matter and energy in chemical reactions respond to harmonics of resonant frequencies much the way musical instruments do. We can stimulate the resonant frequency of the atom (NOF_{atom}) indirectly, using its' harmonics. This is because the harmonic frequency heterodynes with the resonant frequency *of the atom itself* (NOF_{atom}). Say, for instance our laser is tuned to 800 Thz and our atom resonates at 400 Thz. Heterodyning the two frequencies gives us:

$$800 \text{ Thz} - 400 \text{ Thz} = 400 \text{ Thz}.$$

The 800 Thz (the atom's first harmonic), heterodynes with the atom's own resonant frequency, to produce the atom's own resonant frequency. Thus, the

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first harmonic indirectly resonates with the atom's NOF, and stimulates the atom's resonant frequency as a first generation heterodyne.

Of course, the two frequencies will also heterodyne in the other direction, producing:

$$800 \text{ Thz} - 400 \text{ Thz} = 1,200 \text{ Thz}.$$

The 1,200 Thz frequency is not the resonant frequency of the atom. Part of the laser's energy will heterodyne to produce the resonant frequency of the atom. The other part of the laser's energy heterodynes to a different frequency, that does not itself stimulate the resonant frequency of the atom. That is why the stimulation of an object by a harmonic frequency of particular strength or amplitude, is always less than the stimulation by its' own exact resonant (NOF) frequency at the same strength.

The preceding discussion highlights the fact that the same fundamental process of heterodyning governs all the interactions of matter, energy, and their combinations. It was this very similarity in process that prompted Albert Einstein to write several important papers in 1905 modeling atomic events using statistical methods of chemical dynamics. His papers provided the springboard for the later development of relativity and quantum theories. One of these papers described interactions of energy with matter in his explanation of the photoelectric effect[5]. He postulated that electromagnetic energy (ie. a beam of light) was made up of small packets of energy, called photons. Based on the photon concepts in his landmark paper, textbooks now teach that the energy E of a photon is related to its' frequency f, by the equation,

$$E = hf,$$

in which h is a universal constant, called Planck's constant. When a packet or photon of electromagnetic (EM) energy strikes an atom, it may transfer its energy to the atom if their frequencies match. Then the photon ceases to exist as an individual packet of energy. It blends and merges with the electron cloud of the atom, just like a spoonful of water blending into a cup of water.

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[5] Einstein A: On a Heuristic Point of View Concerning the Production and Transformation of Light. *Annalen der Physik.* 1905.

Einstein believed that quantum mechanical descriptions were not the whole story, and that they might someday be replaced by a more complete theory. Over his objections, his energy quanta theories were used to develop theories in which the entire concept of the quantum state was inherently statistical. He is often quoted as cautioning, "God does not play dice with the universe." There may yet be good reason to heed that admonition.

The original intent of his work was misunderstood by many. Take for example the modern definition of a photon. Current science teaches that the energy of a photon is equal to Plank's constant multiplied by the frequency. Thus, the higher the frequency, the higher the energy. Textbooks are full of examples and explanations of scientific phenomena based on "high frequency photons" having high energy, as opposed to "low frequency photons" with lower energy by comparison.

But Planck's constant and photon frequency are both arbitrarily defined in units of Joule·seconds and seconds^{-1}, respectively When multiplied, the seconds cancel out and a unit of energy is obtained. The unit of energy, however, is merely the amount of energy *in one second's worth* of EM waves. If one calculates the amount of energy in *one wave* of EM energy, it turns out that all EM energy has the exact same amount of energy per wave, no matter what the frequency (Appendix B). High frequency EM energy has the same amount of energy in one wave, as low frequency EM energy has.

The "high energy photons" simply fit more waves into a second than the low energy photons. Naturally, if all waves have the same amount of energy, and you double the number of waves, you will double the energy. The whole concept of photons with different amounts of energy is an artifact which detracts from an understanding of the processes around us.

So what is going on around us in the process of chemical reactions? Ostwalds's theories on catalysts and bond formation were based on the kinetic theories of chemistry from the turn of the century. We know quite a bit more than Ostwald did when he proposed his theory. We now know that chemical reactions are interactions of matter, and that matter interacts with other matter through heterodyning of frequencies. We know that energy can just as easily interact with matter through this same process of heterodyning. With the advent of spectroscopy (more on that later) we also learned that matter produces electromagnetic energy at the same frequencies at which it vibrates. Energy and matter move about and recombine with other energy or matter, depending on their frequencies. In many respects, both philosophically and mathematically, both matter and energy *are frequency*.

This leads to the inescapable conclusion that since chemical reactions are recombinations of matter driven by energy, they are in effect, driven just as much by frequency.

Well, this all sounds well and good, but if we analyze a reaction, is this what is *really* going on? Actually, it is. And a good reaction to look at is the formation of water from hydrogen and oxygen gases, catalyzed by platinum. Platinum has been known for some time to be a good hydrogen catalyst, although the reason for this has not been well understood.

$$H_2 + \tfrac{1}{2}O_2 \xrightarrow{\quad Pt \quad} H_2O.$$
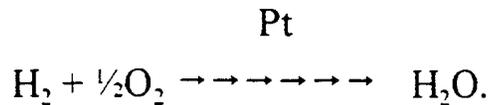
This reaction is proposed to be a chain reaction, dependent on the generation and stabilization of the hydrogen and hydroxy radicals. The proposed reaction chain is:

$$
\begin{array}{c}
\tfrac{1}{2}\,H_2 \\
\downarrow \\
\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow\quad H \\
\uparrow \qquad\qquad \downarrow \\
\uparrow \qquad H + O_2 + H_2 \\
\uparrow \qquad\qquad \downarrow \\
\uparrow \qquad H_2O + OH^{\cdot} \\
\uparrow \qquad\qquad \downarrow \\
\uparrow \qquad OH^{\cdot} + H_2 \\
\uparrow \qquad\qquad \downarrow \\
\leftarrow\leftarrow\leftarrow\leftarrow\leftarrow\leftarrow\leftarrow\quad H + H_2O
\end{array}
$$
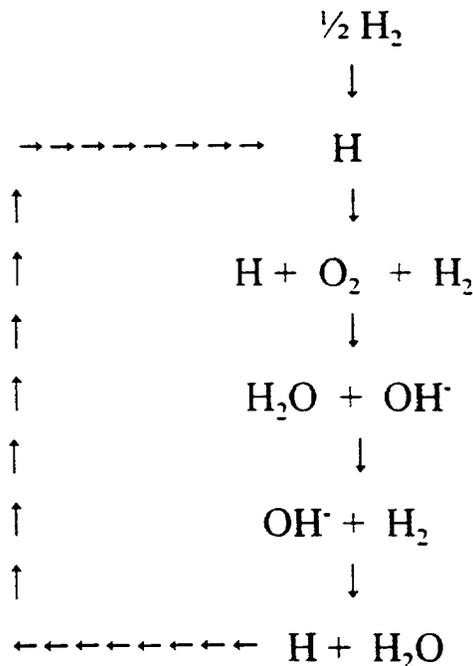
Creation and stabilization of the hydrogen and hydroxy radicals are thought to be crucial to this reaction chain. Under normal circumstances, hydrogen and oxygen gas can be mixed together in a container indefinitely, and they do not form water. Whenever the occasional hydrogen molecule splits apart, the hydrogen atoms do not have enough energy to go out and

react with an oxygen molecule. They simply bond with each other again into another hydrogen molecule.

The trick to catalyzing this reaction is to energize and stabilize the hydrogen intermediates, so they can react with oxygen to form hydroxy intermediates. Then you energize and stabilize the hydroxy intermediates so they can react with more hydrogen molecules. Eventually you end up with water from a chain reaction. How do we stabilize and energize intermediates such as these? The same way nature does - increase their energy levels. Of course we already know that the energy levels of matter can be increased by energy with a matching frequency. In other words, we can stabilize the intermediates by producing resonance with them. Interestingly, that is exactly what platinum does. And in the process of stabilizing the reaction intermediates, platinum allows the reaction chain to continue, and thus catalyzes the reaction.

By now, you are probably wondering just how platinum produces resonance with the reaction intermediates. Quite naturally, it does it by taking advantage of all the ways frequencies interact with each other. Frequencies interact with each other and create resonance either: 1. directly, by exactly matching the frequency; or 2. indirectly, by heterodyning to match the frequency. In other words, platinum vibrates at frequencies which both directly match the natural oscillatory frequencies of the radicals, AND which indirectly match the radical frequencies by heterodyning with the radicals.

The hydroxy radical is a good example of how platinum directly matches the frequency to produce resonance. Hydroxy radicals vibrate strongly at frequencies of 975 THz and 1,060 THz. Platinum also vibrates at 975 THz and 1,060 THz. By directly matching the frequencies of the hydroxy radical, platinum can cause resonance in the hydroxy radical, enabling it to energize and stabilize long enough to take part in chemical reactions.

Hydrogen gives us a good example of matching frequencies by heterodyning. A little background history is in order here. In 1885 a fellow by the name of Balmer discovered that hydrogen vibrates and produces energy at frequencies in the visible light region of the electromagnetic spectrum which can be expressed by a simple formula,

$$1/\lambda = R(1/2^2 - 1/m^2),$$

where λ is the wavelength of the light, R is Rydberg's constant, and m is an

integer greater than or equal to 3 (ie, 3, or 4, or 5, etc.) A few years later, Rydberg discovered that this equation could be adapted to give all the wavelengths in the hydrogen spectrum by changing the $1/2^2$ to $1/n^2$, as in,

$$1/\lambda = R(1/n^2 - 1/m^2),$$

where n is any integer ≥ 1, and m is an integer $\geq n + 1$. For every different number n, you ended up with a series of numbers for wavelength, and the names of various scientists were assigned to the series. For instance, when n=2 and m$\geq$3, the energy is visible light and the series is called the Balmer series. The Lyman series is in the ultraviolet with n=1, and the Paschen series is in the infra-red with n=3.

These early scientists found the units of frequency difficult to work with, so they did everything in wavelengths (λ) and wavenumbers (which are the inverse ($1/\lambda$) of wavelength.) By the time Einstein and Schrodinger were done, they had gone to using energy level diagrams to describe all this. (See Figure 7., for energy level diagrams of the hydrogen atom)[6]. People did not think about the actual frequencies anymore. Instead, all the interest was in wavefunctions, energy levels, orbitals, quantum numbers, and Hamiltonians. That was unfortunate, because this switch in nomenclature caused scientists to miss some of the really fun things going on between matter and energy.
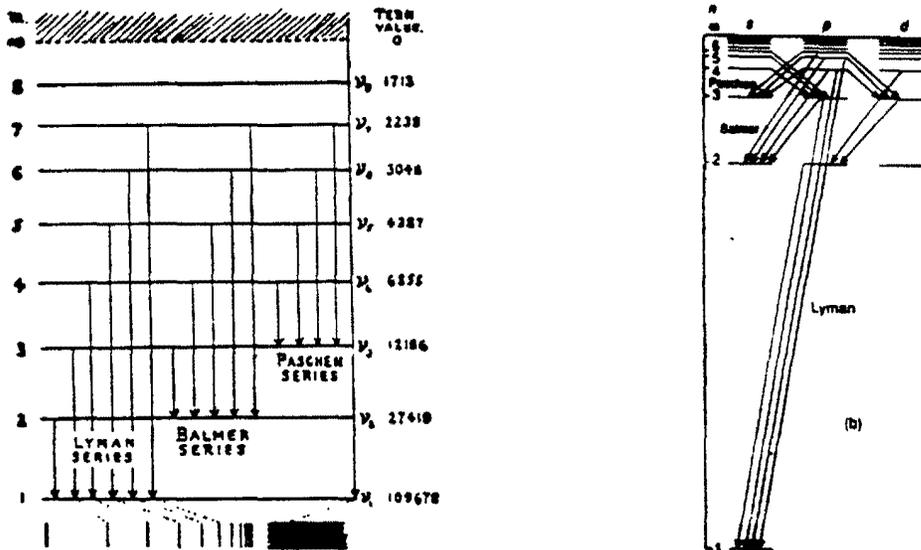
Figure7. - Hydrogen energy level diagrams

[6] Atomic Spectra: Softley TP. Oxford Sci Publ. 1994 & Atomic Spectra: Johnson RC. John Wiley & Sons. 1952.

Take a glance at what hydrogen looks like when we take the very same information used to make energy level diagrams, and graph the actual frequencies and intensities instead (Figures 8.-10.) The X axis shows the frequencies produced by hydrogen, while the Y axis gives the relative intensity for each frequency. The frequencies are plotted in terahertz (10^{12} Hz) and are rounded to the nearest Thz. The intensities are plotted on a relative scale of 1 to 1,000. The highest intensity frequency that hydrogen atoms produce is 2466 Thz. This is the peak of the curve to the far right. We will call this the first curve. It sweeps down and to the right, from 2466 Thz at a relative intensity of 1,000, to 3237 Thz at a relative intensity of only 15.

The second curve starts at 456 Thz with a relative intensity of 300, and sweeps down and to the right. It ends at a frequency of 781 Thz, with relative intensity of 5. Every curve in hydrogen has this same downward sweep to the right. Progressing from right to left, we number the curves I through V; going from high to low frequency, and from high to low intensity. (The reason for this backwards numbering will be apparent momentarily.)

The hydrogen frequency chart really gives you quite a different feel for the hydrogen atom, and looks a lot simpler, than the energy level diagram with all the arrows going this way and that. It is easy to visualize how the frequencies are organized into the different curves. In fact, there is one curve for each of the series described by Rydberg. The big curve farthest out to the right - curve I - contains the frequencies in the Lyman series, originating from what quantum mechanics calls the first energy level. The second curve from the right - curve II - equates to the second energy level, and so on.

Now the interesting thing about the curves in the hydrogen frequency chart is that they are composed of additions and subtractions. Take, for instance, the smallest curve at the far left, labeled curve V (Figure 9. - Magnification of lower hydrogen frequencies). Curve V has two frequencies in it, 40 Thz and 64 Thz, with relative intensities of 6 and 4, respectively. The next curve - IV - starts at 74 Thz, goes to 114 and ends with 138 Thz. The additions go like this,

$$40 + 74 = 114$$
$$64 + 74 = 138.$$

The frequencies in curve IV are the sum of the frequencies in curve V plus the peak intensity frequency in curve IV.
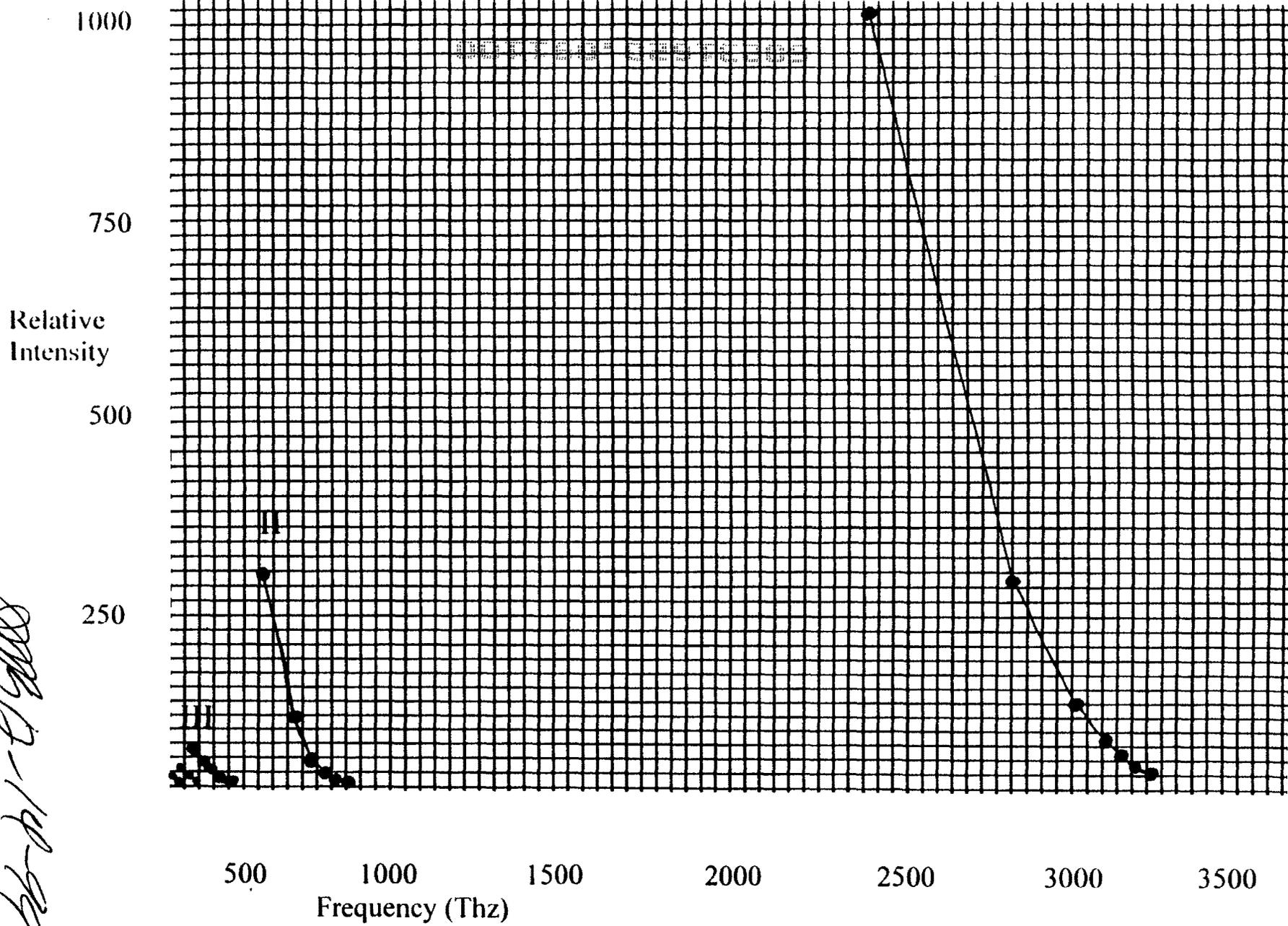
Figure 8. - Frequency diagram of hydrogen
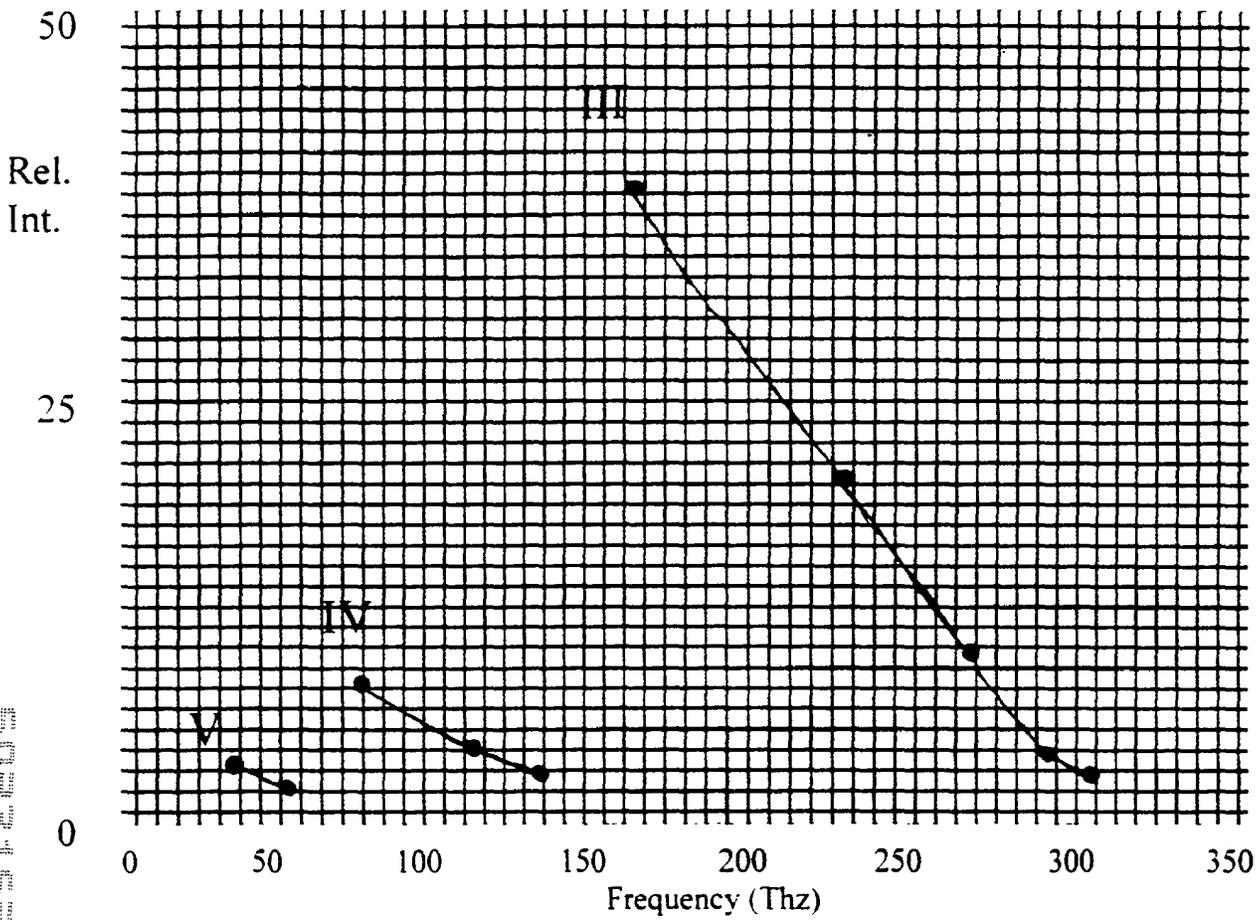
Figure 9. - Magnification of lower hydrogen frequencies

Figure 10. - Frequencies and intensities for hydrogen

Frequency Curves -Thz (relative intensity)

V	IV	III	II	I
40 (6)	74 (15)	160 (40)	456 (300)	2466 (1000)
64 (4)	114 (8)	234 (20)	616 (80)	2923 (300)
	138 (5)	274 (12)	690 (30)	3082 (100)
		298 (7)	731 (15)	3156 (50)
		314 (5)	755 (8)	3196 (30)
			770 (6)	3220 (20)
			781 (5)	3236 (15)

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Another way of looking at it is that the frequencies in curve IV, minus the frequencies in curve V, yield the peak of curve IV:

$$114 - 40 = 74;$$
$$138 - 64 = 74.$$

This is not just a coincidental set of additions or subtractions in curves IV and V. Every curve in hydrogen is the result of adding each frequency in any one curve, with the highest intensity frequency in the next curve.

These hydrogen frequencies are found in both the atom itself, and in the electromagnetic energy it radiates. The frequencies of the atom and its energy, add and subtract in regular fashion. Remember what adding and subtracting of matter and energy is? It is heterodyning. So, not only do matter and energy heterodyne interchangeably, but matter heterodynes its' own energy *within* itself.

It doesn't stop there either. Wonder where the peak frequencies come from? They are heterodynes of heterodynes. Look at the peak frequency in the biggest curve, the one at the farthest right, curve no. I. The frequency is 2,466 THz. Divide 2,466 by 4 and you get 616 THz,

$$2,466\ Thz \div 4 = 616\ Thz, \quad or, \quad 4 \times 616\ THz = 2,466\ THz.$$

Let's talk about the 4 part first. We already know from our discussion about heterodyned frequencies and harmonics, that you end up with even multiples of the starting frequency (from 400 we got the first harmonic at 800 (400 X 2), and the third harmonic at 1,600 (400 X 4)). The even integer multiples are octave harmonics. Multiplying a frequency by four (4) is a natural result of the heterodyning process. This means that 2,466 THz is the third harmonic of 616 Thz. It is a second generation heterodyne - a two octave harmonic of 616 Thz.

The peak of curve II, frequency 456 Thz, is the third harmonic of 114 Thz in curve IV. The peak of curve III, frequency 160 Thz, is the third harmonic of 40 Thz in curve V. The peaks of the curves are heterodynes between the curves, and are also harmonics of individual frequencies.

OK, so 2,466 Thz is a harmonic of 616 Thz. What about 616 Thz? Well, it results from the addition of 456 and 160. But 456 is itself a heterodyne and harmonic, and so is 160. What you end up with is the situation that the biggest, highest intensity frequency in the entire hydrogen

spectrum. namely 2,466 THz, is a second generation heterodyne of some eighth and ninth generation heterodynes. The whole hydrogen spectrum turns out to be an incestuously heterodyned set of frequencies and harmonics.

All this heterodyning and harmonizing has an interesting effect. Look at the intensities of the curves as you move from low to high frequencies, from curve V to curve I. The intensities increase - a lot. The heterodyned frequency curves amplify the vibrations and energy of hydrogen. In many respects. the hydrogen atom is just one big energy amplification system.

We know what the highest set of frequencies is for hydrogen, but what about the low end? Theoretically, this heterodyne process could go on forever. If 40 is the peak of a curve, that means it is 4 times a lower number, and it also means that the peak of the previous curve is 24 (64-40 = 24). It is possible to mathematically extrapolate backwards and downwards this way to derive lower and lower frequencies. Peaks of successive curves to the left are 24.2382, 15.732. and 10.786 Thz - all generated from the heterodyne process. These frequencies are in complete agreement with the Rydberg formula for energy levels 6, 7, and 8, respectively. Not a lot of attention is given these low frequencies. They just are not as exciting as the higher intensity frequencies.

This may all seem somewhat far afield, but it turns out to have a direct bearing on platinum, and on how platinum interacts with hydrogen. It all has to do with hydrogen being an energy amplification system. It is like money in the bank. Put a dollar in the bank today, and you will have one dollar in the bank. But if you had put a dollar in the bank back in 1835, when Berzelius proposed the catalytic force, you would have hundreds of dollars today. Just so, stimulate hydrogen with 2466 Thz at 1000 intensity and you will have 2466 Thz at 1,000 intensity. But if you stimulate hydrogen with 40 Thz at 1,000 intensity, by the time it is amplified back out to curve I, you will have 2466 Thz at 167,000 intensity.

Understood this way, those low frequencies of low intensity suddenly look very interesting. Extend the hydrogen spectrum back to 10.786 Thz, and then compare the hydrogen frequencies to the platinum frequencies. You will find that many of the platinum frequencies are direct matches or multiples (harmonic heterodynes) of the hydrogen frequencies (Appendix A). Seventy frequencies of platinum (40%) are resonant or harmonic frequencies of at least 19 frequencies of hydrogen (80%). Platinum causes massive resonance in the hydrogen atom.

A further look at the individual hydrogen frequencies is even more

informative. Platinum resonates with most, if not all of the hydrogen frequencies with one notable exception, the highest intensity curve at the far right in the frequency chart, curve I representing energy level 1, and beginning with 2,466 Thz. Platinum does not resonate with the ground state of the hydrogen atom. It resonates with the lower frequencies in the upper energy levels.

With that little bit of information we have solved an ongoing mystery in physical chemistry. Ever since lasers came out, the physical chemists had a hunch that there had to be some way to catalyze a reaction using lasers. They decided that the highest intensity frequency of an atom (such as 2,466 Thz of hydrogen) would give them the biggest bang for the buck. If you are just looking at energy level diagrams it makes sense. So they have been tuning their lasers ever since to the ground state frequencies. Not surprisingly, their experiments have been minimally successful in catalyzing reactions.

Of course, platinum, the quintissential hydrogen catalyst, does not resonate with the ground state of hydrogen. It resonates with the upper energy level frequencies - lots of them. Perhaps this is why platinum is such a good hydrogen catalyst. The hydrogen atom acts as a big energy amplification system. A little bit of energy, at a low frequency in a high energy level, can go a long way. By the time it works its way from curve IV or V, back out to curve I, it can have tremendous intensity and really shake things up. So that is how such a small amount of catalyst can have such a profound effect - by resonating with upper energy levels of its target.

Most of the attempts of the last forty years to catalyze reactions with lasers have used *one frequency* from the reactant's *first energy level*. But platinum does not do this. It resonates with *many frequencies* from the *upper energy levels* (lower frequencies). There is a name given to the process of stimulating many upper energy levels - it is called a laser.

Einstein worked out the statistics on this at the turn of the century[7]. Take a bunch of atoms at the ground energy level (E_1) and resonate them to an excited energy level (E_2). Call the number of atoms in the ground state N_1 and the number of excited atoms N_2, with the total N_{total}. Since there are only two possible states the atoms can occupy:

$$N_{total} = N_1 + N_2.$$

Physical Chemistry: McQuarrie DA & Simon JD, Univ. Sci. Books, Sausalito, CA, 1997.

If you go through all the mathematics using temperature (kelvin) and the Boltzmann constant, you arrive at:

$$\frac{N_2}{N_{total}} = \frac{N_2}{N_1 + N_2} < \frac{1}{2}$$

In a two level system there will never be more than 50% of the atoms in the higher energy level, E_2, at the same time.

If, however, you take the same bunch of atoms and energize them at three (3) or more energy levels (a multi-level system), it is possible to get *more than 50%* of the atoms energized above the first level. Call the ground and energized levels E_1, E_2, and E_3 respectively, and the numbers of atoms N_{total}, N_1, N_2, and N_3. Under certain circumstances, the number of atoms at energy level 3 (N_3) can be more than the number at the second energy level (N_2). When this happens, it is called a "population inversion". Population inversion means that more of the atoms are at higher energy levels, than at lower levels.

What is so special about a population inversion? It causes amplification of light energy. In a two-level system, if you put in one photon, you get one photon out. In a system with 3 or more energy levels and population inversion, if you put in one photon, you get out 5, 10, or 15 photons (Fig. 11 below). It all depends on the number of levels and just how energized you get them. All lasers are based on this simple concept of producing a population inversion in a group of atoms, by creating a multi-level energized system amongst the atoms. Lasers are simply devices to amplify electromagnetic wave energy (light). Laser is actually an abbreviation for Light Amplification System for Emitting Radiation.

Two level system   Multi-level system
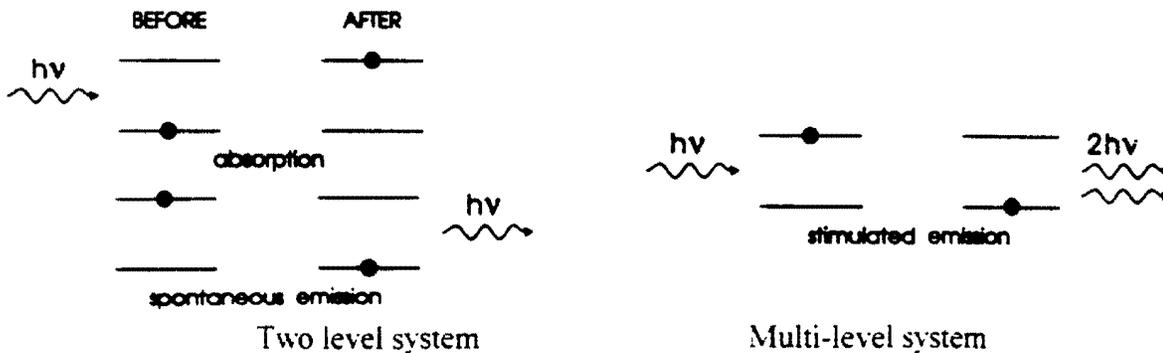
Figure 11[8].- Light amplification with stimulated emission/population inversion

8 Spectra of Atoms and Molecules: Bernath PF. Oxford Univ. Press. 1995.

This takes us back to platinum and hydrogen. Platinum energizes 19 frequencies in hydrogen (80% of the total hydrogen frequencies). We only need three frequencies for a population inversion. Hydrogen is stimulated at 19! This is a multi-level system, if ever there was one. Next consider that seventy platinum frequencies do the stimulating. On average, every hydrogen frequency involved is stimulated by 3 or 4 (70/19) different platinum frequencies - both direct resonant and/or indirect resonant harmonic frequencies. Platinum provides ample stimulus, atom per atom, to produce population inversion in hydrogen. Finally, consider the fact that every time a stimulated hydrogen atom emits some electromagnetic energy, that energy is of a frequency that matches and stimulates platinum in return.

Platinum and hydrogen both resonate with each other in their respective multi-level systems. Together, platinum and hydrogen form an atomic scale laser - an energy amplification system on the atomic level. In so doing, they amplify the energies that are needed to stabilize both the hydrogen and hydroxy intermediates, thus catalyzing the reaction. Platinum is such a good hydrogen catalyst, because it forms a lasing system with hydrogen on the atomic level, amplifying their respective energies.

OK, so now we know how platinum catalyzes reactions. Getting back to our original discussion of matter heterodyning, this seems to be a basic matter:matter interaction. An atom of platinum interacts with an atom of hydrogen or a hydroxy radical. And that is exactly what modern chemistry has taught for the last one hundred years, based on Ostwald's theory of catalysis. The modern textbooks teach that catalysts must participate in the reaction by binding to the reactants, in other words, they teach a matter:matter interaction is required for catalysts. This is taught in the following steps:

1. Reactant diffusion to the catalyst site;
2. Bonding of reactant to the catalyst site;
3. Reaction of the catalyst-reactant complex;
4. Bond rupture at the catalytic site (product); and
5. Diffusion of the product away from the catalyst site.

But Ostwald's theory of catalysis was formulated before lasers were ever built. That had to wait for AT&T in 1958. Fortunately, there have been many scientific advances since that theory of catalysis was first formulated. We now know, for instance, that energy:energy frequencies can interact, as well as energy:matter frequencies. We also know that matter radiates energy, with the energy frequencies being identical to the matter frequencies. So,

platinum vibrates at the frequency of 1,060 THz, and it also radiates electromagnetic energy at 1,060 THz. Once you start looking at it this way, the distintion between energy frequencies and matter frequencies starts to look less and less important.

We can produce resonance in the reaction radicals by letting them come in contact with another bit of matter vibrating at the same frequencies, such as a platinum atom. This is consistent with the current theory of catalysis by Ostwald. Or (and here is the interesting part) we can produce resonance in the radicals by zapping them with just the platinum *energy*, which also vibrates at the same frequencies. Matter, or energy, it makes no difference as far as the frequencies are concerned. So we don't need the actual physical catalyst to speed up a reaction. Its energy pattern and frequencies will do just fine. In other words, you can duplicate the action of the catalyst, by duplicating its energy frequencies.

Think back to our reaction combining hydrogen and oxygen gases, to produce water. Traditionally, that is done with a physical platinum catalyst. We can also catalyze the reaction using only the energy pattern of platinum. This is not a physical catalyst, in the true sense. It is a different kind of catalyst. An energy field that duplicates frequency(s) from a physical catalyst is called a spectral catalyst.

The name "spectral" comes from the field of science concerned with measuring the frequencies of energy and matter. That field is called spectroscopy, and the pattern of energy or electromagnetic frequencies emitted or absorbed by an atom or molecule is called its spectral pattern, or spectrum. So, for the purposes of keeping things straight from here on out, whenever we are talking about the matter:matter interaction of catalysts in the standard chemical theory sense, we will call that a "physical catalyst", because it is physically present as matter in the reaction. And whenever we are referring to the electromagnetic energy (ie. spectral) pattern of a catalyst, we will call that a "spectral catalyst."

The field of spectroscopy actually has much to teach us about how matter and energy vibrate. The spectra of atoms and molecules are broadly classified into three (3) different groups - electronic, vibrational, and rotational. The electronic spectra are said to result from transitions of electrons from one energy level to another, and have the highest frequencies, occuring in the ultraviolet (UV), visible, and infrared (IR) regions of the EM spectrum. Electronic spectra occur in both atoms and in molecules.

The vibrational spectra are said to result from stretching of bonds

between individual atoms within molecules. An example of this would be the vibrational spectra resulting from the various stretching modes of the hydrogen atoms attached to oxygen, in the water molecule. Vibrational spectra can occur only in molecules, because by definition they must occur *between* bonded atoms. This means that atoms such as hydrogen and platinum do not have vibrational spectra - they have only electronic spectra. Vibrational frequencies are generally in the IR region.

Lastly, rotational spectra occur chiefly in the microwave or radiowave regions of the EM spectrum, and are thought to result from rotation of molecules in space. As a result, a gas phase is necessary to support generation of a traditional rotational spectrum. Molecules found only in solid or liquid phases are generally not able to rotate freely in space, and thus do not produce rotational spectra.

Interestingly, some atoms and molecules normally found in only solid or liquid phases (such as metals) produce microwave and radiowave frequencies anyway. These frequencies tend to vary with the size and shape of the substance, and are thought to be antenna-type transmitter effects, rather than true rotational frequencies. Because these antenna frequencies are not rotational frequencies in the classical sense, many people dismiss their importance. Never-the-less, they are probably important to the subject of catalysis and chemical reactions.

The various spectral modes do not act in isolation from each other. Stimulation in one spectral mode, can lead to excitation in another mode. For example, if water is stimulated with its' rotational microwave frequency, it will also become stimulated in its vibrational and electronic modes, albeit to a lesser extent. If sufficiently powerful, a rotational stimulus can produce a vibrational or electronic transition. Thus there is an interlocking continuum of effects between rotational, vibrational, and electronic energy transitions of molecules, and the atoms of which they are composed.

Whenever we talk about a spectral catalyst duplicating any of a physical catalyst's energy pattern, we are referring to *all* the different frequencies produced by a physical catalyst; including electronic, vibrational, rotational, and antenna frequencies. To catalyze, control, or direct a chemical reaction then, all we need to do is duplicate one or more frequencies from a physical catalyst, with an energy field. The actual physical presence of the catalyst is not necessary. A spectral catalyst can replace a physical catalyst.

A spectral catalyst can also augment or promote the activity of a physical catalyst. The exchange of energy at particular frequencies, between

hydrogen. hydroxy, and platinum is what drives the conversion to water. Platinum and hydrogen interact and create a minature atomic scale lasing system that amplifies their energies. The addition of these same energies to a reaction system, using a spectral catalyst, does the same thing. It amplifies the hydrogen and platinum energies by adding to them. Thus, a spectral catalyst can augment a physical catalyst, as well as replace it.

Horseshoes and Harmonics

Some things in life are all or none phenomena. Being pregnant is one of those things: you either are, or you aren't (pregnant that is.) In other endeavors. such as horseshoes and hand grenades. being right on target is nice, but it is also good just to be close. Resonance and heterodyning of energy and matter are like horseshoes and hand grenades. Being right on the target frequency is ideal, but being close to the target frequency can also produce some powerful effects.

Take for example, the effects of platinum on the hydroxy radical. Hydroxy radicals vibrate strongly at frequencies of 975 THz and 1,060 THz. Platinum also vibrates at 975 THz and 1,060 THz. By directly matching the frequencies of the hydroxy radical. platinum causes resonance in the hydroxy radicals, stabilizing them long enough for them to take part in the chemical reaction which leads to the formation of water.

We can duplicate platinum's stabilizing effects on the hydroxy radical by using lasers tuned to 975 Thz and 1,060 Thz. But what if our lasers could only be tuned to 972 Thz and 1,070 Thz? Would our lasers still stabilize the hydroxy radicals? The answer is yes. This is because of the resonance qualities of objects and matter.

All objects, be they atom or elephant have resonant frequencies, their natural oscillatory frequencies. Energy which either directly matches, or matches via heterodyning with the NOF (resonant frequency) of the object will transfer to and combine with the object. The more exact the match, the more energy will transfer. If we use energy waves to exactly and directly match the resonant frequency of an object then a lot of energy will transfer and combine with the object. If the frequencies are just slightly different, then slightly less energy will transfer. If the frequencies are more different, then even less energy will transfer. Finally, one reaches a point where the frequencies are so different that essentially no energy transfers at all.

This can be shown by a simple diagram (Fig. 12 below). It is a basic bell-shaped curve produced by comparing how much energy an object absorbs, with the frequency of the energy. It is called a resonance curve. The energy transfer is maximal at the resonant frequency (f_0) The farther you get from the resonant frequency, the lower the energy transfer. At some

point the energy transfer will fall to only 50% of that at the resonant frequency. The frequency above the resonant frequency, at which energy transfer is only 50% is called f_2. The frequency below the resonant frequency, at which 50% energy transfer occurs, is called f_1.

f_0

f_1

f_2

Amplitude
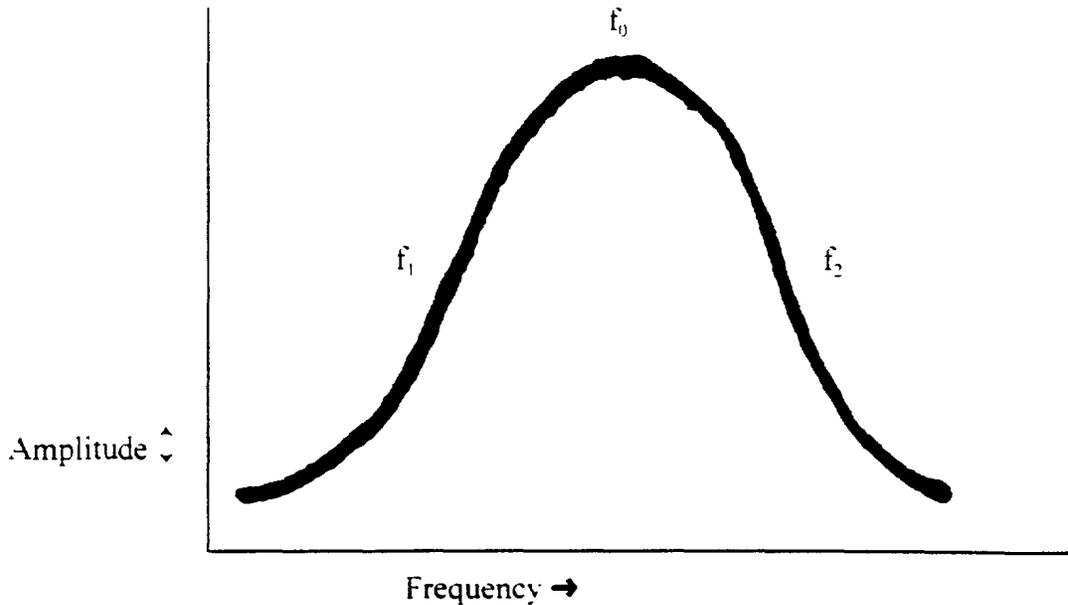
Frequency →

Figure 12. Resonance curve. (f_0 = resonant frequency. f_2 = upper frequency at 50% amplitude. and f_1 = lower frequency at 50% amplitude.)

The resonant characteristics of different objects can be compared using the information from this simple resonance curve. One of these useful characteristics is called the "resonance quality" or "Q" factor. To find out what the resonance quality is for an object we calculate:

$$Q = \frac{f_0}{(f_2 - f_1)}$$

If the bell-shaped resonance curve is tall and narrow, then ($f_2 - f_1$) will be a very small number and Q, the resonance quality, will be high (Fig. 13.a.). This would be the case with a good quartz crystal resonator. If the resonance curve is low and broad, as would be the case for a marshmallow, then the spread or difference between f_2 and f_1 will be very large. Dividing the resonant frequency by this large number will produce a much lower Q value (Fig. 13. b.).

Amplitude ↕

Frequency ➡

a) Resonance curve with high Q

Amplitude ↕

Frequency ➡

b) Resonance curve with low Q
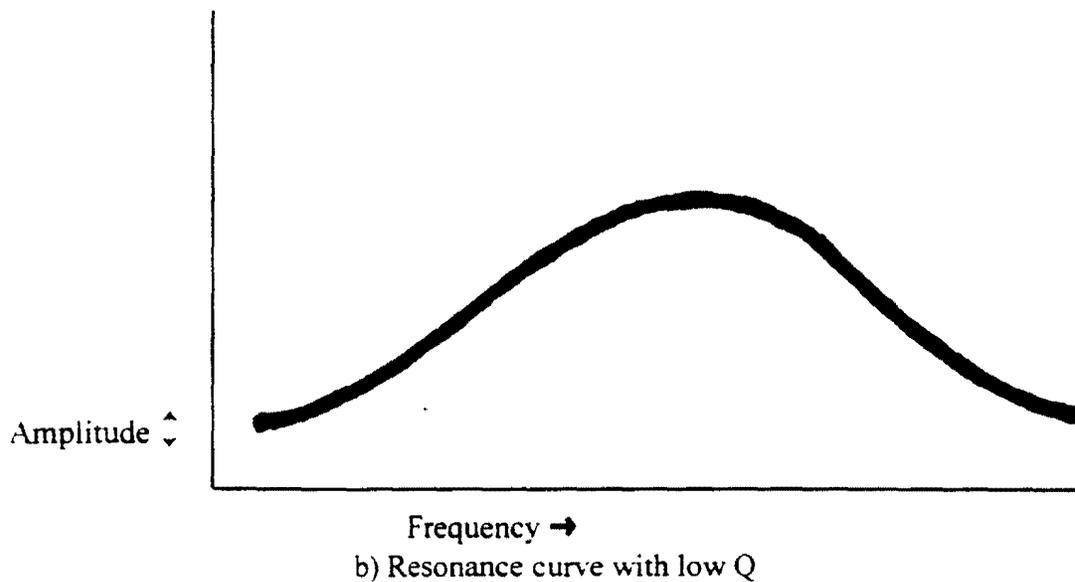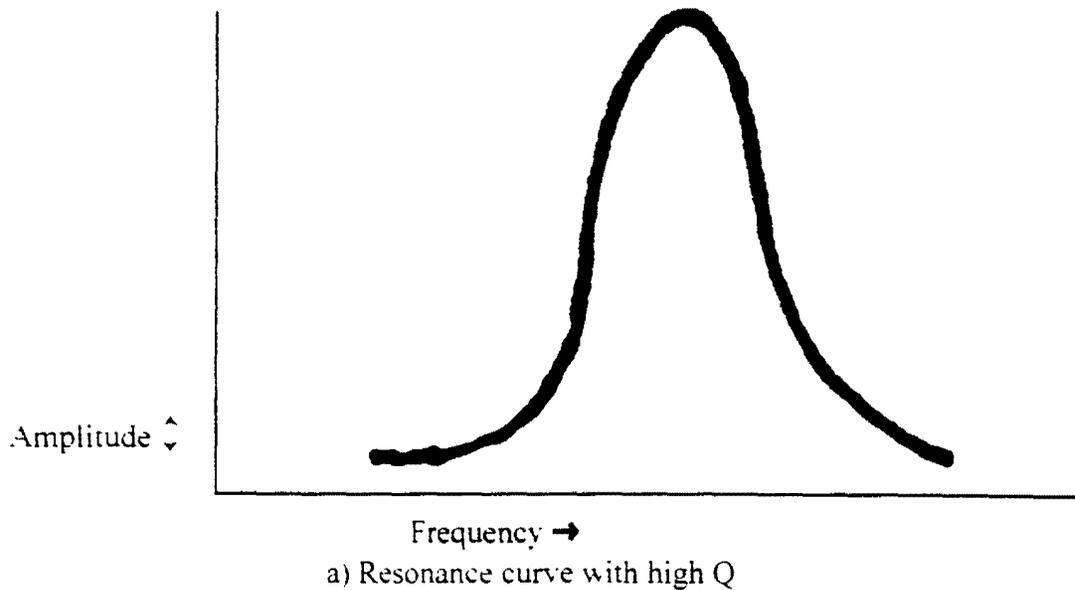
Figure 13. Resonance curves with different resonance quality factors. Q. a) Narrow resonance curve with high Q; b) Broad resonance curve with low Q. $(Q = f_0 / f_2 - f_1)$

All this talk of Q values may seem a bit far afield, but is does relate back to our horseshoes example. Atoms and molecules have resonance curves just like larger objects such as quartz crystals and marshmallows. If you want to stimulate an atom (such as hydrogen in our reaction) you can use an exact resonant frequency produced by hydrogen. You don't have to use

that exact frequency however. You can use a frequency that is merely close to a hydrogen resonant frequency. There will not be quite as much of an effect as using the exact frequency, because less energy will be transferred, but there will still be an effect. The closer you are to the resonant frequency, the more the effect. The farther away you are from the resonant frequency, the less effect you will see. So as with horseshoes and hand grenades, chemical reactions are great if you are right on target with a resonant frequency, but it is also good just to be close.

Harmonics present a similar situation. They are created by heterodyning (adding and subtracting) of frequencies. Take our imaginary atom vibrating at 400 Thz and expose it to 800 Thz electromagnetic energy. The frequencies will subtract and add:

$$800 \text{ Thz} - 400 \text{ Thz} = 400 \text{ Thz}$$

And

$$800 \text{ Thz} + 400 \text{ Thz} = 1200 \text{ Thz}.$$

In this first generation heterodyne, at most only 50% of the energy appears to resonate with the atom's frequency of 400 Thz. The other 50% of the energy goes into producing 1200 Thz and looks like it is wasted. Viewed this way, harmonics appear to be rather inefficient means of stimulating resonance.

The energy transfer from a harmonic is actually quite a bit more than 50% however. We must look beyond the first generation heterodyne to other generations to understand this. The 1200 Thz heterodyne for which 50% of the energy seems wasted, will heterodyne with other frequencies also, such as 800 Thz, and:

$$1200 \text{ Thz} - 800 \text{ Thz} = 400 \text{ Thz}.$$

Also, the 1200 Thz will heterodyne with 400 Thz:

$$1200 \text{ Thz} - 400 \text{ Thz} = 800 \text{ Thz},$$

producing 800 Thz, and the 800 Thz will heterodyne with 400 Thz:

producing 400 Thz again. When other generations of heterodynes of the seemingly wasted energy are taken into consideration, the amount of energy transferred by a first harmonic frequency is much greater than 50%. It is not as much as the energy transferred by direct resonance, but it is still enough to produce a noticeable effect. (Fig. 14.) In this regard, harmonics in chemical reactions are also like horseshoes. Being right on target with a resonant frequency is nice, but a harmonic is also good.

Fundamental resonant frequency curve

Harmonic frequency curve

Amplitude
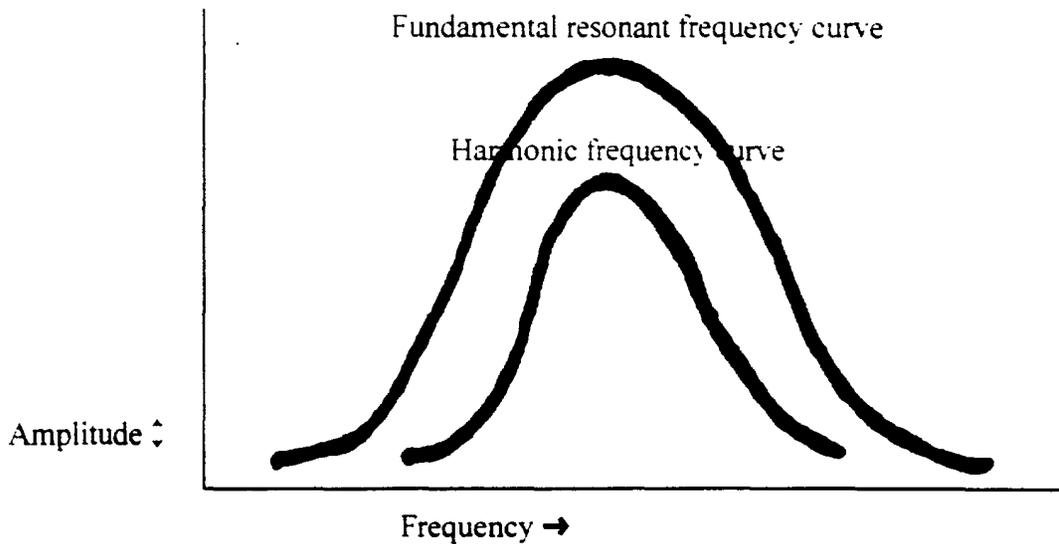
Frequency →

Figure 14. Energy transfer at fundamental resonant frequency using resonant frequency and harmonic frequency.

The last situation we consider is a harmonic horseshoe. In other words, if a resonant effect is produced: 1) by being *close* to the resonant frequency; or 2) by being a *harmonic* of the resonant frequency; is it possible to produce an effect simply by being *close* to the *harmonic* frequency? The answer is yes. The amplitude of the energy transfer will be less on both accounts, but you will still produce an effect. For example, say the harmonic produces 70% amplitude of the fundamental resonant frequency. You are also using a frequency which is merely close to the harmonic, at 90% on the harmonic's resonance curve, then your total effect will be 90% of 70%, or 63% total effect.

Duplicating the Catalyst Mechanism of Action

Some of the best ideas in science come from copying nature. Antibiotics are a good example of the success that can be achieved by copying nature. Dr. Alexander Fleming, the discoverer of antibiotics, had a messy laboratory. Some fungus got into his bacteria culture dishes and "contaminated" them. Fortunately for modern medicine, the good doctor noticed that no bacteria were growing around the fungus. He soon learned that the fungus produced a substance that killed bacteria, and that he could copy the fungus mechanism of action and kill bacteria in sick people by using antibiotics. Since then, an entire science of antibiotic pharmacology has grown up around the simple concept of duplicating nature's processes.

We can apply this same simple concept to extend our control over chemical reactions. In many respects, the spectral catalyst itself is a result of this simple concept. To catalyze, control, or direct a chemical reaction, we need only duplicate one or more frequencies from a physical catalyst. The actual physical presence of the catalyst is not necessary. This is accomplished by understanding the underlying mechanism inherent in catalysis - namely the exchange of energy at certain frequencies. In other words, we copy the mechanism that nature has built into the catalytic process. The result is spectral catalysts.

Can we apply the simple concept of copying nature yet again to control reactions? The answer is yes. A closer look at the catalyst process reveals several opportunities for duplicating catalyst mechanisms of action, and hence improving our spectral catalysts and our control of chemical reactions.

For example, consider our reaction with hydrogen and oxygen producing water, using platinum as a catalyst. In the **Background** section we learned that platinum accomplishes this task several ways:

1. It directly resonates with and energizes reaction intermediates (atomic hydrogen and the hydroxy radical);

2. It harmonically resonates with and energizes a reaction intermediate (atomic hydrogen);

3. It energizes a reaction intermediate at multiple upper energy levels, setting up an atomic scale laser system (atomic hydrogen).

Can we take advantage of this knowledge to improve our catalyst systems? Yes! The frequencies of atomic platinum are in the ultraviolet, visible light, and infra-red regions of the electromagnetic spectrum. The electronic spectra of all atoms are in these regions. These very high electromagnetic frequencies produce a bit of a problem for large-scale and

industrial applications. Wave energies of very high frequency do not penetrate matter very well. The tendency of a wave energy to be absorbed rather than transmitted, is called attenuation. High frequency wave energies have high attenuation. They will not penetrate deeply into an industrial size reaction vessel. Duplicating the exact frequencies of platinum into a big industrial reaction vessel will be a slow process because the energy will be quickly absorbed at the edges of the container.

What we really need to quickly get energy into a big industrial sized container is a lower frequency energy, that will penetrate farther into the vat of chemicals. We can do this quite neatly by copying nature. Remember, the spectra of atoms and molecules are broadly classified into three (3) different groups - electronic, vibrational, and rotational. The electronic spectra of atoms and small molecules are said to result from transitions of electrons from one energy level to another, and have the highest frequencies, occurring in the ultraviolet (UV), visible, and infrared (IR) regions of the EM spectrum. The vibrational spectra are said to result from stretching of bonds between individual atoms within molecules, and occur in the infra-red and microwave regions. Rotational spectra occur in the microwave and radiowave regions of the EM spectrum, from rotation of molecules in space.

If we could use a microwave or radiowave frequency, we could spectrally catalyze a platinum-catalyzed reaction in large quantities. But platinum does not produce frequencies in the microwave or radiowave portions of the spectrum. So how can we catalyze a platinum-catalyzed reaction using microwaves? We simply copy the mechanism of action of platinum, and move it to the microwave part of the spectrum.

The mechanism is: energizing a reaction intermediate. The reaction intermediates are: atomic hydrogen and the hydroxy radical. Atomic hydrogen has a high frequency electronic spectrum. The hydroxy radical, on the other hand, is a small molecule, and has vibrational and rotational spectra as well as an electronic spectrum. Thus the hydroxy radical produces frequencies in the microwave part of the electromagnetic spectrum.

We copy the mechanism of action of platinum - namely resonating with a reaction intermediate. We resonate with the hydroxy radical. Instead of resonating with hydroxy in its electronic spectrum, as physical platinum does, we use one of hydroxy's frequencies in the microwave part of the spectrum. Hydroxy has a microwave frequency at 21.4 Ghz[9]. Energizing a reaction

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[9] *Microwave Spectroscopy* Townes CH & Schawlow AL. Dover Publ.. NY. 1975.

system of hydrogen and oxygen gas with a spectral catalyst at 21.4 Ghz will catalyze the formation of water. In this case we copied the mechanism of action of the physical catalyst platinum, and moved the mechanism to a more convenient portion of the electromagnetic spectrum.

Look at the second item on our list - harmonically energizing a reaction intermediate. What if we wanted to use a bank of lasers to catalyze our hydrogen oxygen reaction. but the frequency range of our lasers was only from 1500 to 2000 Thz. What then? Platinum does not produce frequencies in that part of the EM spectrum. The two hydroxy frequencies that platinum resonates with, 975 and 1060 Thz, are outside that range. Likewise, the hydrogen spectrum goes from 40 Thz up to 3236 Thz, but it does not have any frequencies between 1500 and 2000 Thz (Figs. 8-10).

The answer is simple. We copy the mechanism of action of platinum and adapt it to our available equipment. We use harmonics of the reaction intermediates in the portion of the EM spectrum available to us with our lasers. For the hydroxy radical, with frequencies of 975 and 1060 Thz, the first harmonics are 1950 and 2120 Thz, respectively. Thus, some of our lasers can be tuned to 1950 Thz to resonate harmonically with the hydroxy radical. The first harmonics of three different hydrogen frequencies also fall within our desired range. The fundamental frequencies are 755, 770, and 781 Thz and the first harmonics are 1510, 1540, and 1562 Thz, respectively. Thus, some of our lasers can be tuned to the first harmonics 1510, 1540, and 1562 Thz.

Depending on how many lasers we have, we can go to third or fourth harmonics as well. The third harmonic of the hydrogen frequency 456 Thz falls at 1824 Thz, nicely within our part of the spectrum. Similarly, the fourth harmonic of the hydrogen frequency 314 Thz is 1570 Thz, again within our desired frequency range. In summary, we see that once again, we can duplicate a mechanism of action of a physical catalyst and move it to a portion of the electromagnetic spectrum that is more convenient for us.

What about the third item on our list - energizing a reaction intermediate at multiple upper energy levels, setting up an atomic scale laser system? Think about our example above with the bank of lasers. Lets say we have ten lasers. There are 4 first harmonics within our equipment frequency range of 1500 to 2000 Thz. Should we set all ten lasers to these 4 harmonics only. or should we set some of the lasers to third, fourth, and higher harmonics?

A mechanism that physical platinum uses is to resonate with multiple

upper energy levels of the reaction intermediate. The more upper energy levels, the better. This creates an atomic scale laser system with *amplification* of the electromagnetic energies being exchanged between the atoms of platinum and hydrogen. This amplification of energy catalyzes the reaction at a much faster rate than it would ordinarily proceed. We can take advantage of this mechanism to catalyze the reaction with our available equipment.

Rather than setting all ten lasers to the 4 first harmonics and energizing only 4 energy levels, we want to energize as many different energy levels as possible. We do this by setting each of the ten lasers to a different frequency. Even though the physical platinum is not present, the energizing of multiple upper energy levels in the hydrogen will amplify the energies being exchanged between the atoms, and the reaction system will form its' own laser system between the hydrogen atoms. This will allow the reaction to proceed at a much faster rate than it ordinarily would. Once again, we have copied nature by duplicating one of her mechanisms of action.

The preceding discussion on duplicating catalyst mechanisms of action is far from an exhaustive review of the subject. There are many factors and variables that affect both catalyst performance, and chemical reactions in general. We can learn many interesting things from modern chemistry about the mechanisms of catalysts and chemical reactions. For instance, the same catalyst, mixed with the same reactant, but exposed to different conditions such as temperature or pressure, will produce different products. Consider the following example[1]:

$$> 300° C$$
1. Cyclohexene $\xrightarrow{\hspace{3cm}}$ Benzene + $2H_2$
$$\text{Pd catalyst}$$

$$< 300° C$$
2. Cyclohexene $\xrightarrow{\hspace{3cm}}$ Benzene + 2Cyclohexane
$$\text{Pd catalyst}$$
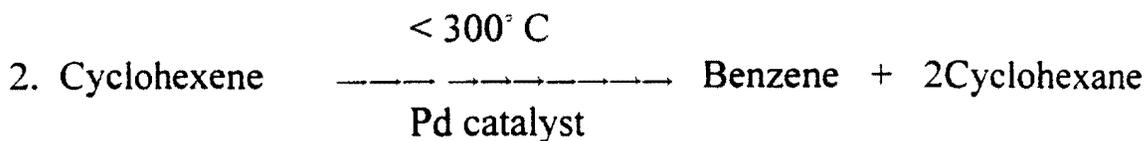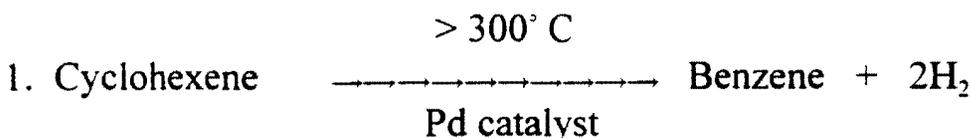
The same catalyst with the same reactant, produces quite different products - molecular hydrogen or cyclohexane - depending on the reaction temperature. If catalyst activity is merely a matter of the frequencies it

produces, then how can this be? If a physical catalyst actually catalyzes a reaction by virtue of the electromagnetic spectral pattern it emits, then why would temperature affect catalyst activity?

The answer to this question again comes from advances in the field of spectroscopy. Many factors are known to affect the direction and intensity with which a physical catalyst guides a reaction. Temperature is but one of these factors. Other factors include pressure, volume, surface area, solvents and support materials, contaminants, catalyst size and shape, reaction vessel size and shape, electric fields, magnetic fields, and acoustic fields. These factors all have one thing in common. They change the spectral frequency patterns of atoms and molecules. Some of these changes are so well studied that entire branches of spectroscopy have been designed around them. The next several sections will discuss each factor and its' influence on catalyst mechanisms of action, and chemical reactions in general.

Temperature

Let's start with temperature. At very low temperatures, the spectral pattern of an atom or molecule has clean crisp peaks (Fig. 15.a.). As the temperature increases, the peaks begin to broaden, producing a bell curve type of spectral pattern (Fig. 15.b.). At even higher temperatures, the bell curve broadens even more, to include more and more frequencies on either side of the primary frequency (Fig. 15.c). This phenomenon is called "broadening".

These spectral curves are very much like the resonance curves we discussed in the previous section. Spectroscopists use resonance curve terminology to describe spectral frequency curves for atoms and molecules (Fig. 16). The frequency at the top of the curve- f_0 - is called the resonance frequency. There is a frequency (f_2) above the resonance frequency and another (f_1) below it, at which the energy or intensity is 50% of that for the resonant frequency f_0. When we discussed resonance curves we used the ratio of:

$$\frac{f_0}{f_2 - f_1}$$

to calculate the resonance quality, Q, for a resonance curve. Spectroscopists use the frequencies a little bit differently. The quantity (f_2 - f_1) is a measure
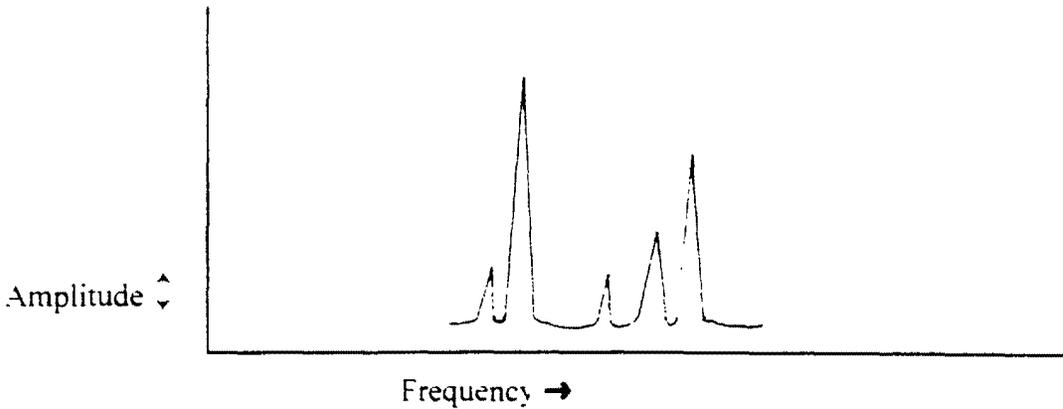
Frequency →

a) Spectral pattern at low temperature.

Frequency →

b) Spectral pattern at moderate temperature.

Frequency →
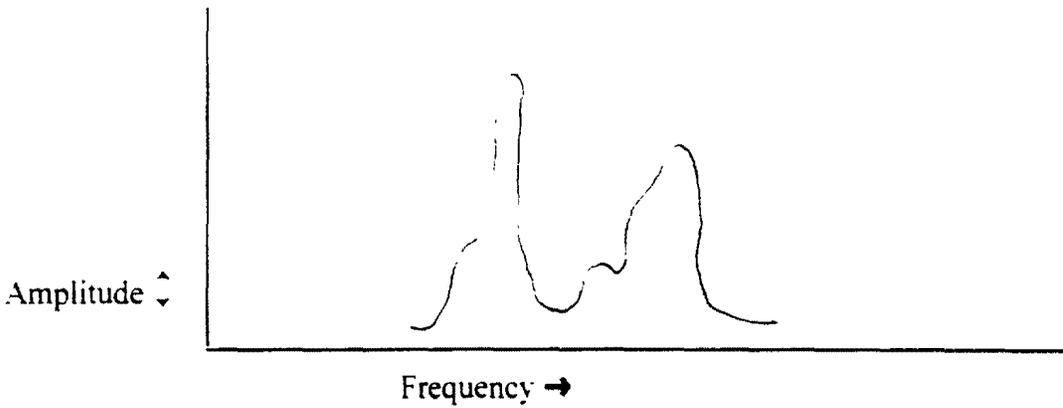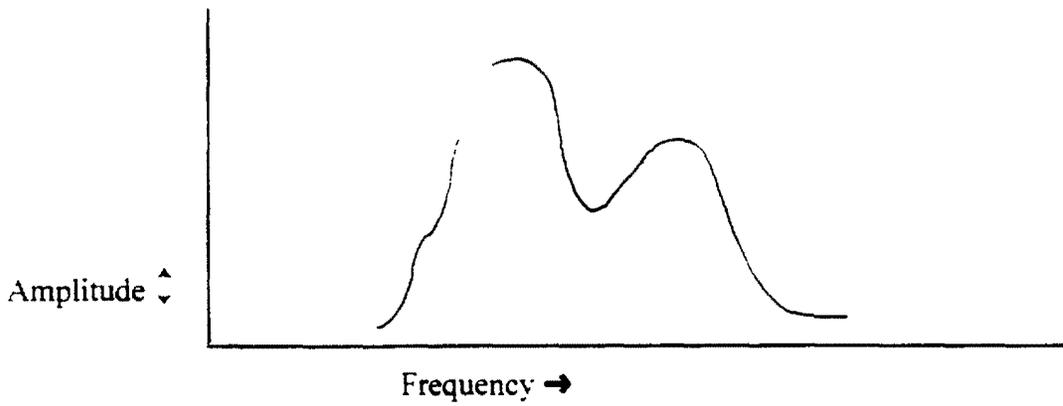
c) Spectral pattern at high temperature.

Figure 15. Spectral patterns at different temperatures. the effects of temperature on spectral emissions. a) Spectral pattern at low temperatures with crisp narrow peaks. b)Spectral pattern at moderate temperature with broader peaks. c) Spectral pattern at high temperature with much broadening of peaks.

of how wide or narrow the spectral frequency curve is. Spectroscopists call this quantity (f_2 - f_1) the "line width". A spectrum with narrow curves has a small line width, while one with wide curves has a large line width.
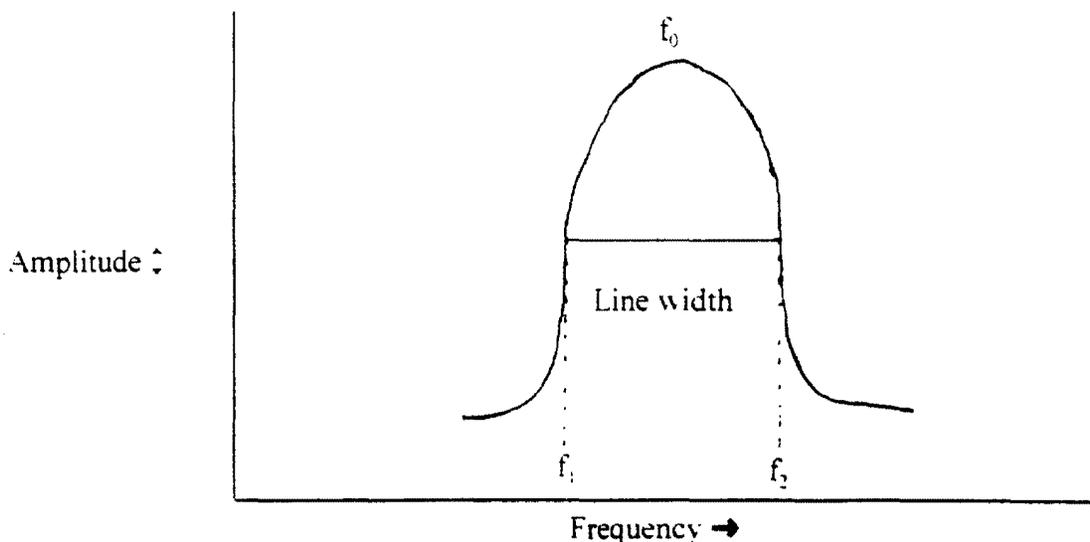
Figure 16. Spectral curve showing line width (f_2 - f_1).

Temperature affects the line width of spectral curves. Line width can affect catalyst performance and chemical reactions. At low temperatures, the spectral curves of chemical species will be separate and distinct, with little transfer of resonant energy (Fig. 17.a). As the line widths of the chemical species get broader and broader, their spectral curves may start to overlap with matching frequencies (Fig. 17.b.). When the frequencies match at higher temperatures, resonant transfer of energy takes place and the reaction can proceed in a different direction than it otherwise would have at a lower temperature.

Besides affecting the line width of the spectral curves, temperature also can change the resonant frequency and the amplitude of the curves. For some chemical species the resonant frequency will shift as temperature changes. This can be seen in the infrared absorption spectra and blackbody radiation graphs in Figure 18. Atoms and molecules do not all shift their resonant frequencies by the same amount or in the same direction, at the same temperatures. This can affect catalyst performance. If a catalyst resonant frequency shifts more with increased temperature than the resonant frequency of its target chemical, then resonance may be created where none previously existed. (Fig. 18.c.)

Frequency →
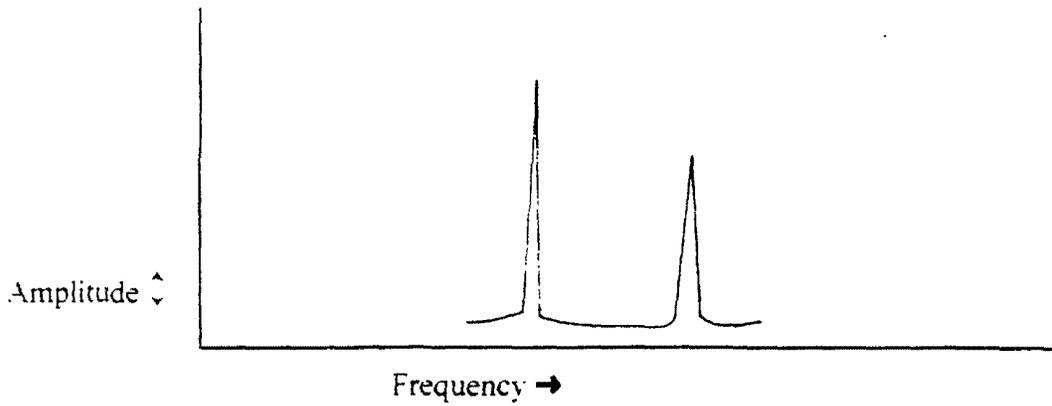
a) Separate and distinct spectral curves at low temperature.
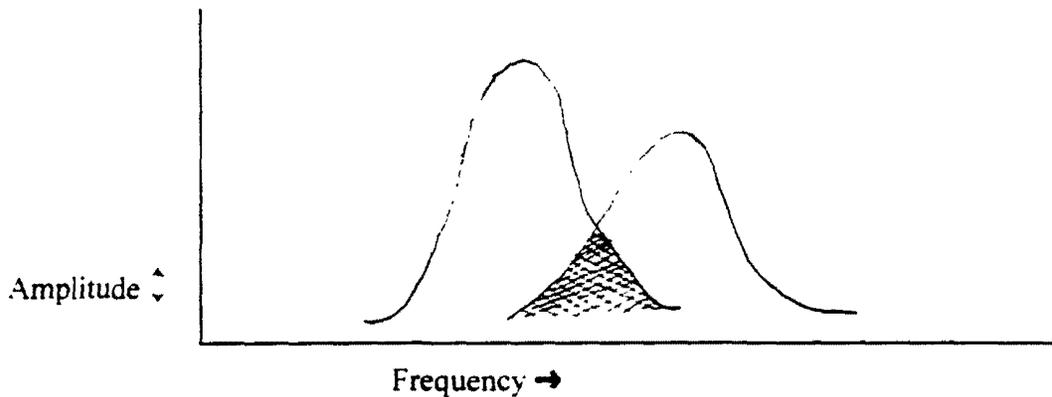
Frequency →

b) Overlapping spectral curves at higher temperature. allowing resonant energy transfer.

Figure 17. Effects of temperature on spectral curve line widths and resonant transfer of energy.
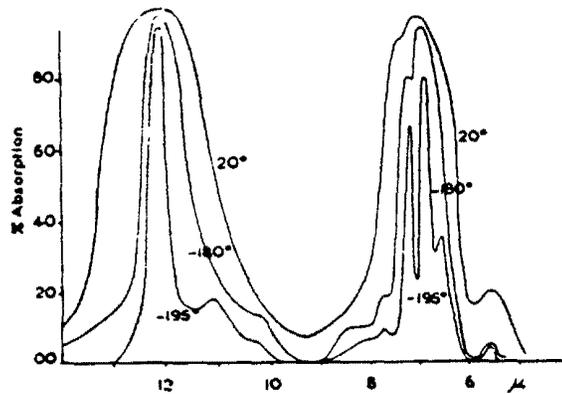
a) Lowering of resonant frequency (increasing wavelength) as temperature increases in right hand set of curves.

Figure 18. Effects of temperature on resonant frequency. a. Influence of temperature on the resolution of infrared absorption spectra[10]

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[10] *Chemical Spectroscopy.* Brode W.R. John Wiley & Sons 1943, p.273
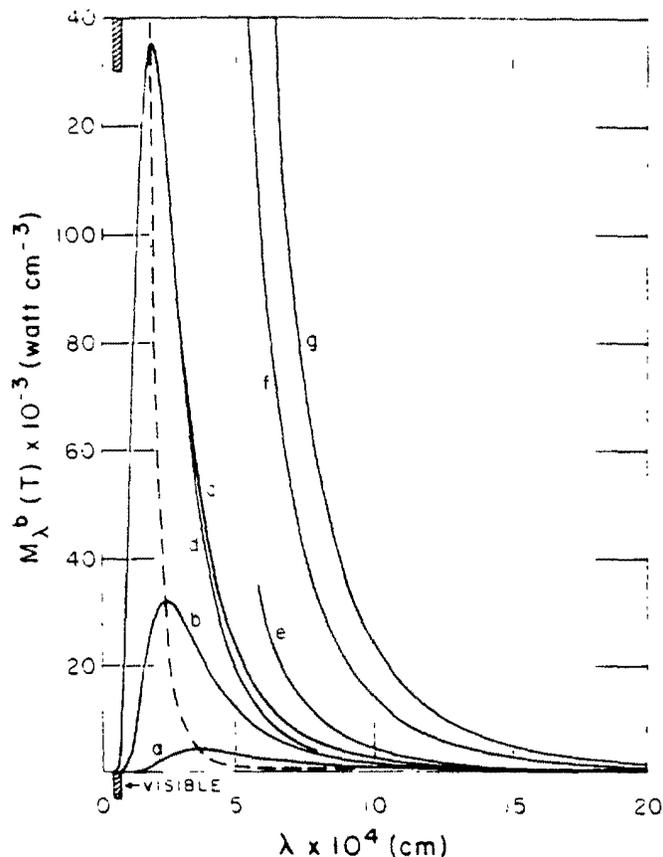
18.b. Spectral radiant emittance of a blackbody: (a) 800 K. (b) 1200 K. (c) 1600 K. (d) 1600 K (Wien). (e) 1600 K (Rayleigh). (f) 6000 K. (g) 10,000 K. The decrease of resonance wavelength. and hence increase of resonance frequency. is shown by the dashed curve.[11]
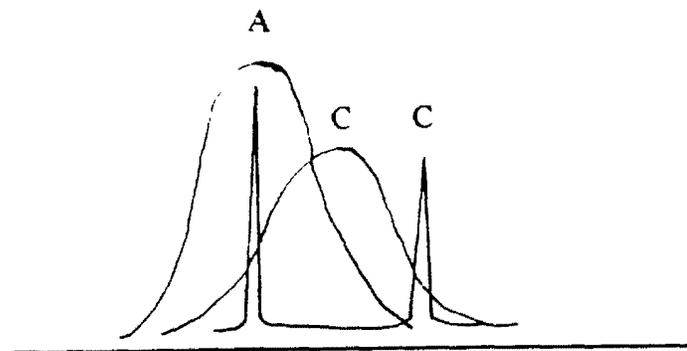
Figure 18.c. At low temperature the catalyst (C) does not resonate with target chemical species (A). At high temperature. the catalyst's resonant frequency shifts and resonance exists between C and A.

The amplitude or intensity of a spectral line may be affected by temperature also[9]. For instance, linear and symmetric rotor molecules will *increase* intensity as the temperature is lowered. Conversely, rotational or vibrational spectra may *decrease* intensity as the temperature is lowered. These changes of spectral intensity can affect catalyst performance. Consider

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[11] *Encyclopedia of Physics Blackbody Radiation* Lerner RG & Trigg GL. VCH Publishers, NY. 1991

the example where a low intensity spectral curve of a catalyst is resonant with a chemical target's frequency. Only small amounts of energy can be transferred from the catalyst to the target chemical. Say that as the temperature increases, the amplitude of the catalyst's curve increases also. In this case the catalyst can transfer much larger amounts of energy to the chemical target. If the chemical target is the intermediate chemical species for an alternative reaction route, the type and ratio of end products may be affected.

Look at our cyclohexene palladium reaction again. At temperatures *below* 300 C the products are benzene and hydrogen gas. When the temperature is *above* 300 C the products are benzene and cyclohexane. Temperature is affecting the palladium and/or the rest of the reaction system (including reactants, intermediates, and products) is such a way that an alternative reaction pathway leading to the formation of cyclohexane is favored above 300 C. This could be a result of increased line width, altered resonance frequencies, or changes in spectral curve intensities for any of the chemical species in the reaction system.

It is important to consider the spectral catalyst frequencies *under the reaction conditions we want to duplicate.* Say for instance that at temperatures above 300 C, the reaction system is unaffected but the palladium has an increased line width, lower resonant frequency, and increased intensity. Also say for instance that the wider line width and lower resonant frequency interact with an intermediate important for the formation of cyclohexane. If we wanted to spectrally catalyze the formation of cylcohexane at room temperature, we would need to use the wider, lower spectral catalyst frequency for palladium *above 300 C.*

Thus it can be important to understand the reaction system dynamics in designing and determining a spectral catalyst. Otherwise, one is reduced to using random, trial and error or feedback-type analyses which; although they will eventually identify the spectral catalyst frequencies, will be very time-consuming. The trial and error techniques for determining spectral catalysts also have the added drawback, that having once identified a frequency, one is left with no idea of what it means[12]. If one wishes to modify the reaction, another trial and error analysis becomes necessary rather than a simple, quick calculation.

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[12] *Science.* Vol 279. March 20, 1998, p. 1947-8.

Pressure

Pressure and temperature are directly related to each other. Everyone · probably remembers the ideal gas law from high school chemistry:

$$PV = nRT,$$

where P is pressure, V is volume, n is the number of moles of gas, R is the gas constant, and T is the absolute temperature (Celsius plus 273˚). All things being equal, if temperature increases, so does pressure. Given this similarity between the effects of pressure and temperature in chemical systems, one might wonder if they have similar effects on spectral emission patterns. The answer is yes. Increased pressure causes broadening and other changes in spectral curves, just as increased temperature does (Fig. 19).
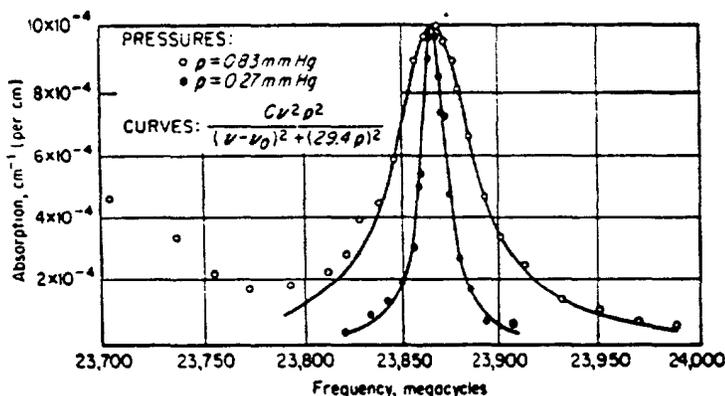
Figure 19. Effect of pressure broadening on the NH$_3$ 3.3 absorption line[9].

Mathematical treatments of pressure broadening are generally grouped into either collision or statistical theories[9]. In collision theories, the assumption is made that most of the time an atom or molecule is so far from other atoms or molecules that their energy fields do not interact. Occasionally, however, the atoms or molecules come so close that they collide. In this case, the atom or molecule may undergo a change in wave phase function, or a change to a different energy level. Collision theories treat the significant radiation as occurring only when the atom or molecule is far from others, and is not involved in a collision. Because collision theories ignore spectral frequencies during collisions, they fail to accurately predict chemical behavior at more than a few atmospheres of pressure, when collisions are frequent.

Statistical theories, however, consider spectral frequencies before, during, and after collisions. They are based on calculating the probablilities that various atoms and molecules are interacting with or perturbed by other atoms or molecules. The drawback with statistical treatments of pressure effects is that they do not do a good job of accounting for the effects of molecular motion. In any event, neither collision or statistical theories adequately predict the rich interplay of frequencies and heterodynes that take place as pressure is increased.

Experimental work has demonstrated that increased pressure can have effects similar to those produced by increased temperature, with:

1) broadening of the spectral curve producing increased line width; and

2) shifting of the resonant frequency, f_0.

Unlike temperature, however, pressure changes usually do not affect intensity or energy amplitude (Fig. 20).
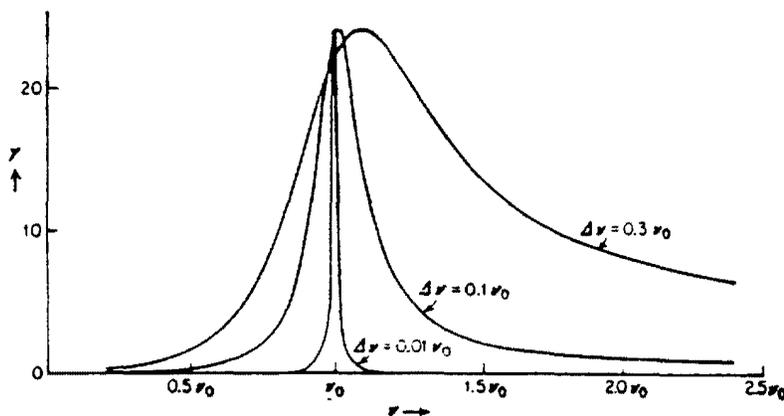
Figure 20. Theoretical shape of pressure-broadened lines for three different pressures[9]. The intensity is unchanged. $\Delta\nu=0.01\nu_0$ is the lowest pressure and $\Delta\nu=0.3\nu_0$ the highest pressure curve.

Pressure broadening differs from temperature broadening in one other significant aspect. The curves produced by pressure broadening can be less symmetric than the temperature affected curves. Consider the shape of the three curves in the theoretical work above (Fig. 20). As the pressure increases, the curves become less and less symmetrical. A tail extending into the higher frequencies develops. This upper frequency extension is confirmed

by experimental work (Fig. 21).
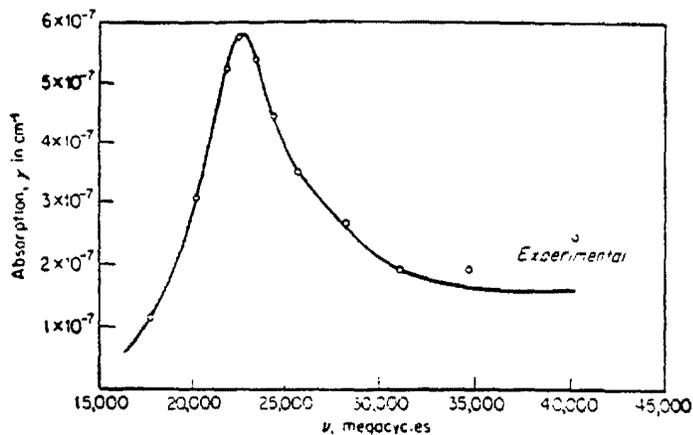
a)
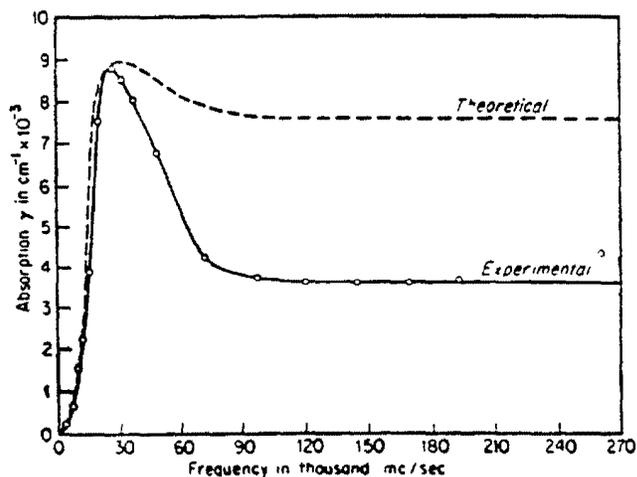
b)

Figure 21. Experimental confirmation of upper frequency tail produced at increased pressures[9].
a) Absorption by water vapor in air (10 g of H_2O per cubic meter); b) Absorption in NH_3 at 1 atm
pressure.

Pressure broadening effects on spectral curves are broadly grouped into
two types: resonance or "Holtsmark" broadening, and "Lorentz" broadening[13].
Holtsmark broadening is secondary to collisions between atoms of the same
element, and thus the collisions are considered to be symmetrical. Lorentz
broadening results from collisions between atoms or molecules which are
different. The collisions are asymmetric, and the resonant frequency, f_0, is
often shifted to a lower frequency. This shift in resonant frequency is shown

[13] _Atomic Absorption Spectroscopy_ Ed. Haswell SJ Elsevier Science Publ 1991

in Fig. 20.

The changes in spectral curves and frequencies that accompany changes in pressure can affect catalysts and chemical reactions. At low pressures, the spectral curves will be fairly narrow and crisp, and nearly symmetrical about the resonant frequency. As pressures increase, the curves may broaden, shift, and develop high frequency tails. At low pressures the spectral frequencies in the reaction system might be so different for the various atoms and molecules that there is no resonant effect. At higher pressures, the combination of broadening, shifting and extension into high frequencies can produce over-lapping between the spectral curves, with creation of resonance where none previously existed. The reaction system may proceed down one path or another, depending on the changes in spectral curves produced by the pressure changes. One reaction path may be resonant, and hence proceed at moderate pressure, while another reaction path may be resonant and predominate at higher pressures. As with temperature, it is important to consider the spectral catalyst frequencies and mechanisms *under the reaction conditions we want to duplicate*.

Surface Area

Traditionally, the surface area of the catalyst is considered to be important because the available surface area controls the number of available binding sites. The more exposed binding sites, the more catalysis, or so the theory goes. In light of the spectral mechanism underlying the activity of physical catalysts, surface area may be important for another reason.

Many of the catalytically active frequencies produced by physical catalysts are in the visible light and ultraviolet regions. These high frequencies have very poor penetrance in large reaction vats full of chemicals. The high frequency spectral emissions from a catalyst such as platinum or palladium will not travel very far in a reaction system before they are absorbed. Thus, an atom or molecule must be fairly close to a physical catalyst to interact with its' electromagnetic radiation.

Surface area affects the probability that a particular chemical species, will be close enough to the physical catalyst to interact with its electro-magnetic spectral emission. With small surface area, few atoms or molecules will be close enough to interact. As surface area increases, so too does the probability that more atoms or molecules will be within range. Thus, rather than increasing the available number of binding sites, large surface area

increases the volume of the reaction system exposed to the spectral catalyst frequencies.

Catalyst Size and Shape

In a related line of reasoning, catalyst size and shape are classically thought to affect physical catalyst activity. Particle size selectivity of reactions has been used to steer catalytic pathways for several years[14]. As with surface area, certain particle sizes are thought to stabilize a maximum of active binding sites and thus maximize the reaction rate[14].

Catalyst size and surface area are often intertwined theoretically. Maximum catalyst activity is said to require maximum surface area, and maximum surface area obtains from bits of catalyst as small as possible[1]. Extremely fine powders of small catalyst particles are not stable however. They have a tendency to coalesce into larger particles, thereby reducing surface tension and remaining thermodynamically stable. When this happens during use of a catalyst, it is called "sintering". Sintering is thought to reduce the number of active binding sites by reducing the surface area.

In light of the spectral mechanism underlying the activity of physical catalysts, catalyst size and shape may be important for other reasons. One is due to a phenomenon called "self absorption"[13]. When a single atom or molecule produces its'classical spectral pattern it radiates electromagnetic energy which travels out from the atom or molecule into neighboring space (Fig. 22.). As more and more atoms or molecules group together, radiation from the center of the group of is absorbed by its' neighbors and never makes it out into space. Depending on the size and shape of the group of atoms, self absorption can cause a number of changes in the spectral emission pattern (Fig. 23.). These changes include a shift in resonant frequency and self-

Figure 22. Radiation from a single atom vs. radiation from a group of atoms.

[14] Physics Today. Catalysis and Surface Science. Ertl G & Freund HJ, Jan 1999. p 32-8

reversal patterns.
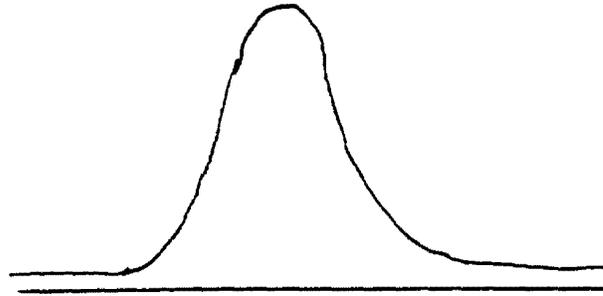
a) Normal spectral curve produced by a single atom

b) Resonant frequency (f_0) shift from self absorption

c) Self-reversal spectral pattern produced by self absorption in a groups of atoms

d) Self-reversal spectral pattern produced by self absorption in a groups of atoms

Figure 23. Effects of self absorption on the spectral emission patterns of groups of atoms or molecules. a) spectral pattern of a single atom: b) resonant frequency shift: c&d) self-reversal.

Catalyst size and shape are also important to spectral emission patterns because of the antenna-type transmitter effects produced by many atoms and molecules, particularly metals such as many of the catalysts. As with antennas in general, the larger the metallic structure, the lower the frequency with which it resonates. So too, the larger the size of the catalyst, the lower the antenna-type frequencies it will produce.

The changes in spectral curves and frequencies that accompany changes in catalyst size and shape can affect catalysts and chemical reactions. For single atoms, such as in a gas phase, the spectral frequencies in the reaction system might be so different for the various atoms and molecules that there is no resonant effect. With larger groups of atoms, such as in a solid phase, the combination of resonant frequency shifting and self-reversal can produce or eliminate over-lapping between the spectral curves of chemical species, either creating or destroying conditions of resonance, respectively. The reaction system may proceed down one path or another, depending on the changes in spectral curves produced by the particle sizes. One reaction path may be resonant, and hence proceed at moderate catalyst particle size, while another reaction path may be resonant and predominate at larger catalyst sizes. As with other factors, it is important to consider the spectral catalyst frequencies and mechanisms *under the reaction conditions we want to duplicate*.

The changes in spectral curves and frequencies that accompany changes in catalyst size and shape are relevant for practical applications. Industrial catalysts are manufactured in a range of sizes and shapes, depending on the design requirements of the process and the type of reactor used[1]. Catalyst activity is proportional to the surface area of the catalyst bed in the reactor[1]. Surface area increases as the size of the catalyst particles decreases[1]. Seemingly, the smaller the catalyst particles, the better for industrial applications. This is not always the case, however. When a very fine bed of catalyst particles is used, high pressures are required to force the reacting chemicals across the catalyst bed. The chemicals go in the catalyst bed under high pressure, and come out the other side at low pressure. This large difference between entry and exit pressures is called a "pressure drop". A compromise is often required between catalyst size, catalyst activity, and pressure drop across the catalyst bed.

The use of spectral catalysts allows for much finer tuning of this compromise. For instance, a large catalyst size can be used so that pressure drops across the catalyst bed are minimized. At the same time, the high level of catalyst activity obtained with a smaller catalyst size can still be obtained.

by *augmenting* the physical catalyst spectrally.

Say for instance that a 10 mm catalyst has 50% of the activity of a 5 mm catalyst. With a 5 mm catalyst, however, the pressure drop across the reactor is so great that the reaction cannot be economically performed. The compromise in the factory has been to use twice as much 10 mm catalyst, to obtain the same amount of activity as with the original amount of 5 mm catalyst. We fine tune the compromise: use the original amount of 10 mm catalyst and augment with a spectral catalyst. Catalyst activity is doubled by the spectral catalyst, giving us the same degree of activity as with the 5 mm catalyst. The size of the catalyst is larger, retaining the favorable reactor vessel pressure conditions for us. We can perform the reaction economically, using half as much catalyst as we did in the past.

Another way to approach the problem is to do away with the catalyst all together. We simply put a fiberoptic sieve, with very large pores, in a flow-through reactor vessel. The pore size is so large that there is virtually no pressure drop across the sieve, compared to the drop accompanying the 5 mm or even the 10 mm catalyst. The spectral catalyst is emitted through the fiberoptic sieve, catalyzing the reacting species as they flow by.

Industrial catalysts are also manufactured in a range of shapes, as well as sizes. Shapes include spheres, irregular granules, pellets, extrudate, and rings[1]. Some shapes are more expensive to manufacture than others, while some shapes have superior properties (catalyst activity, strength, and less pressure drop) than others. While spheres are inexpensive to manufacture, packed beds of spheres produce high pressure drops and the spheres are not very strong. Rings, on the other hand, have superior strength and activity and produce very little pressure drop, but they are also very expensive to produce.

Spectral catalysts allow us greater flexibility in choosing catalyst shape. Instead of using a packed bed of inexpensive spheres, with the inevitable high pressure drop and resulting mechanical damage to the catalyst particles, we can use a single layer of spheres augmented with a spectral catalyst. Our catalyst is inexpensive, activity is maintained, and large pressure drops are not produced, thus preventing mechanical damage and extending the useful life of our spheres. Similarly, we can use far smaller numbers of catalyst rings, and obtain the same or greater catalyst activity by supplementing with a spectral catalyst. The process can proceed at a faster flow-through rate because the catalyst bed will be smaller.

The use of spectral catalysts to augment existing physical catalysts has the following advantages:

- it allows use of less expensive shaped catalyst particles;
- it allows use of fewer catalyst particles overall;
- it allows use of stronger shapes of catalyst particles;
- it allows use of catalyst particle shapes with better pressure drop characteristics.

The use of spectral catalysts to replace existing physical catalysts has similar advantages:

- it eliminates the use and expense of catalyst particles altogether;
- it allows use of spectral catalyst delivery systems that are stronger;
- it allows use of spectral catalyst delivery systems with superior pressure drop characteristics.

Solvents

Generally, the term solvent is applied to liquid mixtures for which the solvent is a liquid and the solute (reacting chemical species or catalyst) can be a gas, liquid, or solid[15]. (Although less common, solvents can also be gases or solids, as well as liquids.) Solvents are grouped into three broad classes - aqueous, organic, and nonaqueous. If an aqueous solvent is used, it means that the solvent is water. Organic solvents include hydrocarbons such as alcohols and ethers. Nonaqueous solvents are inorganic non-water substances. Many catalyzed reactions take place in solvents.

Because solvents are themselves composed of atoms and molecules, they can have pronounced effects on chemical reactions. Solvents are atoms and molecules, and thus emit their own spectral frequencies. These solvent frequencies undergo the same basic processes discussed earlier, including heterodyning, resonance, and harmonics. Spectroscopists have known for years that a solvent can dramatically affect the spectral frequencies produced by its' solutes. Likewise, chemists have known for years that solvents can affect catalyst activity. Unfortunately, the spectroscopists and chemists did not associate these long studied changes in solute frequencies with changes in catalyst activity. These changes in solute frequencies include spectral curve broadening, changes of curve intensity, gradual or abrupt shifting of the resonant frequency f_0, and even abrupt rearrangement of resonant frequencies.

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[15] Concise Encyclopedia of Science & Technology. Ed. Parker SP. McGraw-Hill. 1992.
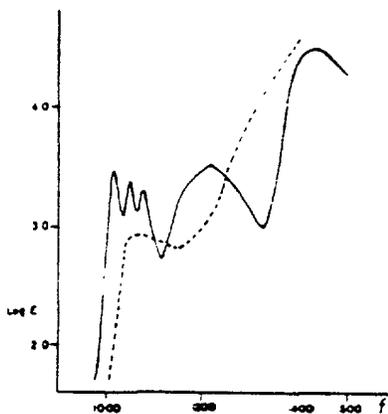
a) Absorption spectra of phthalic acid in hexane (dotted) and alcohol (solid).
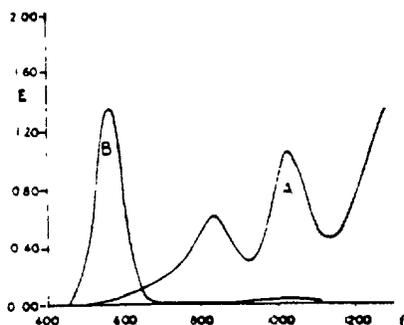
b) Absorption spectra of iodine in alcohol (A) and carbon tetrachloride (B).
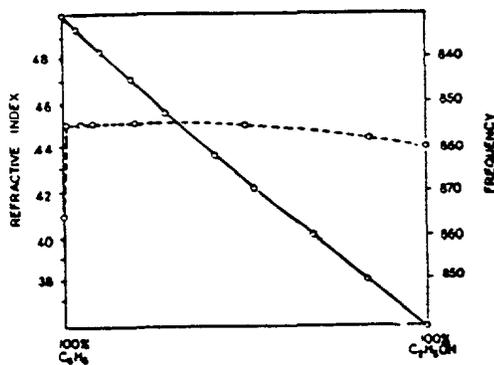
c) Effect of mixtures of alcohol and benzene on the absorption frequency of phenylazophenol. Dotted line is frequency.

Figure 24. Effects of solvents on spectral patterns of chemical species solutes[10].

Looking at Fig. 24.a.. consider a reaction taking place in alcohol, in which the catalyst resonates with phthalic acid at 1250, the large solid curve in the middle. If we change the solvent to hexane. the phthalic acid no longer

1250, it will no longer resonate with the phthalic acid. The change in solvent will make our catalyst ineffective.

Similarly, consider Fig. 24.b., wherein iodine produces a high intensity curve at 580 when dissolved in carbon tetrachloride. In alcohol, the iodine produces instead, a moderate intensity curve at 1050 and a low intensity curve at 850. Let's say we are performing a reaction using a catalyst that resonates directly with the iodine in carbon tetrachloride at 580. Assuming the catalyst spectral pattern does not change, if we change the solvent to alcohol, the catalyst will no longer work. Its' frequency of 580 will no longer match and resonate with the new iodine frequencies of 850 and 1050. Of course there is always the possibility that the catalyst will change its spectral pattern with a change of solvent. The catalyst could change in a similar manner to the iodine, in which case it will continue to catalyze the reaction regardless of the change in solvent. Conversely, the catalyst spectral pattern could change in a direction opposite to the iodine's. The catalyst will again fail to catalyze our original reaction. There is also the possibility that the change in the catalyst could bring it into resonance with a different chemical species and help the reaction proceed down an alternative reaction pathway.

Finally, consider the graph in Fig. 24.c. showing a variety of solvent mixtures ranging from 100% benzene at the far left, to a 50:50 mixture of benzene and alcohol in the center, to 100% alcohol at the far right. The solute is phenylazophenol. The phenylazophenol has a frequency of 855 for most of the solvent mixtures. For 100% alcohol and for 50:50 benzene:alcohol the frequency is 855 or 98:2 benzene:alcohol the frequency is still 855. At 99.5:0.5 benzene:alcohol however, the frequency abruptly changes to 880. A catalyst active in 100% benzene by resonating with the phenylazophenol at 880, will lose its activity is there is even a slight amount of alcohol in the solvent. Once again, it is important to consider the spectral catalyst frequencies and mechanisms **under the reaction conditions we want to duplicate**.

Support Materials

Catalysts can be either unsupported or supported. An unsupported catalyst is a formulation of the pure catalyst, with no other molecules present. Unsupported catalysts are rarely used industrially because they generally have low surface area and hence low activity. The low surface area results from sintering. or coalesence of small molecules of the catalyst into larger

molecules, in a process which reduces surface tension of the particles. An example of an unsupported catalyst is platinum alloy gauze, which is used for the selective oxidation of ammonia to nitric oxide.[1] Another example is small silver granules, used to catalyze the reaction of methanol with air, to form formaldehyde.[1] When the use of unsupported catalysts is possible, their advantages include straightforward fabrication and easy installation in industrial processes.

A supported catalyst is a formulation of the catalyst with other molecules, the other molecules acting as a supporting skeleton for the catalyst. Traditionally, the support molecules are thought to be inert, providing a simple physical scaffolding for the catalyst molecules. Thus, one of the functions of the support material is to give the catalyst shape and mechanical strength. The support material is also said to reduce sintering rates.[1] If the support is as finely divided as the catalyst, the support will act as a "spacer" between the catalyst particles, and hence prevent sintering. An alternative theory holds that an interaction takes place between the catalyst and support, thereby preventing sintering.[1] This theory is supported by the many observations that catalyst activity is altered by changes in support material structure and composition.

Supported catalysts are generally made by one of three methods: impregnation, precipitation, and crystallization. Impregnation techniques use preformed support materials, which are then exposed to a solution containing the catalyst or its precursors. The catalyst or precursors diffuse into the pores of the support. Heating or another conversion process drives off the solvent and transforms the catalyst or precursors into the final catalyst. The most common support materials for impregnation are refractory oxides such as aluminas and aluminium hydrous oxides. These support materials have found their greatest use for catalysts that must operate under extreme conditions such as steam reforming[1], because they have great mechanical strength.

Precipitation techniques use concentrated solutions of catalyst salts (usually metal salts).[1] The salt solutions are rapidly mixed and then allowed to precipitate in a finely divided form. The precipitate is then prepared using a variety of processes including washing, filtering, drying, heating, and pelleting. Often a graphite lubricant is added. Precipitated catalysts have high catalytic activity secondary to high surface area, but they are generally not as strong as impregnated catalysts.

Crystallization techniques produce support materials called zeolites. The structure of these crystallized catalyst zeolites is based on SiO_4 and AlO_4

.tetrahedral units[1] (Fig. 25).

O   O   O   O
 \   /   \   /
  \   /   \   /
   \   /   \   /
     Al   Si
   /   \   /   \
  /   \   /   \
 /   \   /   \
O   O   O   O
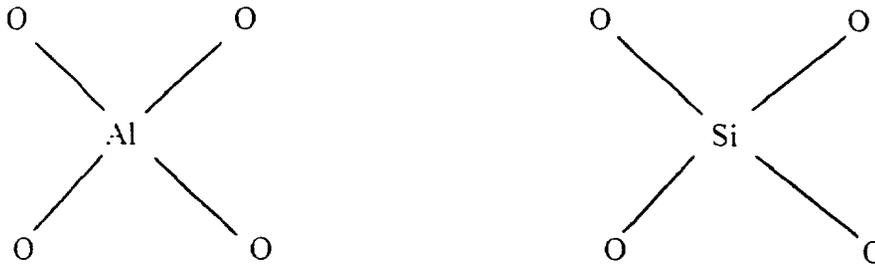
Figure 25 - Tetrahedral units of silicon and alumina

These units link in different combinations to form structural families, which include rings, chains, and complex polyhedra. For instance, the SiO_4 and AlO_4 tetrahedral units can form truncated octahedron structures, which form the building blocks for A, X, and Y zeolites (Fig. 26).
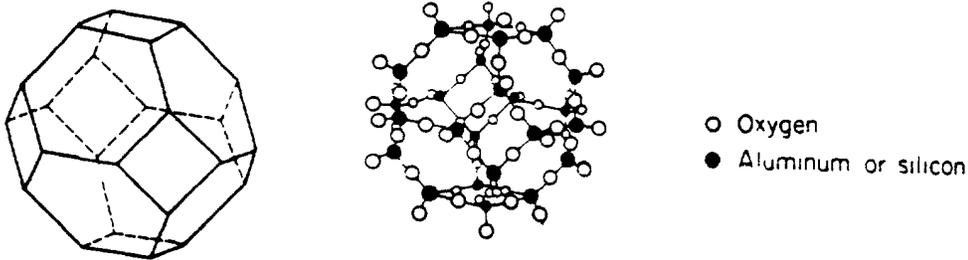
O Oxygen
● Aluminum or silicon

a) Truncated octahedron structure with lines representing oxygen atoms and corners are Al or Si atoms[16]
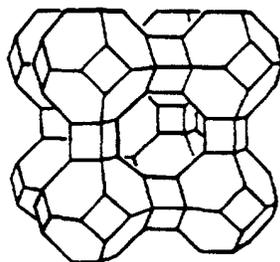
b) Zeolite A - Truncated octahedrons joined by oxygen bridges between square faces
Figure 26 - Zeolite structures using silicon and aluminum tetrahedral units as building blocks.[1]

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[16]Chemistry of Catalytic Processes. Gates BC et al: McGraw-Hill, 1979.
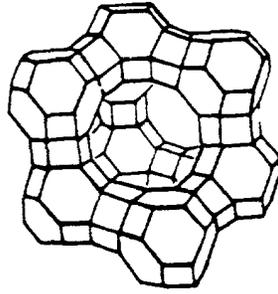
c) Zeolites X and Y - Truncated octahedrons joined by oxygen bridges between hexagonal faces

Figure 26 - Zeolite structures using silicon and aluminum tetrahedral units as building blocks.[1]
a) Truncated octahedron structure with lines representing oxygen atoms and corners are
Al or Si atoms; b) Zeolite A - Truncated octahedrons joined by oxygen bridges between square
faces; c) Zeolites X and Y - Truncated octahedrons joined by oxygen bridges between
hexagonal faces.

The crystalline structure of zeolites gives them a well defined pore size and structure. This differs from the varying pore sizes found in impregnated or precipitated support materials. Zeolite crystals are made by mixing solutions of silicates and aluminates and the catalyst. Crystallization is generally induced by heating. The structure of the resulting zeolite depends on the silicon/aluminum ratio, their concentration, the presence of added catalyst, the temperature, and even the size of the reaction vessels used.[1] Zeolites generally have greater specificity than other catalyst support materials - ie. they do not just speed up the reaction. They also steer the reaction towards a particular reaction path.

Support materials can affect the activity of a catalyst. Traditionally these effects have been attributed to geometric factors. There are undoubtedly spectral factors as well. It has been well established that solvents affect the spectral patterns produced by their solutes. Solvents can be liquids, solids, or gases. Support materials are nothing more than solid solvents for catalysts. As such, support materials will affect the spectral patterns produced by their solute catalysts.

Consider a glass of Cool-Aid. The liquid water is the solvent. The solutes are sugar, flavoring, and coloring. Now imagine freezing an ice cube of the Cool-Aid. The water is still the solvent, but it is a solid now, instead of a fluid. The solid water solvent still contains the same solutes of sugar, flavoring, and coloring.

Just as dissolved sugar can be placed into a solid phase solvent,

catalysts are placed into support materials that are solid phase solvents. These support material solid solvents have the same spectral effects on catalysts that liquid solvents have. Support materials can change spectral frequencies of their catalyst solutes by causing spectral curve broadening, changes of curve intensity, gradual or abrupt shifting of the resonant frequency f_0, and even abrupt rearrangement of resonant frequencies.

It is no surprise then that changes in support materials can have dramatic effects on catalyst activity. The support materials affect the spectral frequencies produced by the catalysts. The changes in catalyst spectral frequencies produce varying effects on chemical reactions and catalyst activity, including accelerating the rate of reaction and also guiding the reaction on a particular reaction path.

Poisoning

Poisoning of catalysts occurs when the catalyst activity is reduced by adding a small amount of another chemical species[1]. Traditionally, poisoning is attributed to chemicals with available electrons, and to adsorption of the poison onto the catalyst surface where it physically blocks reaction sites. Neither of these theories satisfactorily explains poisoning however.

Consider the case of nickel hydrogenation catalysts[1]. They are completely deactivated if only 0.1% sulphur compounds by weight are adsorbed onto them. Could 0.1% sulphur really contribute so many electrons as to inactivate the nickel catalyst? Could 0.1% sulphur really occupy so many reaction sites that it completely deactivates the catalyst? Neither explanation is satisfying.

Poisoning phenomena can be more logically understood in terms of spectral catalysts. Remember the example in the solvent section using a benzene solvent and phenylazophenol as the solute? In pure benzene the phenylazophenol has a spectral frequency of 880. The addition of just a few drops of alcohol (0.5%) abruptly changes the phenylazophenol frequency to 855. If we were counting on the phenylazophenol to resonate at 880, we would say that the alchohol had poisoned it. The addition of small quantities of other chemical species can change the resonant frequencies (f_0) of catalysts and reacting chemicals. The addition of another chemical species can act as a poison to take the catalyst and reacting species out of resonance.

Besides changing resonant frequencies of chemical species, adding small amounts of other chemicals can also affect the spectral intensities of the

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catalyst and other atoms and molecules in the reaction system, either increasing or decreasing them. Consider cadmium and zinc mixed in an alumina-silica precipitate[10] (Fig. 27). A normal ratio between the cadmium 3252.5 line and the zinc 3345.0 line was determined. Addition of sodium, potassium, lead, and magnesium had no effect on the Cd/Zn intensity ratio. Addition of copper reduced the relative intensity of the zinc line and increased the cadmium intensity. Conversely, addition of bismuth increased the relative intensity of the zinc line while decreasing cadmium.
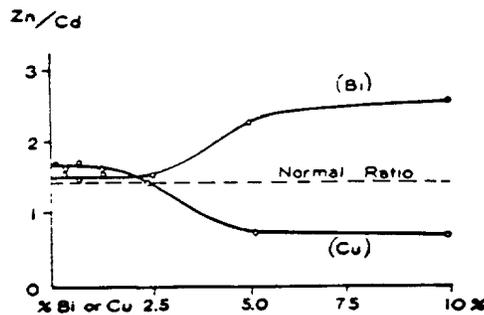
Figure 27 - Influence of copper and bismuth on the zinc/cadmium line ratio[10].

Also, consider the effect of small amounts of magnesium on a copper aluminum mixture[10] (Fig. 28). Magnesium, 0.6%, causes marked reductions in line intensity for copper and for aluminum. At 1.4% magnesium, spectral intensities for both copper and aluminum are reduced by about a third. If the copper frequency is important for catalyzing a reaction, adding this small amount of magnesium would dramatically reduce the catalyst activity. We would say the copper catalyst had been poisoned by the magnesium.
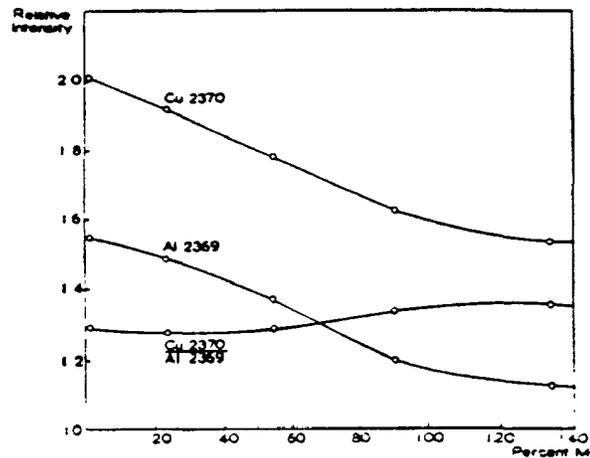
Figure 28 - Influence of magnesium on the copper aluminum intensity ratio[10].

In summary, poisoning effects on catalysts are due to spectral changes. Adding a small amount of another chemical species to a catalyst and reaction system can change the resonance frequencies or the spectral intensities of one or more chemical species. The catalyst might remain the same, while a crucial intermediate is changed. Likewise, the catalyst might change, while the intermediate stays the same. They might both change, or they might both stay the same and be oblivious to the added species.

Promoters

Just as adding a small amount of another chemical species to a catalyst and reaction system can poison the activity of the catalyst, the opposite can also happen[1]. When an added species enhances the activity of a catalyst, it is called a promoter. For instance, adding a few percent calcium and potassium oxide to iron-alumina compounds promotes activity of the iron catalyst for ammonia synthesis. Promoters act by all the mechanisms discussed in **Solvents, Support Materials,** and **Poisoning**. Not surprisingly, some support materials actually are promoters. Promoters enhance catalysts and specific reactions by changing spectral frequencies and intensities. While a catalyst poison takes the reacting species out of resonance, the promoter brings them into resonance. Likewise, instead of reducing the spectral intensity of crucial frequencies, the promoter increases the crucial intensities.

If we wanted phenylazophenol to react at 855 in a benzene solvent, we would add alcohol and call it a promoter. If we wanted the phenylazophenol to react at 880, we would consider the alcohol a poison. Thus understood, the differences between poisons and promoters are a matter of perspective, and depend on which reaction paths and products we want. They both act by the same underlying spectral mechanisms.

Concentration

Concentrations of chemical species are known to affect reaction rates and dynamics. Concentration affects catalyst activity. These effects are explained by the probabilities that various chemical species will collide with each other. At high concentrations of a particular species, there are a lot of individual atoms or molecules. The more atoms or molecules, the more likely

they are to collide with something else. This statistical treatment may not explain the entire situation. Take a look at Figure 29., with various concentrations of N-methyl urethane in a carbon tetrachloride solution. At low concentrations the spectral lines have low intensity. As the concentration is increased, the intensities of the spectral curves increase also. At 0.01 molarity the spectral curve at 3460 cm^{-1} is the only prominent frequency. At 0.15 molarity, the curves at 3370 and 3300 cm^{-1} are also prominent.
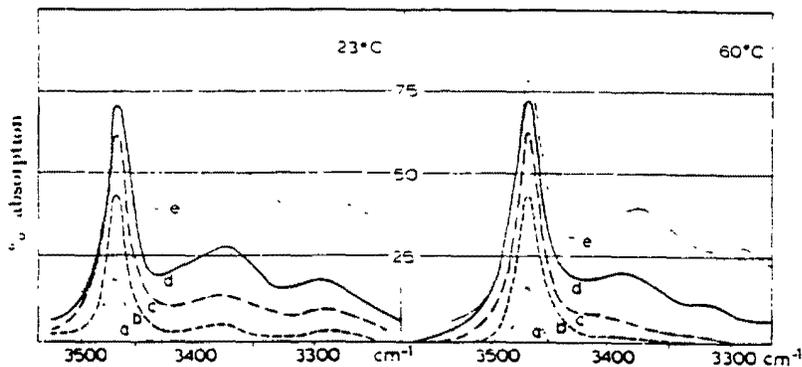
Figure 29. Concentration effects on the v (N-H) frequencies of N-methyl urethane in carbon tetrachloride solutions.[17] A) 0.01 M; b) 0.03 M; c) 0.06 M; d) 0.10 M; e) 0.15 M.

As the concentration of a chemical species is changed, the spectral character of that species in the reaction mixture changes also. Suppose that 3300 and 3370 cm^{-1} are important frequencies for a desired reaction path. At low concentrations, we will not see our desired reaction. If we increase the concentrations however (and hence the intensities of the relevant frequencies) the reaction will proceed down the desired path.

Fine Structure Frequencies

In the **Background** section we discussed spectroscopy, that field of science concerned with measuring the frequencies of energy and matter. Three broad classes of atomic and molecular spectra were reviewed. Electronic spectra, which are from electron transitions, have frequencies in the ultraviolet (UV), visible, and infrared (IR), and occur in atoms and molecules. Vibra-

[17] Infra-Red Spectroscopy and Molecular Structure M Davies. Elsevier Publ. Co., 1963.

tional spectra are from bond stretching between individual atoms within molecules, are in the IR, and occur only in molecules. Rotational spectra are from rotation of molecules in space, have microwave or radiowave frequencies, and occur only in molecules. This is the standard set of spectra found in any general book on spectroscopy.

This is also an over-simplification. The truth of the matter is slightly more complicated, but much more interesting. There are actually two other sets of spectra - the fine structure spectra and the hyperfine structure spectra. They occur in atoms and molecules, and extend from the infrared down to the low radio regions. These spectra are often mentioned in chemistry and spectroscopy books as an aside, because chemists tend to focus more on the traditional types of spectroscopy (electronic, vibrational, and rotational).

The fine and hyperfine spectra are found more often in publications by physicists and radio astronomers. For instance, cosmologists map the locations of interstellar clouds of hydrogen, and collect data regarding the origins of the universe by detecting signals from outerspace at 1.420 GHz, which is a hyperfine splitting frequency for hydrogen. Most of the large databases about the microwave and radio frequencies of molecules and atoms have been developed by astronomers and physicists, rather than by chemists. The microwave spectroscopy book cited in this paper was written by two physicists, not chemists. Because of this gap between chemists and physicists, use of the fine and hyperfine spectra in chemistry has been neglected by many.

Take another look at the frequency diagrams for hydrogen (Fig. 8 & 9) in the **Background** section. The Balmer series, frequency curve II, starts out with a frequency of 456 THz (Fig 30.a). Let's suppose we can look at this individual frequency in greater detail, with a spectral magnifying glass of sorts. We would find that instead of there being just one crisp narrow curve at 456 THz, there are really 7 different curves, very close together, that make up our curve at 456 THz. Figure 30.b. shows the emission spectrum for the 456 THz curve in hydrogen.[6] A high resolution laser saturation spectrum gives us even more detail, like a spectral microscope, as shown in Figure 30.c.[6] The seven different curves positioned very close together, which we see only when we look at the spectrum with very fine resolution, are fine structure curves or frequencies.
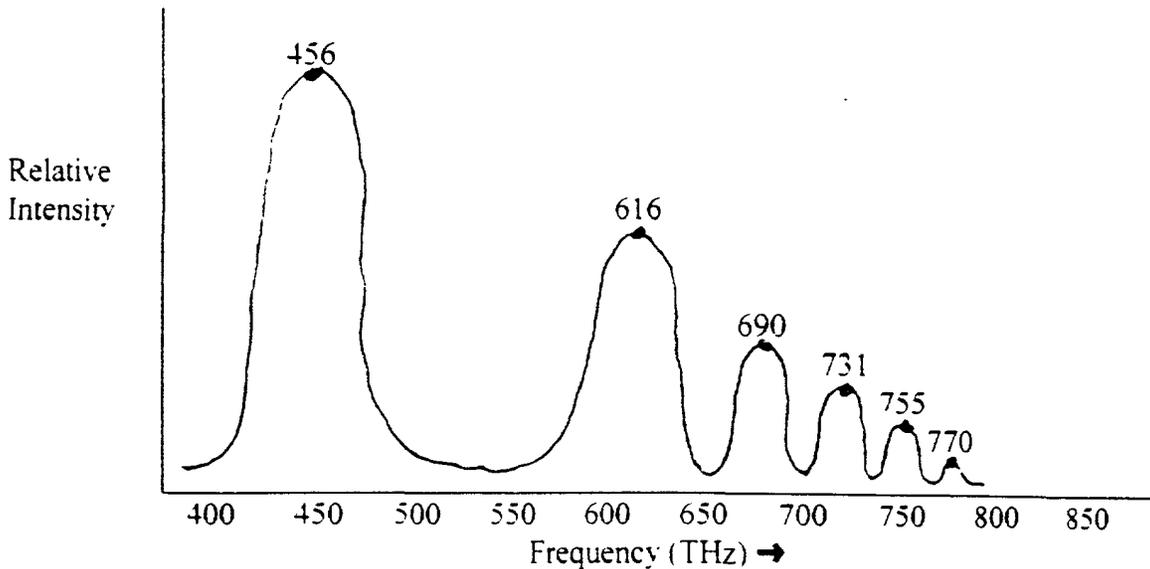
a) Balmer series II for hydrogen. frequency on X axis and relative intensity on Y axis.
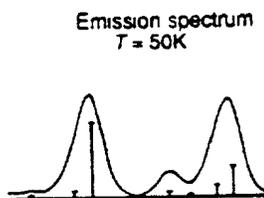
b) Emission spectrum for the 456 THz frequency of hydrogen.
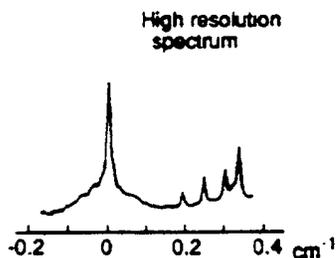
c) High resolution laser saturation spectrum for the 456 THz frequency of hydrogen.

Figure 30. Fine structure spectra for the 456 THz frequency from hydrogen.[6] Spectra taken at 70 K to reduce broadening of the lines. a) Portion of hydrogen electronic spectrum. b) Positions of the seven underlying fine structure components are indicated with bars. c) The strong line is 15.233.0702 cm^{-1} (456 THz) and the horizontal scale is relative to that wavenumber.[18]

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[18] These frequencies differ slightly from the frequencies in the NIST database. The frequencies listed in this figure are from " *Atomic Spectra* " by TP Softley. rather than the NIST database.

The hydrogen 456 THz frequency is composed of seven different fine structure frequencies. A group of several frequencies very close together like this is called a multiplet. Although there are seven different fine structure frequencies, they are all grouped around two major frequencies. These are the two tall, high intensity curves seen in Fig. 30.b. These two high intensity curves are also seen in Fig. 30.c. at zero cm^{-1} (456.676 THz), and at relative wavenumber 0.34 cm^{-1} (456.686 THz). When what appears to be a single frequency is composed predominantly of two slightly different frequencies, the two frequencies are called a doublet, and the frequency is said to be split. The difference or split between the two predominant frequencies in the hydrogen 456 THz doublet is 0.34 cm^{-1} wavenumbers, or 10.2 GHz (0.0102 THz). This frequency, 10.2 GHz, is called the fine splitting frequency for hydrogen's 456 THz frequency.

Thus the individual frequencies seen in ordinary electronic spectra are composed of two or more distinct frequencies spaced very close together. The distinct frequencies spaced very close together are called fine structure frequencies. The difference, between two fine structure frequencies that are split apart by a very slight amount, is a fine splitting frequency (Fig. 31). Now you may think this is starting to get rather far afield from spectral catalysts. In case you are wondering where this is all going, please note for future reference that the operative word here is "difference", and the difference between any two frequencies is a heterodyne.
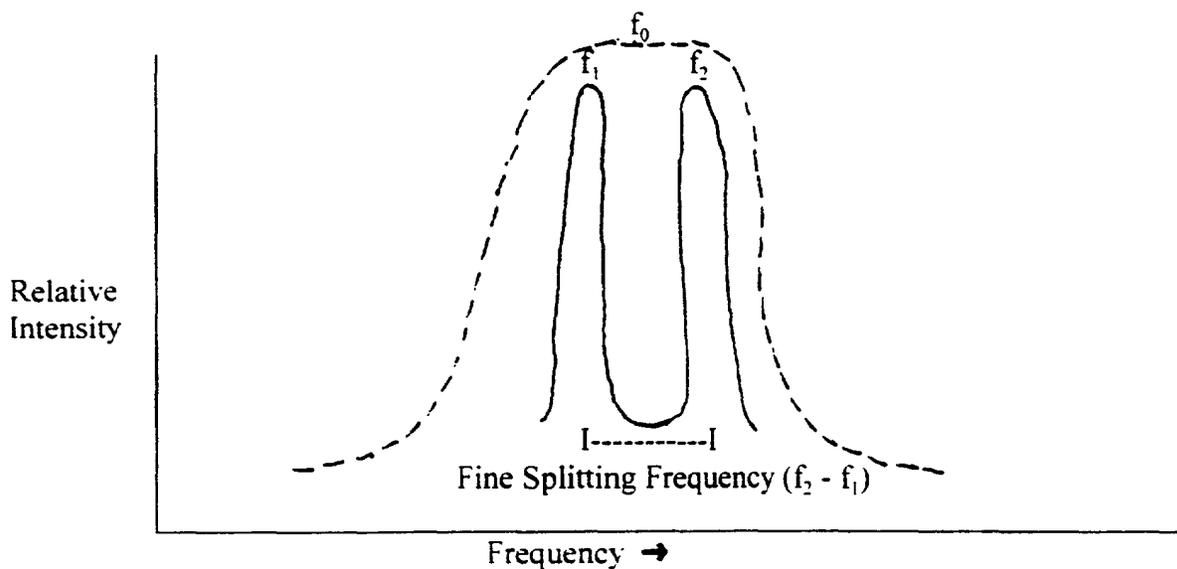
Figure 31. Fine structure. Dotted line (---) is electronic spectrum frequency, f : solid lines (__) are fine structure frequencies, f_1 and f_2. The difference (heterodyne) between the fine structure frequencies ($f_2 - f_1$) is the fine splitting frequency.

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Almost all the hydrogen frequencies in Figs. 8 and 9 are doublets or multiplets. This means that almost all the hydrogen electronic spectrum frequencies have fine structure frequencies AND fine splitting frequencies (heterodynes). Some of the fine splitting frequencies (heterodynes) for hydrogen are listed in Figure 32. These fine splitting heterodynes range from the microwave down into the upper reaches of the radio region.

FIGURE 32. - Fine Splitting Frequencies for Hydrogen

Frequency (THz)	Orbital	Wavenumber (cm^{-1})	Fine splitting Frequency
2466	2p	0.365	10.87 GHz
456	n2→3	0.34	10.20 GHz
2923	3p	0.108	3.23 GHz
2923	3d	0.036	1.06 GHz
3082	4p	0.046	1.38 GHz
3082	4d	0.015	448 MHZ
3082	4f	0.008	239 MHZ

There are more than 23 fine splitting frequencies (heterodynes) for just the first (I) series in hydrogen. Lists of the fine splitting heterodynes can be found in the classic 1949 reference "*Atomic Energy Levels*" by Charlotte Moore[19]. This seminal reference also lists 133 fine splitting heterodyned intervals for carbon, whose frequencies range from 14.1 THz (473.3 cm^{-1}) down to 12.2 GHz (0.41cm^{-1}) . Oxygen has 287 fine splitting heterodynes listed, from 15.9 THz (532.5 cm^{-1}) down to 3.88 GHz (0.13 cm^{-1}). The 23 platinum fine splitting intervals detailed are from 23.3 THz (775.9 cm^{-1}) to 8.62 THz in frequency (287.9 cm^{-1}).

Diagrammatically, the magnification and resolution of an electronic frequency into several closely spaced fine frequencies is depicted in Figure 33. The electronic orbit is designated by the orbital number n = 1, 2, 3, etc. The fine structure frequency is designated as α. A quantum diagram for hydrogen fine structure is in Figure 34.[20] Figure 35. shows the multiplet splittings for the lowest energy levels of carbon, oxygen, and fluorine.[19]

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[19] Atomic Energy Levels. As Derived From the Analyses of Optical Spectra. Vols. I-III. Charlotte E. Moore Circular of the National Bureau of Standards 467. June 15. 1949.

[20] Spectra of Atoms and Molecules. PF Bernath. Oxford University Press. 1995.
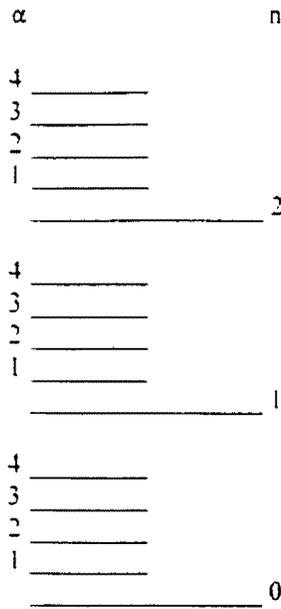
Figure 33. Diagram of atomic electron levels (n) and fine structure frequencies (α).
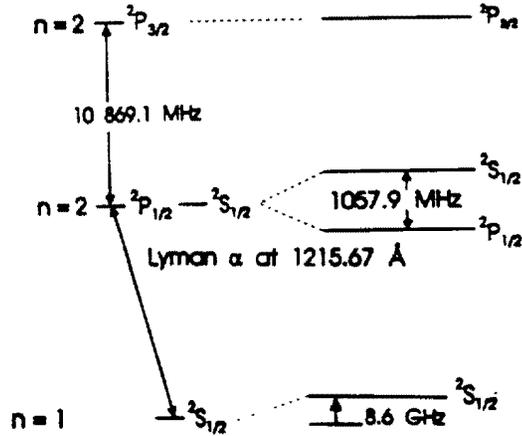
Figure 34. Fine structure of the n = 1 and n = 2 levels of the hydrogen atom.[19]
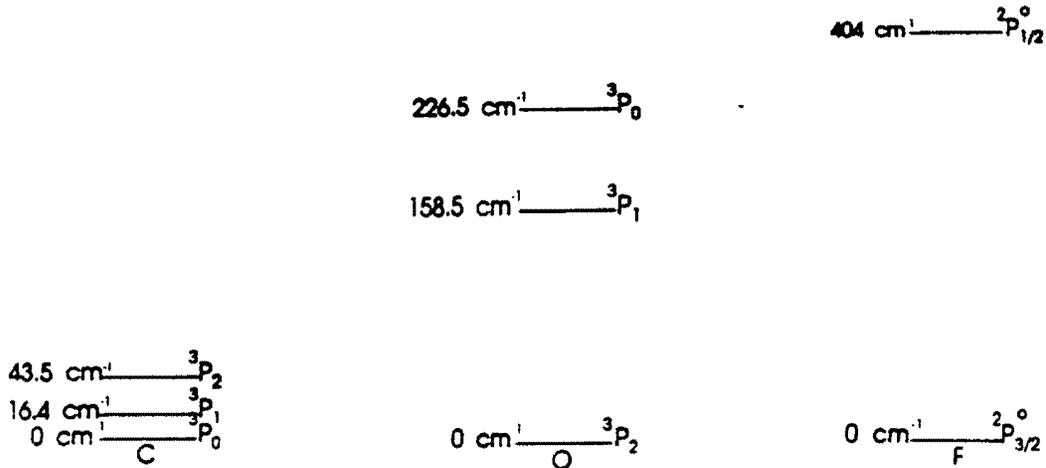
Figure 35. The multiplet splittings for the lowest energy levels for Carbon. Oxygen. and Fluorine. 43.5 cm⁻ = 1.3 THz. 16.4 cm⁻¹ = 490 GHz. 226.5 cm⁻¹ = 6.77 THz. 158.5 cm⁻¹ = 4.74 THz. 404 cm⁻ = 12.1 THz.

Now that you know atoms have fine structure frequencies, which are split apart by differences or intervals (heterodynes) called fine splitting frequencies, you are probably beginning to wonder about molecules as well. Molecules also have fine structure frequencies. The origin and derivation for molecular fine structure and splitting is a little different from that for atoms, but the graphical and practical results are quite similar. In atoms, the fine structure frequencies are said to result from the interaction of the spinning electron with its' own magnetic field. Basically, this means the electron cloud of a single atomic sphere, rotating and interacting with its' own magnetic field, produces the atomic fine structure frequencies. In the literature, you will find this referred to as "spin-orbit coupling". For molecules, the fine structure frequencies are the actual rotational frequencies of the electronic or vibrational frequencies. So the fine structure frequencies for atoms and molecules both result from rotation. In the case of atoms, it is the atom spinning and rotating around itself, much the way the earth rotates around its axis. In the case of molecules, it is the molecule spinning and rotating head-over-heels, like a candy bar tumbling through the air.

Take a look at Figure 36. This shows the infrared absorption spectrum of the SF_6 vibration band near 28.3 THz (10.6 μm wavelength, wavenumber
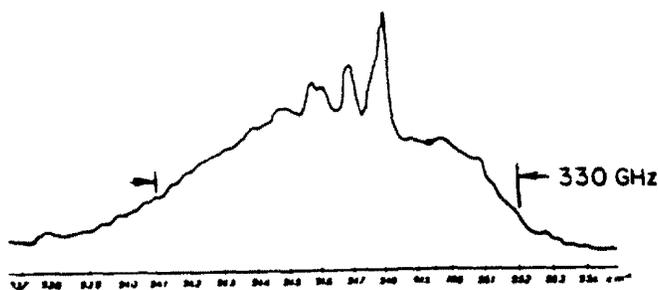
Figure 36. The vibration band of SF_6 at wavelength 10 μm.[2]

948 cm^{-1}) of the SF_6 molecule.[2] The molecule is highly symmetrical and rotates like a top. The spectral tracing was obtained with a high resolution grating spectrometer. There is a broad band between 941 and 952 cm^{-1} (28.1 and 28.5 THz) with three sharp spectral curves at 946, 947, and 948 cm^{-1} (28.3, 28.32, and 28.34 THz). Now what if we take a narrow slice of the broad band and look at it in more detail?

Figure 37.a. shows a narrow slice being taken from between 949 and 950 cm^{-1}, which is blown up to show more detail below and in 37.b. A tunable semiconductor diode laser was used to obtain the detail. There are many more spectral curves which appear when we look at the spectrum in finer detail. These curves are called the fine structure frequencies for this molecule.
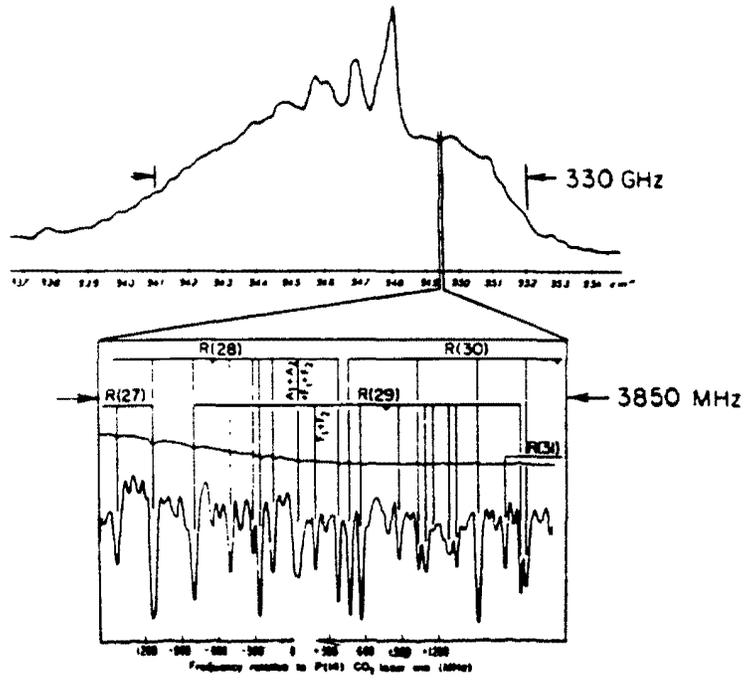
a) Slice from vibration band of SF$_6$.
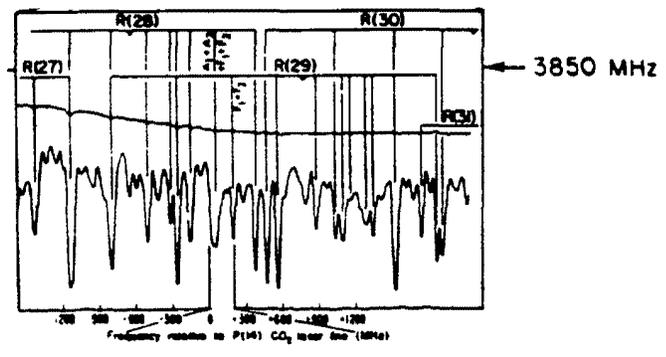
b) Fine structure frequencies shown in detail.

Figure 37. A narrow slice from the vibration band of SF$_6$, blown up to show more detail, with the fine structure frequencies.

The total energy of an atom or molecule is the sum of its' electronic, vibrational, and rotational energies. The simple Planck equation discussed in the **Background** section:

$$E = hf,$$

can be rewritten as follows:

$$hf = E = E_e + E_v + E_r$$

where E is the total energy, E_e the electronic energy, E_v the vibrational energy, and E_r the rotational energy. Diagrammatically, this looks like Figure 37. for molecules. The electronic energy, E_e, involves a change in the orbit of one of the electrons in the molecule.[10] It is designated by the orbital number n = 0, 1,
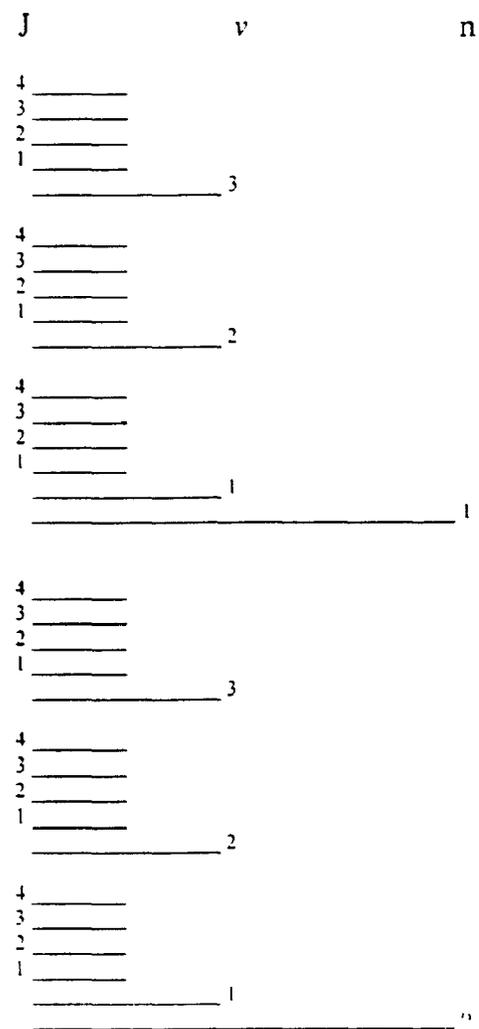
Figure 38. Diagram of rotational (J), vibrational (v), and electronic (n) energy levels for a molecule.

2, 3, etc. The vibrational energy, E_v, is produced by a change in the vibration rate between two atoms within the molecule[10], and is designated by a vibrational number $v = 1, 2, 3$, etc. Lastly, the rotational energy, E_r, is the energy of rotation caused by the molecule rotating around its' center of mass[10]. The rotational energy is designated by the quantum number $J = 1, 2, 3$, etc., as determined from angular momentum equations.

Thus, when we look at the vibrational frequencies of SF_6 in more detail, we see the fine structure molecular frequencies. These fine structure frequencies are actually produced by the molecular rotations, J, as a subset of each vibrational frequency. Just as the rotational levels J are evenly separated in Figure 38, they are also evenly separated when plotted as frequencies.

This may by easier to understand by looking at some other frequency diagrams. Figure 39 shows the rotational spectrum for hydrogen chloride[21]. In Fig. 39.a., the separate waves that look like teeth on a comb, are the individual rotational frequencies. The whole big wave (the whole comb) that goes from 20 to 500 cm^{-1} is the entire vibrational frequency. At low resolution, this would look like a single frequency peaking at 20 cm^{-1} (598 GHz) (Fig. 39.b.). This is very similar to the way atomic frequencies such as 456 THz look like just one frequency at low resolution, but turn out to be several different frequencies at higher magnification.

| 500 | 380 | 260 | 140 | 20 |
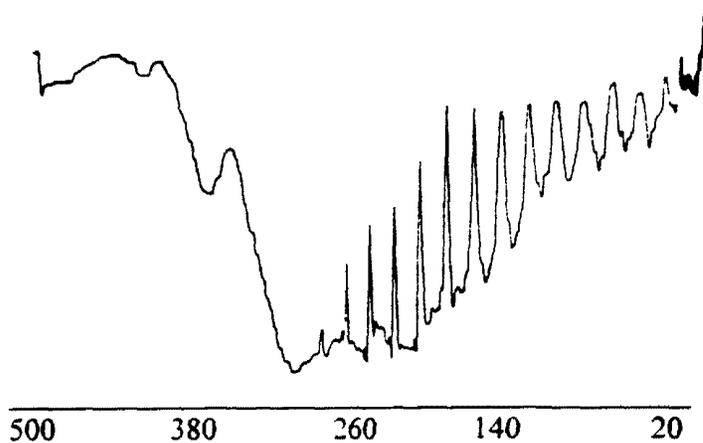
a)

[21] Infra-red Spectroscopy and Molecular Structure. M Davies. Elsevier Publ. Co. 1963.

| 500 | 380 | 260 | 140 | 20 |
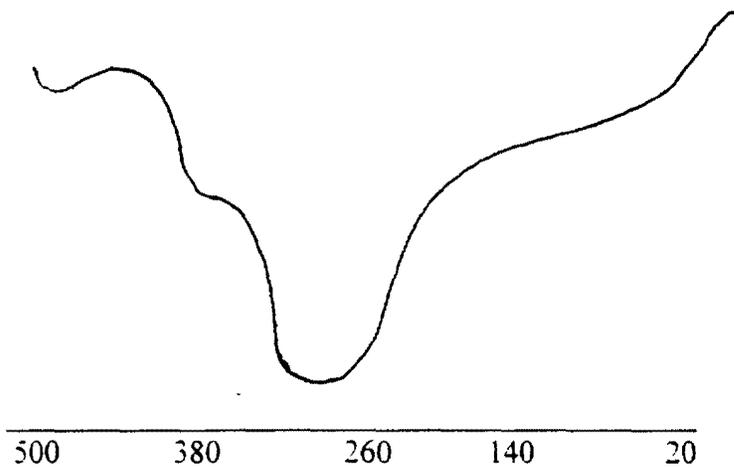
b)

Figure 39. The rotational spectrum for hydrogen chloride showing fine structure detail. a) Pure rotational absorption spectrum of gaseous hydrogen chloride recorded with an interferometer. b) The same spectrum at low resolution.

In Figure 40, the rotational spectrum (fine structure) of hydrogen cyanide is shown.[20] Note again the regular spacing of the rotational levels. (This spectral tracing is oriented the opposite of what we are used to. It uses transmission rather than emission on the horizontal Y axis, so our familiar intensity notation increases as you go down on the Y axis, rather than up.)
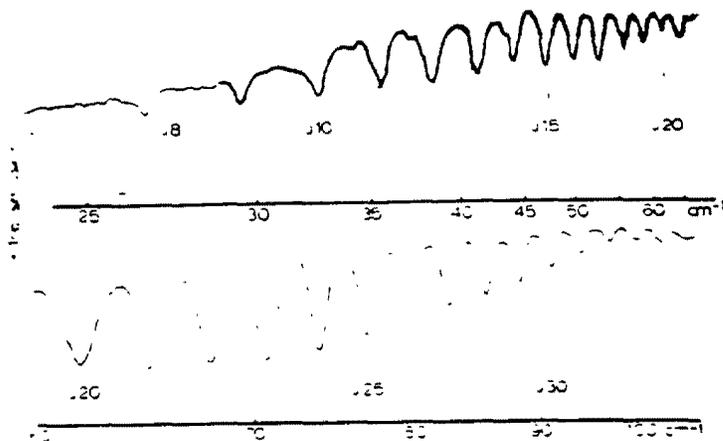
Figure 40. The rotational spectrum for hydrogen cyanide. "J" is the rotational level.

Finally, for a veritable symphony of rotational frequencies, take a look at Figure 41, showing a vibrational band for FCCF[22]. All of the fine sawtooth spikes are the fine structural frequencies, corresponding to the rotational frequencies. Note the regular spacing of the rotational frequencies. Also note the undulating pattern of the rotational frequency intensity, as well as the alternating pattern of the rotational frequency intensities.
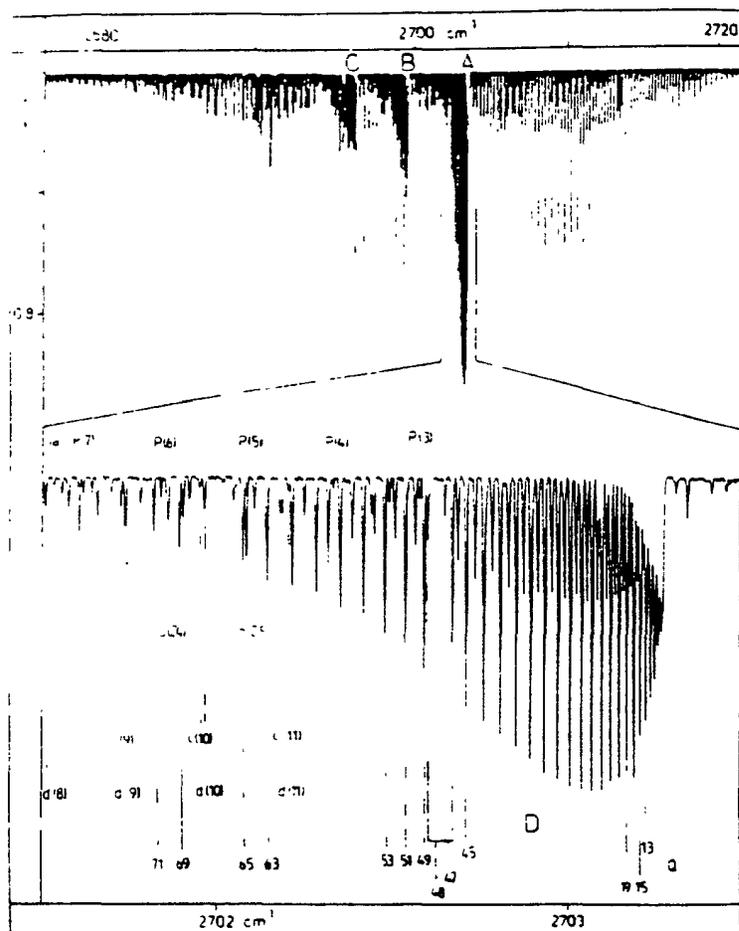
Figure 41.[21] The $v_1 - v_5$ band of FCCF. v_1 is vibrational level one, and v_5 is vibrational level 5. The vibrational level frequencies heterodyne (add and subtract) just like all frequencies. The additive heterodyne of v_1 and v_5 are depicted in the spectral band showing the frequency band at "A" $(v_1 - v_5)$. $B = v_1 - 2v_5$.

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[22] Vibration-Rotational Spectroscopy and Molecular Dynamics. Ed. D Papousek. World Sci., 1997

Consider the actual rotational frequencies (fine structure frequencies) for the ground state of carbon monoxide listed in Figure 42.

Figure 42. Rotational Frequencies and Derived Rotational Constant for CO in the Ground State[23]

J Transition	Frequency (MHZ)	Frequency (GHz)
0 → 1	115,271.204	115
1 → 2	230.537.974	230
2 → 3	345,795.989	346
3 → 4	461,040.811	461
4 → 5	576,267.934	576
5 → 6	691,472.978	691
6 → 7	806,651.719	807

$$B_0 = 57,635.970 \text{ MHZ}$$

Each of the rotational frequencies is regularly spaced approximately 115 GHz apart. Now the quantum theorists will explain this as being due to the fact that the rotational frequencies are related to Planck's constant and the moment of inertia (center of mass for the molecule) by the equation:

$$B = \frac{h}{8\pi^2 I}$$

where B is a rotational constant, h is Planck's constant, and I is the moment of inertia for the molecule. From there they go to a frequency equation for the rotational levels that looks like this:

$$f = 2B(J + 1)$$

where f is the frequency, B is the rotational constant, and J is the rotational level. Thus the rotational spectrum (fine structure spectrum) for a molecule turns out to be a harmonic series of lines with the frequencies all spaced or

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[23] Microwave Molecular Spectra. 3rd Edition. W Gordy & RL Cook, Wiley & Sons. 1984.

split (heterodyned) by the same amount. The physicists call this amount "2B", and they call "B" the "rotational constant". In charts and databases of molecular frequencies, B is usually listed as a frequency such as MHZ. This is graphically represented for the first four rotational frequencies in CO in Figure 43.
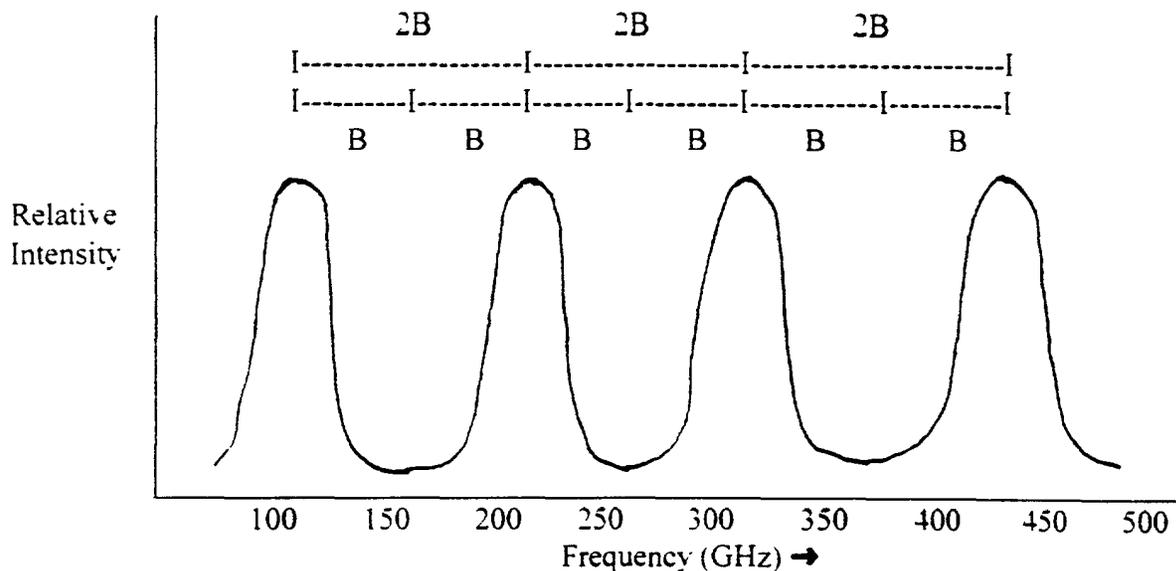
Figure 43. Graphical representation of fine structure spectrum showing the first four rotational frequencies for CO in the ground state. The difference (heterodyne) between the molecular fine structure rotational frequencies is 2 X the rotational constant B (ie. $f_2 - f_1 = 2B$). In this case B = 57.6 GHz (57,635.970 MHZ).

Now this is interesting for several reasons. The rotational constant B listed in so many databases is equal to one half of the difference between rotational frequencies for a molecule. That means that B is the first *subharmonic* frequency to the fundamental frequency - 2B - which is the heterodyned difference between all the rotational frequencies. The rotational constant B listed for carbon monoxide is 57.6 GHz (57,635.970 MHZ). This is basically half of the 115 GHz difference between the rotational frequencies. If we want to stimulate a molecule's rotational levels we can use 2B, which is the fundamental first generation heterodyne, or we can use just B, which is the first subharmonic of that heterodyne.

This is interesting for another reason as well. If you talk to a spectroscopist or physicist, they will tell you that if you want to use microwaves, you will be restricted to stimulating levels at or near the ground state of the molecule (n = 0 in Figure 37.). They will say that as you progress upward in Figure 38 to the higher electronic and vibrational levels, you are going to be

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necessarily in the infra-red, visible, and ultraviolet regions. The reason this is so interesting is that it is not true.

Take a look at Figure 38 again. The rotational frequencies are evenly spaced out no matter what electronic or vibrational level you look at. The even spacing in this diagram was not done just to make it look pretty. The rotational frequencies *actually are* evenly spaced out as you progress upwards through all the higher vibrational and electronic levels. Take a look at Figure 44. which lists the rotational frequencies for lithium fluoride (LiF) at several different rotational AND vibrational levels.

Figure 44. Rotational Frequencies for Lithium Fluoride (LiF)[20]

Vibrational level	Rotational Transition	Frequency (MHZ)
0	0 → 1	89,740.46
0	1 → 2	179,470.35
0	2 → 3	269,179.18
0	3 → 4	358,856.19
0	4 → 5	448,491.07
0	5 → 6	538,072.65
1	0 → 1	88,319.18
1	1 → 2	176,627.91
1	2 → 3	264,915.79
1	3 → 4	353,172.23
1	4 → 5	441,386.83
2	0 → 1	86,921.20
2	2 → 3	173,832.04
2	3 → 4	260,722.24
2	4 → 5	347,581.39
3	1 → 2	171,082.27
3	2 → 3	256,597.84
3	3 → 4	342,082.66

The differences between rotational frequencies, no matter what the vibrational level. is roughly 86.000 to 89,000 MHZ (86-89 GHz). By using a

microwave frequency between 86,000 MHZ and 89,000 MHZ, one can stimulate the molecule from the ground state levels, all the way up to its' highest levels.

Remember in the **Background** section where we talked about the experiment performed by Cirac and Zoller? They used a wire composed of metal atoms. The wire had a natural oscillatory frequency (NOF). The individual metal atoms also had unique oscillatory frequencies. The NOF of the atoms and the NOF of the wire heterodyned by adding and subtracting, the way all frequencies heterodyne,

$$NOF_{atom} - NOF_{wire} = Subtracted\ Frequency_{atom-wire}.$$

When they stimulated an atom on the wire with the Subtracted Frequency$_{atom-wire}$, it heterodyned (added) with the NOF$_{wire}$ to produce NOF$_{atom}$, the natural oscillatory frequency of the atom,

$$Subtracted\ Frequency_{atom-wire} + NOF_{wire} = NOF_{atom}.$$

The rotational frequencies of molecules can be manipulated the same way. The first rotational level has a natural oscillatory frequency (NOF) of 89,740 MHZ. The second rotational level has a NOF of 179,470 MHZ.

$$NOF_{rotational\ 1 \to 2} - NOF_{rotational\ 0 \to 1} = Subtracted\ Frequency_{rotational\ 2-1}.$$

$$179,470\ MHZ - 89,740\ MHZ = 89,730\ MHZ.$$

The NOFs of the rotational frequencies heterodyne by adding and subtracting, the way all frequencies heterodyne. The two rotational frequencies heterodyne to produce a subtracted frequency. This subtracted frequency happens to be exactly twice as big as the derived rotational constant "B" listed in nuclear physics and spectroscopy manuals. When you stimulate the first rotational frequency in the molecule with the Subtracted Frequency $_{rotational\ 2-1}$, it will heterodyne (add) with the NOF$_{rotational\ 0 \to 1}$ (first rotational frequency) to produce NOF$_{rotational\ 1 \to 2}$, the natural oscillatory frequency of the molecule's second rotational level.

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Subtracted Frequency $_{rotational\ 2-1}$ + NOF$_{rotational\ 0\rightarrow1}$ = NOF$_{rotational\ 1\rightarrow2}$

$$89{,}730\ \text{MHZ} \quad + \quad 89{,}740\ \text{MHZ} \quad = \quad 179{,}470\ \text{MHZ}$$

Since the rotational frequencies are evenly spaced harmonics, the subtracted frequency will also add with the second level NOF to produce the third level NOF. It will add with the third level NOF to produce the fourth level NOF. And so on and so on. By using one single microwave frequency you will stimulate all the rotational levels in a vibratory band.

Now if you excite all the rotational levels for a vibrational frequency, you will excite the vibrational frequency also. And if you excite all the vibrational levels for an electronic level, you will excite the electronic level as well. Thus, one can drive up into the highest levels of the electronic and vibrational structure of the molecule using a single microwave frequency. That is why the spectroscopists are wrong in stating that the use of microwaves restricts you to the ground state of the molecule. If you are trying to resonate **directly** with an upper vibrational or electronic level you cannot use a microwave frequency. If, however, you imitate a mechanism of action from the catalysts - namely resonating with target species **indirectly** through heterodynes, you can use a microwave frequency to energize an upper level vibrational or electronic state. With an understanding of the simple processes of heterodyning it becomes readily apparent why microwave frequencies do not really limit one to the ground state levels of molecules.

Catalysts use this trick, of stimulating target species indirectly by zapping them with heterodyned frequencies (harmonics). Catalysts also stimulate the target species by direct resonance with the fundamental frequency of interest. Here the rotational frequencies give us a bonus. Take a look at the first frequency in Figure 42. The first rotational frequency for CO is 115 GHz. The heterodyned difference between rotational frequencies is also 115 GHz. The first rotational frequency and the heterodyned difference between frequencies are identical. All of the upper level rotational frequencies are harmonics of the first frequency. This relationship is not as apparent when one deals only with the rotational constant "B", but a frequency based analysis makes it easier to see.

Take a look at the first level rotational frequencies for LiF as well. It is nearly identical to the heterodyned difference between it and the second level rotational frequency. The rotational frequencies are sequential harmonics of the first rotational frequency.

Now if you stimulate a molecule with a frequency equal to 2B, the heterodyned harmonic difference between rotational frequencies, you will kill two birds with one stone. You will resonate with all the upper rotational frequencies *indirectly* through heterodynes, and you will also resonate *directly* with the first rotational frequency.

There are a whole host of constants used in spectroscopy that relate in some way or another to the frequencies of atoms and molecules, just as the rotational constant "B" relates to the harmonic spacing of rotational fine structure molecular frequencies. The alpha (α) rotation-vibration constant is a good example of this. The alpha rotation-vibration frequency constant is related to slight changes in the frequencies for the same rotational level, when the vibrational level changes. Take a look at the frequencies for the same rotational levels, but different vibrational levels of LiF in Figure 44. This has been reformatted in Figure 45. The frequencies are almost the same, but vary by a few percent as one moves between vibrational levels. The rotational transition 0 → 1 has frequency 89,740.46 MHZ at vibrational level 0. At vibrational level 1, the 0 → 1 transition is 88,319.18 MHZ, and at vibrational level 2 the 0 → 1 transition is 86,921.20 MHZ. These slight differences between the same J rotational level for different vibrational levels are related to harmonics of the alpha frequency constant.

Figure 45. Rotational and Vibrational Frequencies for LiF

Rotational Transition				
0 → 1	89,740.46	88,319.18	86,921.20	
1 → 2	179,470.35	176,627.91	173,832.04	171,082.27
2 → 3	269,179.18	264,915.79	260,722.24	256,597.84
3 → 4	358,856.19	353,172.23	347,581.39	342,082.66
4 → 5	448,491.07	441,386.83		
5 → 6	538,072.65			
Vibrational Level	0	1	2	3

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Consider the rotational and vibrational states for OCS shown in Figure 46.[9] This figure shows the same rotational level (J = 1 → 2) for different vibrational states in the OCS molecule. For the ground vibrational (000) level. J = 1 → 2 transition; and the excited state (100) J = 1 → 2 transition, the difference between the two frequencies is equal to 4 X alpha$_1$ ($4\alpha_1$). In another excited state, the frequency difference between the ground vibrational (000) level. J = 1 → 2 transition, and the center of the two l-type doublets 4 X alpha$_2$ ($4\alpha_2$). In a higher excited vibrational state, the frequency difference between (000) and (02^00) is 8 X alpha$_2$ ($8\alpha_2$). Thus it can be seen that the rotation-vibration constants "α" are actually harmonic molecular frequencies. Stimulating a molecule with an α frequency or a harmonic of it will either directly resonate with or indirectly heterodyne harmonically with various rotational-vibrational frequencies for the molecule.
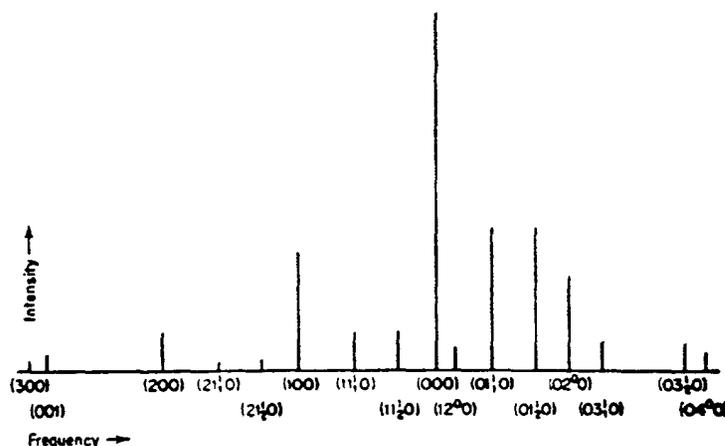
Figure 46[9]. Rotational transition J = 1 → 2 for the triatomic molecule OCS. The vibrational state is given by vibrational quantum numbers in brackets ($v_1 v_2 v_3$), v_2 having a superscript $|l|$. In case $l = 1$. a subscript 1 is applied to the lower-frequency component of the l-type doublet, and 2 to the higher-frequency component. The two lines at (01^10) and (01^10) are an l-type doublet, separated by q_l..

Another interesting constant is the l-type doubling constant. This can also be seen in Figure 45. Just as the atomic frequencies are sometime split into doublets or multiplets, the rotational frequencies are also sometimes split into doublets. The difference between them is call the l-type doubling constant. These constants are usually smaller (lower frequency) than the α constants. For OCS the α constants are 20.56 and 10.56 MHZ, while the l-type doubling constant is 6.3 MHZ. These frequencies are all in the radiowave portion of the electro-magnetic spectrum.

Well after that lengthy (and hopefully not too boring) discourse on fine structure frequencies of atoms and molecules, this seems like a good time to come up for a breath of fresh air, and discuss just what all this has to do with spectral catalysts and chemical reactions. We shall begin by considering the case of atomic fine structure frequencies and splitting frequencies. From there we will move on to applications of molecular fine structure frequencies.

By way of review, the electronic frequencies seen in the atomic spectra are not neat crisp individual curves. If we look at them in sufficient detail, we see that each curve is made up of several other curves spaced so closely together that they just look like one curve or line on a conventional spectrum. The 456 THz frequency for hydrogen is actually made up of 7 different but closely spaced frequencies. These are the fine structure frequencies. The amount that the closely spaced frequencies are split apart is called the fine splitting frequency.

Energy is transferred by two fundamental frequency mechanisms. If the frequencies are the same, then energy transfers by direct resonance. Energy can also transfer indirectly by heterodyning, ie. the frequencies match after having been added or subtracted with another frequency. The direct or indirect resonant frequencies do not have to match exactly. If they are merely close, a lot of energy will still transfer.

In our reaction combining hydrogen and oxygen to form water, we learned that energizing the reaction intermediates of atomic hydrogen and the hydroxy radical are crucial to sustaining the reaction. The catalyst platinum energizes both reaction intermediates by directly and indirectly resonating with them. Platinum also energizes the intermediates at multiple energy levels, creating the conditions for energy amplification. Let's say we want to copy platinum's mechanism of action by making use of atomic fine structure frequencies.

If we directly resonate with the fine structure frequencies we will simply resonate with the same frequencies we discussed earlier with only slight variations between the frequencies (456.676 and 456.686 THz for example). This is no different from what we did earlier and has no advantages to what we already know.

If we indirectly resonate with the fine structure frequencies, however, it is another story altogether. How do we indirectly resonate with the atomic fine structure frequencies? By using the fine splitting frequencies which are

simply the differences or heterodynes between the fine structure frequencies. Look at the hydrogen 456 THz fine structure and fine splitting frequencies for hydrogen (Figures 30, 32, and 34).

$$456.686 \text{ THz} - 456.676 \text{ THz} = 0.0102 \text{ THz} = 10.2 \text{ GHz}$$

If we irradiate hydrogen atoms with 10.2 GHz electromagnetic energy (microwaves), we will energize the 456 THz electronic spectrum frequency by resonating with it indirectly. The 10.2 GHz will add to 456.676 THz to produce the resonant frequency of 456.686 THz. The 10.2 GHz will also subtract from the 456.686 THz to produce the resonant frequency of 456.676 THz. Thus zapping a hydrogen atom with 10.2 GHz will energize its' overall 456 THz frequency.

If we want to use a combination of mimicked catalyst mechanisms, we can try the following: 1) resonate with the hydrogen atom frequencies indirectly through heterodynes (fine splitting frequencies); and 2) resonate with the hydrogen atom at multiple frequencies. We would do this by using a combination of microwave frequencies either simultaneously, in sequence, or in chirps or bursts. For instance we could use the individual microwave frequencies of 10.87 GHz, 10.2 GHz, 3.23 GHz, 1.38 GHz, and 1.06 GHz in a sequence. If we wanted to use radiowave frequencies, we could use 239 and 448 MHZ in sequence. There are many fine splitting frequencies for hydrogen not listed here, so depending on the frequency range of our equipment, we can Tailor the chosen frequencies to the capabilities of our equipment.

Another way to deliver multiple electromagnetic energy frequencies would be to use a lower frequency as a carrier wave for a higher frequency. This can be done for instance by producing 10.2 GHz EM energy in short bursts, with the bursts coming at a rate of 239 MHZ. This can also be done by continuously delivering 10.2 GHZ EM energy and by varying the amplitude at a rate of 239 MHZ.

Thus by mimicking the mechanism of action of catalysts and by making use of the atomic fine structure and splitting frequencies we can energize upper levels of atoms using microwave and radiowave frequencies. By knowingly energizing particular atoms, we catalyze and guide the reactions to desired end products. Depending on the circumstances, the option to use lower frequencies may have many advantages. Lower frequencies have much better penetrance into large reaction spaces and volumes, and may be better

suited to large scale industrial applications. Lower frequencies may be easier to deliver with portable, compact equipment, as opposed to large, bulky equipment for higher frequencies such as lasers. The choice of frequencies may be for as simple a reason as avoiding interference from other sources of EM energy. In any event, an understanding of the basic processes of heterodyning and fine structure splitting frequencies confers far greater flexibility in our design of spectral catalyst systems, than simply reproducing frequency for frequency, the spectrum of a physical catalyst. And it allows us to make full use of the entire range of frequencies in the electromagnetic spectrum.

Last but not least, we will discuss applications of molecular fine structure frequencies. By way of review, the electronic and vibrational frequencies seen in the molecular spectra are not neat crisp individual curves. If we look at them in sufficient detail, we see that each curve is made up of several other curves spaced so closely together that they just look like one curve or line on a conventional spectrum. The closely spaced frequencies are produced by rotational motion of the molecule and are called the fine structure frequencies. The amount that the closely spaced frequencies are split apart is a harmonic of the rotational constant "B". The amount by which various frequencies for the same rotational level vary slightly is a harmonic of the α rotation-vibration constant. When a rotational frequency occurs as a doublet, they are split (heterodyned) by a frequency or harmonic called the l-type doubling constant.

Now let's go back to our hydrogen/oxygen reaction in terms of the molecular fine structure. We want to catalyze the reaction by duplicating the catalyst's mechanism of action in the microwave region. If your equipment is like mine and only goes up to 24 GHz, that does not give you a lot to work with. We know that platinum energizes the reaction intermediates of atomic hydrogen and the molecule hydroxy. The B frequency for hydroxy is 565.8 GHz. That means the actual heterodyned difference between the rotational frequencies is 2B, or 1,131.6 GHz. My equipment will not go that high, or even as high as just the B frequency.

Interestingly, the α constant for hydroxy is 21.4 GHz. That frequency is within the range of my equipment. So you can fill a reaction flask with hydrogen and oxygen gas (we actually did this experiment) and irradiate it with 21.4 GHz. The gigahertz energy is a heterodyne of the rotational frequencies for the same rotational level but different vibrational level. The heterodyned frequency energizes the rotational frequencies, which energize the vibrational frequencies, which energize the electronic frequencies, which

catalyze the reaction.

Now what if my equipment could deliver 565.8 GHz, or even 1,131.6 GHz? We could irradiate the reaction flask with one of those frequencies. All of the rotational levels in the molecule would be energized, from the ground state all the way up. This copies a catalyst mechanism of action in 2 ways. The first way is by energizing the hydroxy radical and sustaining a crucial reaction intermediate to catalyze the formation of water. The second mechanism copied from the catalyst is to energize multiple levels in the molecule. Because the rotational constant B relates to the rotational frequency heterodynes *at all levels* in the molecule. using it also energizes *all levels* in the molecule. This potentiates the establishment of an energy amplification system such as occurs with the physical catalyst platinum.

If we are energizing a molecule with an *l*-type doubling constant, we can use that the same way we would use a fine splitting frequency from an atomic spectrum. The difference between the two frequencies in a doublet is a heterodyne, and zapping the doublet with its' heterodyne (splitting frequency) energizes the basic frequency.

Now if we want to get fancy, we can use combination frequencies and such, as we discussed for atomic fine structure. For instance, we could put in a constant central frequency of 1,131.6 GHz (the heterodyned difference between rotational frequencies for hydroxy) with a vibrato varying around the central frequency by $\pm$ 21.4 GHz (the α constant harmonic for variations between rotational frequencies.) We could use 1,131.6 GHz EM energy in short bursts, with the bursts coming at a rate of 21.4 GHz.

Since there is slight variation between rotational frequencies for the same level, we can use that frequency range to construct bursts. Let's say that the largest B is 565.8 GHz, giving a rotational frequency heterodyne of 1,131.6 GHz. Suppose that the smallest B is 551.2 GHz giving a rotational frequency heterodyne of 1,102 GHz. We can transmit "chirps" starting as 1,100 GHz and increasing in frequency to 1,140 GHz. If we really want to get fancy, we can set the transmitter to "chirp" at a rate of 21.4 GHz.

In any event, there are many ways to make use of the atomic and molecular fine structure frequencies, with their attendant heterodynes and harmonics. An understanding of catalyst mechanisms of action enables us to move our spectral catalyst system from the high frequency ultraviolet and visible light regions. down into the more manageable microwave and radiowave regions. At the very least. it gives us a way to calculate and determine the effects of microwave and radiowave energies on chemical reactions.

Hyperfine Frequencies

Hyperfine frequencies are just like the fine structure frequencies, only different. Fine structure frequencies can be seen by magnifying a portion of a standard frequency spectrum. Hyperfine frequencies can be seen by magnifying a portion of a fine structure spectrum. Fine structure frequencies occur at lower frequencies than the electronic spectra, primarily in the infrared and microwave regions of the electromagnetic spectrum. Hyperfine frequencies occur at even lower frequencies than the fine structure spectra, primarily in the microwave and radio wave regions of the electromagnetic spectrum. Fine structure frequencies are caused by the electron interacting with its' own magnetic field. Hyperfine frequencies are caused by the electron interacting with the nucleus.

Remember the SF_6 molecule we looked at in the fine structure section? The rotation-vibration band and fine structure are shown again in Fig. 47.[2]
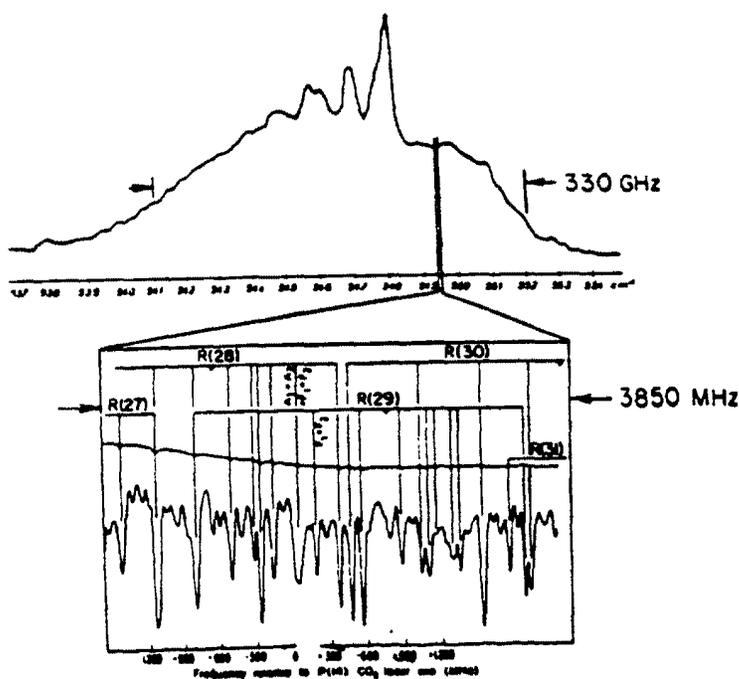
Figure 47. SF_6 rotation-vibration band and fine structure frequencies.[2]

The fine structure frequencies are seen by magnifying a small section of the standard vibrational band spectrum. In many respects, looking at fine structure frequencies is like using a magnifying glass to look at a standard spectrum. When we magnify what looks like a flat and uninteresting portion

of a standard vibrational frequency band, we see many lower frequency curves. These lower frequency curves are the fine structure curves.

Now what would we see if we took a small uninteresting portion of the fine structure spectrum, and magnified it the same way we magnified the regular spectrum? A small portion of the SF_6 fine structure spectrum is magnified below in Figure 48.[2]
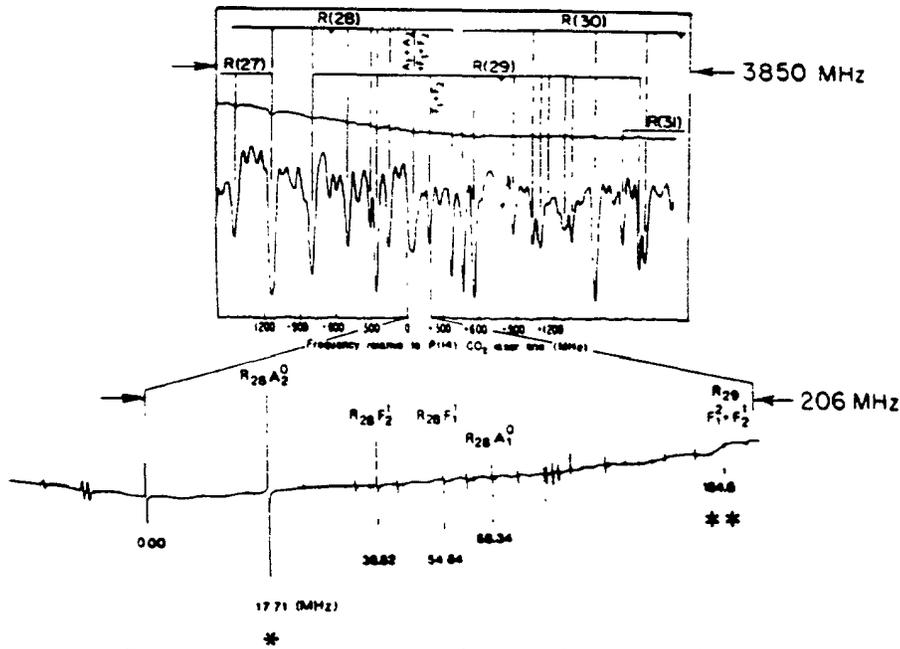
Figure 48. SF_6 fine structure spectrum with a small portion from zero to 300 magnified.[2]

Once again, we see that when a small uninteresting portion of the spectrum is magnified, we see many curves of even lower frequency. This time we magnified the fine structure spectrum, instead of the regular vibrational spectrum. What we see is that there are even more curves of even lower frequency. What if we magnify these other lower frequency curves? Figure 49[2] shows a magnification, of the two curves marked with asterisks in Fig. 48.

What looks like a single crisp curve in Figure 48 turns out to be a series of several curves spaced very close together. These are the hyperfine frequency curves. Remember that when we looked at the 456 THz curve from the electronic spectrum for hydrogen, we discovered that instead of it being a single crisp curve, it was really made up of seven curves spaced very close together (Fig. 30.)? We see the same thing when we magnify a fine structure curve. It is really made up of several more curves spaced very close together.

These other curves spaced even closer together are call the hyperfine frequencies.

Take another look at the spacing of the hyperfine frequencies. The curves are spaced very close together at somewhat regular intervals. The small amount that the hyperfine curves are split apart is called the hyperfine splitting frequency. The hyperfine splitting frequency is a heterodyne. The concept is identical to the idea of the fine splitting frequency. The difference between two curves that are split apart is called a splitting frequency. As always, the difference between two curves is a heterodyned frequency. So hyperfine splitting frequencies are all heterodynes of hyperfine frequencies.
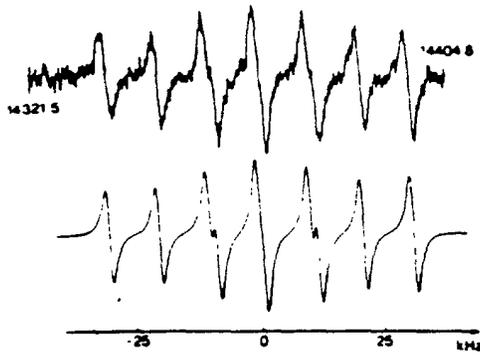
a)
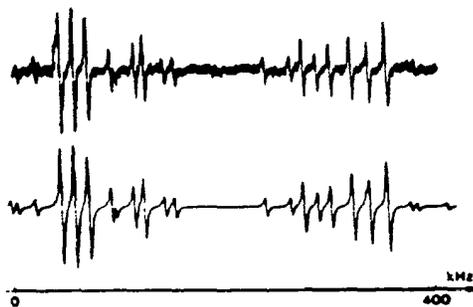
b)

Figure 49. Magnification of two curves from fine structure of SF.. showing hyperfine structure frequencies. Note the regular spacing of the hyperfine structure curves. a) Magnification of curve marked with a single asterisk (*). b) Magnification of curve marked with a double asterisk (**).

Because the hyperfine frequency curves result from a magnification of the fine structure curves, they occur at only a fraction of the frequency seen in the fine structure curves and are thus lower. We need to clarify here this idea of frequencies being *larger* or **smaller**, *higher* or **lower**. When a frequency is *large*, it is said to be a *high* frequency. Conversely, a **small** frequency is **low**. This perspective of frequencies comes mainly from the way we hear sounds. A *large* frequency sound at 20,000 Hz has a *high* pitch. A **small** frequency sound at only 200 Hz has a **low** pitch. The *high* frequency sound - 20,000 Hz - is much *larger* numerically (100 X) than the **low** pitched sound at 200 Hz. Because of the way we hear sounds, we call a *large* frequency number *high*, and a **small** frequency number **low**.

Even though we do not hear electromagnetic waves, we apply the same sort of jargon to the electromagnetic spectrum. An EM frequency of one million hertz is *high* compared to an EM frequency of only one thousand hertz. We call an EM frequency of one thousand hertz **low**. This terminology has an impact on the way we discuss fine and hyperfine frequencies.

Consider the hydrogen atom for which there is an electronic spectrum frequency of 2466 THz. When we magnify the 2466 THz curve to look at the fine structure, we see that it is made of at least two different curves spaced very close together. The two curves are just 0.01087 THz apart, hence the splitting frequency for the 2466 THz curves is 0.01087 THz.. Because the fine structure curves are spaced so close together, they are split apart by only a fraction of a terahertz (10^{12} hertz). Since 0.01087 THz is **smaller** than 2466 THz, it is a **lower** frequency.

If we move the decimal point over three places, 0.01087 THz (10^{12} hertz) becomes 10.87 GHz (10^9 hertz). Gigahertz frequencies are **lower** (**smaller**) than terahertz frequencies. We usually use an exponent with a number, such as 10^9 or 10^{12}, so that we do not have long strings of zeroes with our numbers.

Now getting back to spectral frequencies, if we magnify a regular spectrum we get fine structure frequencies. The fine structure frequencies are really just several curves, spaced very close together around the regular spectrum frequency. If we magnify fine structure frequencies we get hyperfine frequencies. The hyperfine frequencies are really just several more curves, spaced very close together around the fine structure frequency. The closer together the curves are, the smaller the distance or frequency separating them. Now the distance separating any two curves is a heterodyned frequency. So the closer together any two curves are, the **smaller** is the heterodyned

frequency between them. The distance between hyperfine frequencies - the amount that they are split apart - is the hyperfine splitting frequency. It is also called a constant or interval.

The electronic spectrum frequency of hydrogen is 2466 THz. The 2466 THz frequency is made up of fine structure curves spaced 10.87 GHz (0.01087 THz) apart. Thus the fine splitting frequency is 10.87 GHz. Now the fine structure curves are made up of hyperfine curves. These hyperfine curves are spaced just 1420, 178, 59, 52, 23, 18, 7, 4.2, and 2.7 MHz (10^6 hertz) apart. Thus 1420, 178, 59, 52, 23, 18, 7, 4.2, and 2.7 MHz are all hyperfine splitting frequencies for hydrogen. The hyperfine frequencies are spaced even closer together than the fine structure frequencies, so the hyperfine splitting frequencies are **smaller** and **lower** that the fine splitting frequencies.

The hyperfine splitting frequencies are usually written as megahertz (MHz = 10^6 hertz). Most of the frequency numbers are **smaller** than a gigahertz and are much **smaller** than a terahertz.

Thus the hyperfine splitting frequencies are **lower** than the fine splitting frequencies. This means that rather than being in the infra-red and microwave regions, as the fine splitting frequencies are, they are in the microwave and radiowave regions. These lower frequencies are in the MHz (10^6 hertz) and Khz (10^3 hertz) regions of the electromagnetic spectrum. Several of the hyperfine splitting frequencies for hydrogen are shown below in Fig. 50.[6]
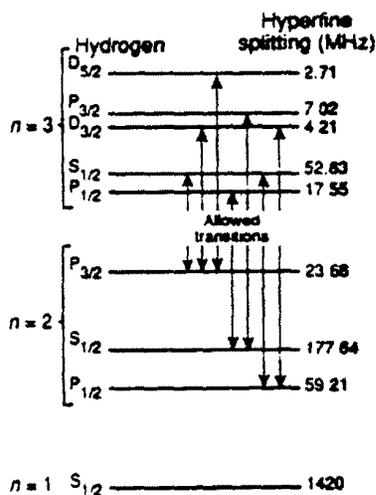
Figure 50.[7] Hyperfine structure in the n = 2 to n = 3 transition of hydrogen. The hyperfine splitting (MHz) are indicated at the right-hand side of each level.

The hyperfine splitting frequency for hydrogen at 1420 MHz has played an important role in the development of science and astronomy. Microwave radiation due to transitions between the hyperfine components of atomic hydrogen in interstellar space[9] was first detected in 1951. The radiation has a wavelength of around 21 cm. It penetrates interstellar space and even the earth's atmosphere rather easily. The movement of various objects in our galaxy, the Milky Way, has been assessed by examining this hyperfine radiation produced by interstellar hydrogen gas. For instance, hydrogen hyperfine frequency observations have shown that in certain directions throughout our galaxy, there are several strips of gas each moving systematically at velocities matching the arms of a rotating spiral nebula[9]. It is from this evidence that astronomers have concluded that our galaxy is formed in the shape of a giant two-armed spiral, similar in shape to the yin-yang shape of oriental tradition.

Let's look at another example of hyperfine frequencies. In Fig. 51, the hyperfine frequencies for CH_3I are shown.[9] These frequencies are a magnification of the fine structure frequencies for the molecule. Since fine structure frequencies for molecules are actually the rotational frequencies, what we are really looking at here is the hyperfine splitting of rotational frequencies. In this particular figure, we are looking at the hyperfine splitting of just the $J = 1 \rightarrow 2$ rotational transition. The splitting between the two tallest curves is less than 100 MHz.
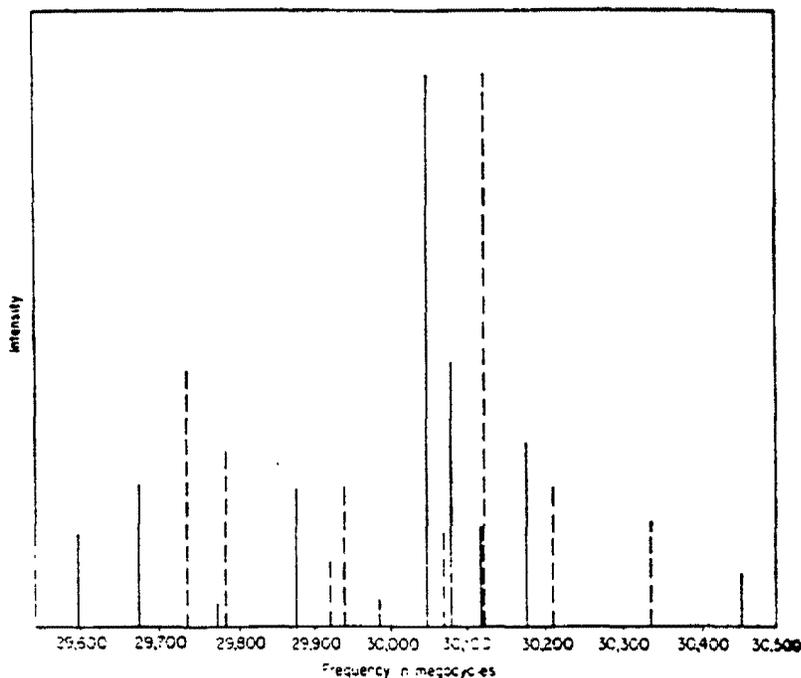
Figure 51. Hyperfine structure in the $J = 1 \rightarrow 2$ rotational transition of CH_3I.

Figure 52[9] shows another example for the molecule ClCN. This set of hyperfine frequencies is from the J = 1 → 2 transition of the ground vibrational state. The scale for "Spectrum under high resolution" shows a bar with the notation 1 mc. This means that the bar represents 1 MHz. This particular reference uses mc for megacycle for megahertz. Notice that the hyperfine frequencies are separated by just a few megahertz, and in a few places by less than even one megahertz.
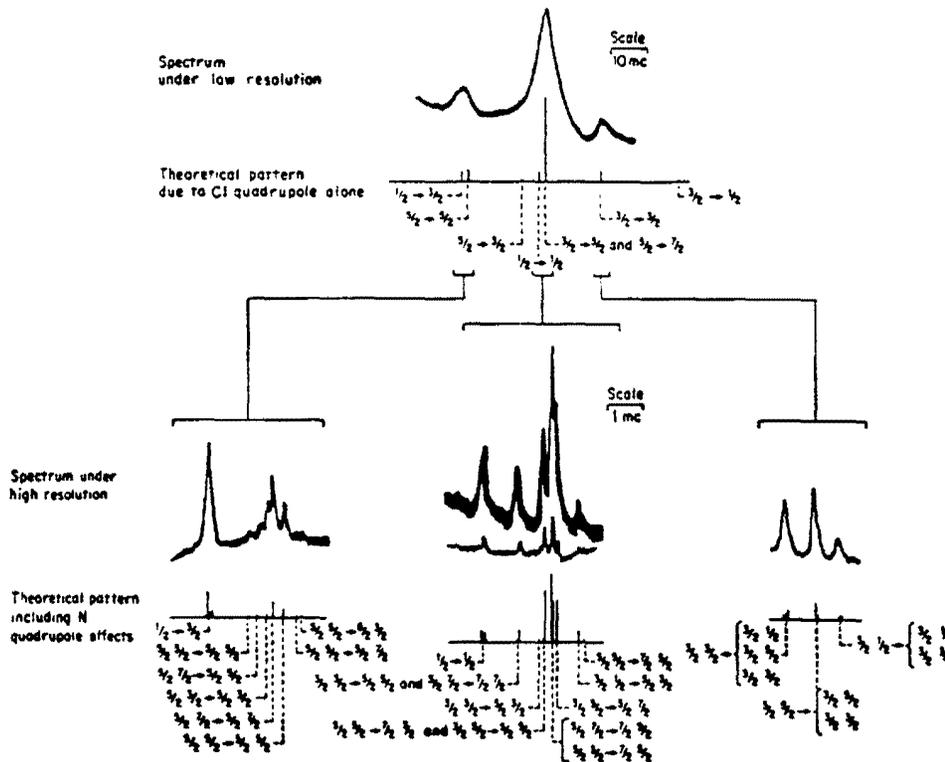
Figure 52.[9] - Hyperfine structure of the J = 1 → 2 transition for ClCN in the ground vibrational state. Experimental values are compared to theoretical patterns.

The energy-level diagram and spectrum of the J = ½ → 3/2 rotational transition for NO is shown in Figure 53.[9] The scale of the "Observed spectrum" is in "Mc", which means it is megahertz (MHz).

In Fig. 54[9], the hyperfine frequencies for NH_3 are shown. Notice that the frequencies are spaced so close together that the scale at the bottom is in kilohertz (Kc/sec). The hyperfine features of the lines were obtained using a beam spectrometer.

Calculated spectrum

Observed spectrum
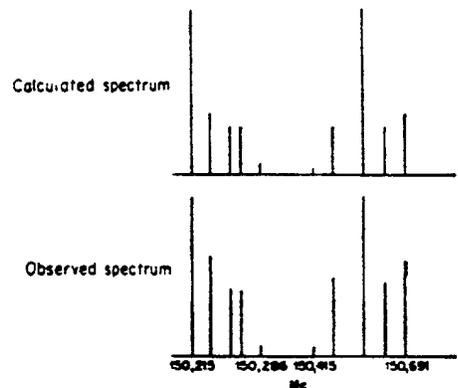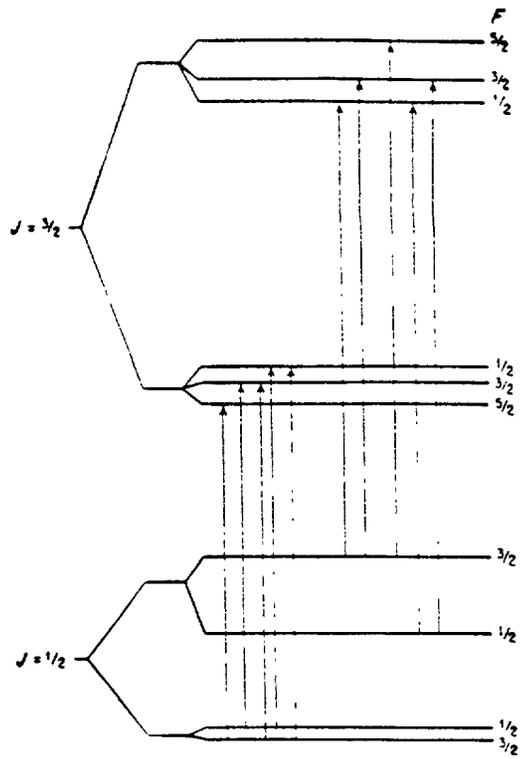
Figure 53.[9] - Energy level diagram and hyperfine frequencies for the NO molecule.
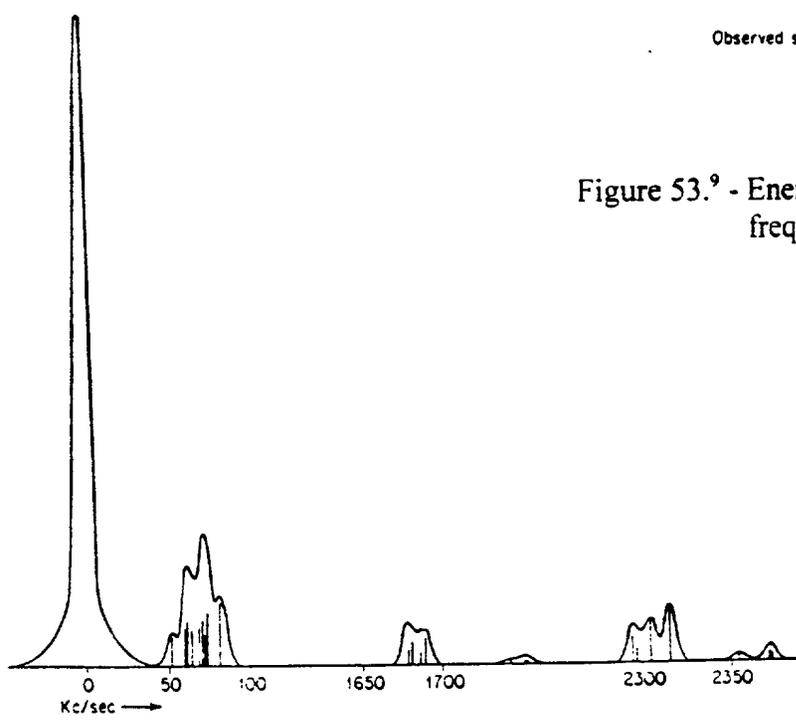
Figure 54.[9] - Hyperfine frequencies for NH₃.

You may remember that the fine structure frequencies are sometimes split into doublets. The same thing happens with hyperfine frequencies. In a place where we would normally expect to find only a single hyperfine frequency curve, there are two curves instead - one on either side of the location where we expected to find the single hyperfine frequency. Hyperfine doubling is shown below in Figure 55[9]. This hyperfine spectrum is also from NH_3, this time the third and fourth (J = 3 and 4) rotational levels. The doubling can be seen most easily in the J = 3 curves. There are two sets of short curves, a tall one, and then two more short sets. Each of the short sets of curves is generally located where we would normally expect to find just one curve. There are two curves instead, one on either side of the main curve location. Each set of curves is a hyperfine doublet.
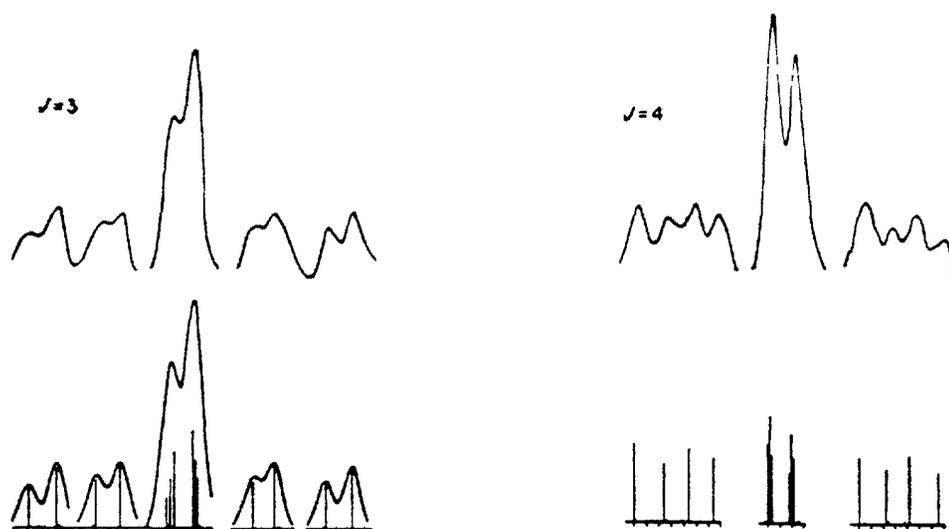
Figure 55.[9] - Hyperfine structure and doubling of the NH_3 spectrum for rotaitonal levels J = 3 and J = 4. The upper curves show experimental data, while the lower curves are derived from theoretical calculations. Frequency increases from left to right in 60 KHz intervals.

There are different notations to indicate the source of the doubling such as l - type doubling, K doubling, and Λ doubling, and they all have their own constants or intervals. Without going into all the nuclear theory behind these various types of doublets, suffice it to say that the interval between any two hyperfine doublet curves is a heterodyne, and thus all of these doubling constants represent frequency heterodynes.

You may recall that the fine structure frequencies were caused by the electron interacting with its' own magnetic field. The general rule of thumb for hyperfine frequencies is that they are caused by the electron interacting

with the magnetic field of the nucleus. It is actually a bit more complicated than that because other factors also contribute to hyperfine structure, such as finite nuclear mass and electric charge distribution in the nucleus, variation of the electron potential from a coulomb potential when electrons are within the nuclear radius, isotropic polarization of the nucleus by electron fields, and nuclear quadropole moments. The predominant factor for the hyperfine frequencies of any particular spectrum, depends on whether the spectrum is for an atom or a molecule, and on the type and arrangement of the various atoms that make up the molecule. Entire books in theoretical physics are written on this very subject, complete with horribly long and complicated equations, so we won't go into all this in a spectral catalyst paper. We will simply use the general rule of thumb that fine structure is caused by the electron interacting with its' own magnetic field, while the hyperfine frequencies are caused by the electron interacting with the nucleus's magnetic field.

Well, now that you know all about hyperfine frequencies, you are probably wondering just what this has to do with spectral catalysts and catalyzing reactions. Or perhaps you have a pretty good idea where this is all going because you noticed that heterodynes keep popping up all over whenever we talk about hyperfine frequencies.

A frequency in an atom or molecule can be stimulated directly or indirectly. Let's say we want to stimulate the 2466 Thz frequency of hydrogen for some reason. We could get an ultraviolet laser and irradiate the hydrogen with 2466 Thz electromagnetic radiation. This would stimulate the atom directly. If we only had microwave equipment, we could use hydrogen's fine structure splitting frequency of 10.87 Ghz. The gigahertz frequency would heterodyne (add or subtract) with the two closely spaced fine structure curves at 2466, and stimulate the 2466 Thz frequency band. This would stimulate the atom indirectly.

Now what if our equipment did not even go up that high? What if our microwave only had a range from 0.5 to 4 Ghz? In this case, we could use the hyperfine splitting frequency for hydrogen at 1.42 Ghz. The 1.42 GHz frequency would heterodyne (add or subtract) with the two closely spaced hyperfine frequency curves at 2466, and stimulate the fine structure curves at the 2466 Thz frequency band. Stimulation of the fine structure curves would in turn lead to stimulation of the 2466 Thz band for the hydrogen atom.

If we had only radio equipment, and no microwaves technology we could use the hyperfine splitting frequencies for hydrogen in the radio wave

portion of the electromagnetic spectrum. We could set up a radio wave pattern with 2.7 MHz, 4.2 MHz, 7 MHz, 18 MHz, 23 MHz, 52 MHz, and 59 MHz. This would stimulate several different hyperfine frequencies for the 2466 Thz band of hydrogen, and it would stimulate them all at the same time. This would cause stimulation of the fine structure frequencies, which in turn would stimulate the 2466 THz electronic band in the hydrogen atom.

Depending on our equipment and design constraints we could use some of the delivery mode tricks we discussed in the fine structure section. For instance, one of the lower frequencies could be a carrier frequency for the upper frequencies. A continuous frequency of 52 MHz could be varied in amplitude at a rate of 2.7 MHz. Or a 59 MHz frequency could be pulsed at a rate of 4.2 MHz. There are all kinds of ways these frequencies can be delivered, including different wave shapes, durations, intensity shapes, duty cycles, etc.

The point is, that when we have identified a frequency that we wish to copy for spectral catalyst purposes, we can stimulate that frequency by moving to whichever portion of the electromagnetic spectrum best suits our equipment and design requirements.

As a small aside, the scientific community has long maintained a schizophrenic perspective on the subject of low frequency electromagnetic waves interacting with matter. When it comes to nuclear physics, they readily admit that a 2.7 MHz frequency, with a wavelength several meters long, can affect an atom no larger than 10^{-10} meters in its' largest diameter. If that matter happens to be in a biologic organism, however, they steadfastly maintain that there is no way for the 2.7 MHz radiation to interact with the organism. They protest that there is no possible mechanism of action for a wavelength several meters long to interact with a human just 2 meters long. This is because for biologic organisms they consider only antenna type interactions, where the dimensions of the structure (human height) must be equivalent to or larger than the wavelength of the electromagnetic radiation.

*If hydrogen in a spectroscopy chamber can be stimulated by 2.7 MHz, then hydrogen in a human can be stimulated by this frequency as well. Once one understands spectral catalysts and the heterodyning effects of fine and hyperfine splitting frequencies on atoms and molecules, one must admit this as another mechanism for the interaction of electromagnetic radiation in **biologic organisms**.*

Biologic scientists divide electromagnetic radiation into ionizing radiation (ultraviolet and X-ray) and nonionizing radiation (visible light, infrared, microwave, and radio wave). Most believe that ionizing radiation can cause potentially damaging changes in biologic organisms, and hence should be avoided. They also believe that nonionizing radiation poses no threat to biologic organisms, as long as high power intensities are avoided, to prevent simple thermal injury from the passage of large amounts of energy.

This ignorance has been further compounded by the fact that even those scientists who DO believe that there are nonthermal effects from nonionizing radiation, haven't the slightest clue as to the mechanisms. They have no concept of the importance of frequency to chemical reactions, much less a concept of how lower frequency radiation can influence higher frequency biochemical events.

Thus the situation has evolved over the last 50 years wherein a minority of scientists consistently find evidence for a nonthermal effect of visible light, infrared light, microwaves, or radio waves. They rarely bother to measure the frequencies of the electrogmagnetic radiation under study, because they don't know that frequency is even important. Their critics assail their experimental and epidemiologic results as flukes and serrendipitous happenstance, because they cannot articulate a mechanism for their results.

As a consequence, the use of electromagnetic devices has proliferated, with no attention to the health effects of the radiation frequencies being used. This has led to an odd mixture of affects, for some of the randomly used frequencies confer a beneficial or protective effect on the biologic organism, while other frequencies produce damaging effects. For the same frequency, one power level may be beneficial, while the other power level may be damaging. Electromagnetic radiation per se is not bad for biologic organsims, but we need to be aware of frequency-specific effects before broadcasting them around the world willy-nilly.

Electric Fields

In the presence of an electric field, spectral frequency lines of atoms and molecules can be split, shifted, broadened, or changed in intensity. The effect of an electric field on spectral lines is called the "Stark Effect", in honor of its' discoverer, J. Stark. In 1913 Stark discovered that the Balmer series of hydrogen (curve II) was split into several different components, while using a high electric field in the midst of his hydrogen flame. In the intervening years, Stark's original observation has evolved into a separate branch of spectroscopy, namely the study of atoms and of molecular structure by measuring the changes in their spectral lines caused by an electric field.

In the preceding sections we learned that fine structure and hyperfine frequencies along with their low frequency splitting or coupling constants were caused by interactions *inside* the atom or molecule, between the electric field of the electron and the magnetic field of the electron or nucleus. The Stark effect is really quite similar, only instead of the electric field coming from *inside* the atom, it comes from *outside* instead. The Stark effect is just the interaction of an external electric field, from *outside* the atom or molecule, with the electric and magnetic fields already *inside* the atom or molecule.

When examining the Stark effect of electric fields, one must consider the effects on atoms, and the effects on molecules. One must also consider the nature of the electric field, such as whether it is static or dynamic. A static electric field is produced by a direct current. A dynamic electric field is time varying, and is produced by an alternating current. If the electric field is from an alternating current, then one must also consider the frequency of the alternating current compared to the frequencies of the atom or molecule.

In atoms, an external electric field perturbs the electron's charge distribution. This disturbance of the electron's own electric field induces a dipole moment in it (slightly lop-sided charge distribution). This lop-sided electron dipole moment then interacts with the external electric field. In other words, the external electric field first induces a dipole moment in the electron field, and then interacts with the dipole. The end result is that the atomic frequencies become split into several different frequencies. The amount the frequencies are split apart depends on the strength of the electric field - the stronger the electric field, the farther apart the splitting. This is shown in Figure 56[6], which diagrams the Stark effect for potassium. Note that the frequency splitting or separation of the frequencies (deviation from zero-field wavenumber) varies with the square of the electric field strength $(V/cm)^2$.
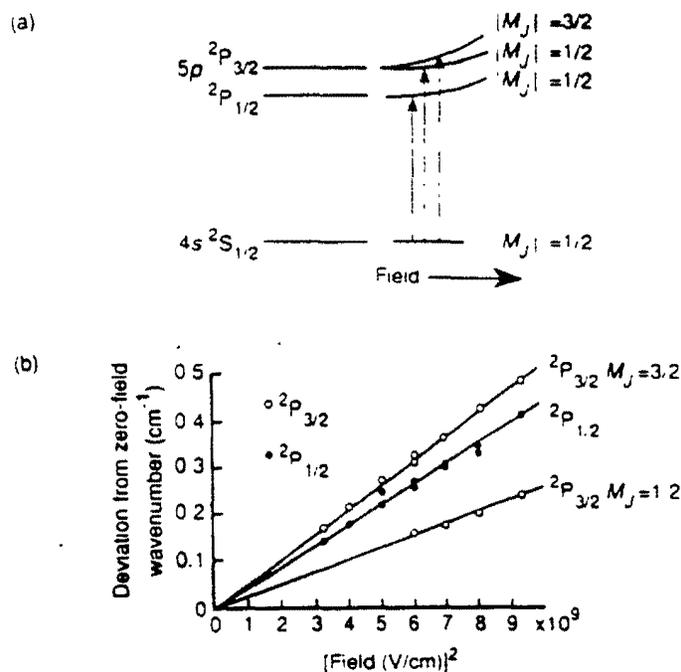
Figure 56[6] - The Stark effect for potassium. a) Schematic dependence of the 4s and 5p energy levels on the electric field. b) A graph plotting the deviation from zero-field positions of the 5p²P1/2,3/2 ← 4s²S1/2 transition wavenumbers against the square of the electric field.

When the splitting varies with the square of the electric field strength, it is called a "second order" Stark effect, or a quadratic Stark effect. Most atoms have second order or quadratic Stark effects. The notable exception to this is hydrogen. In the hydrogen atom the splitting is directly proportional to the electric field strength. This is called a "first order" Stark effect, or a linear Stark effect. Thus hydrogen exhibits linear, first order Stark effects.[24]

The mechanism for the Stark effect in molecules is a little simpler than it is in atoms. Most molecules already have an electric dipole moment (slightly uneven charge distribution). The external electric field simply interacts with the electric dipole moment already inside the molecule. The type of interaction - a first or second order Stark effect - is different for differently shaped molecules. For instance, most symmetric top molecules have first-order Stark effects.[9] Asymmetric rotors usually have second-order Stark effects.[9] Thus in molecules, as in atoms, the splitting or separation of the frequencies due to the external electric field, is proportional either to the electric field strength itself, or to the square of the electric field strength.

[24] Spectrochemical Analysis JD Ingle & SR Crouch. Prentice Hall. Englewood Cliffs, NJ. 1988
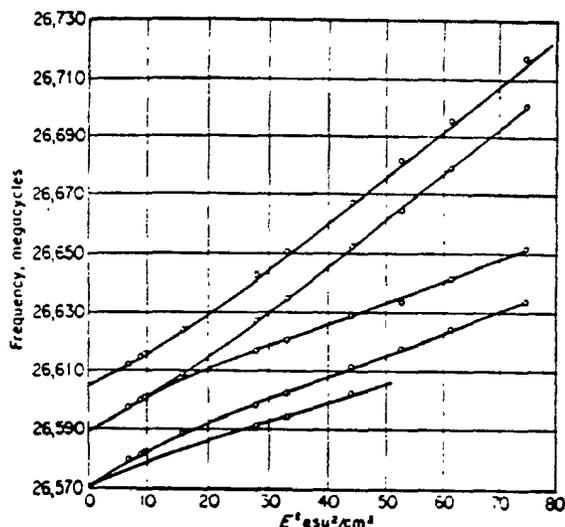
Figure 57[9]. - Frequency components of the J = 0→1 rotational transition for CH_3Cl, as a function of field strength. Frequency is given in megacycles (MHZ) and electric field strength (esu cm) is given as the square of the field, E^2, in $esu^2 cm^2$.

An example of this is shown in Figure 57[9], which diagrams how the molecule CH_3Cl responds to an external electric field. When the electric field is very small (less than 10), the primary effect is shifting of the three rotational frequencies to higher frequencies. As the field strength is increased (between 10 and 20), the three rotational frequencies split into five different frequencies. With continued increases in the electric field strength, the now five frequencies continue to shift to ever higher and higher frequencies. Some of the intervals or differences between the five rotational frequencies remain the same regardless of the electric field strength, while other intervals become progressively larger and higher. Thus a heterodyned frequency might stimulate rotational levels at one electric field strength, but not at another.

Another molecular example is shown in Figure 58[9]. This is a diagram of the Stark in effect in the OCS molecule which we examined in the **Fine Structure Frequencies** section (Figure 46). When we looked at OCS earlier we were looking at the J = 1→2 transition for several different vibrational levels, and at the slight differences in the same rotational frequency for different vibrational levels. The slight differences between the rotational frequencies were harmonics of the α constant. In Figure 58, we are looking at just one frequency, from the several frequencies shown in Figure 46. That one frequency is a single frequency when there is no external electric field. When an electric field is added, however, the single rotational frequency splits into two. The stronger the electric field is, the wider the splitting is between

the two frequencies. One of the new frequencies shifts up higher and higher, while the other frequency shifts lower and lower. Because the difference between the two frequencies changes when the electric field strength changes, a heterodyned frequency might stimulate the rotational level at one electric field strength, but not at another.
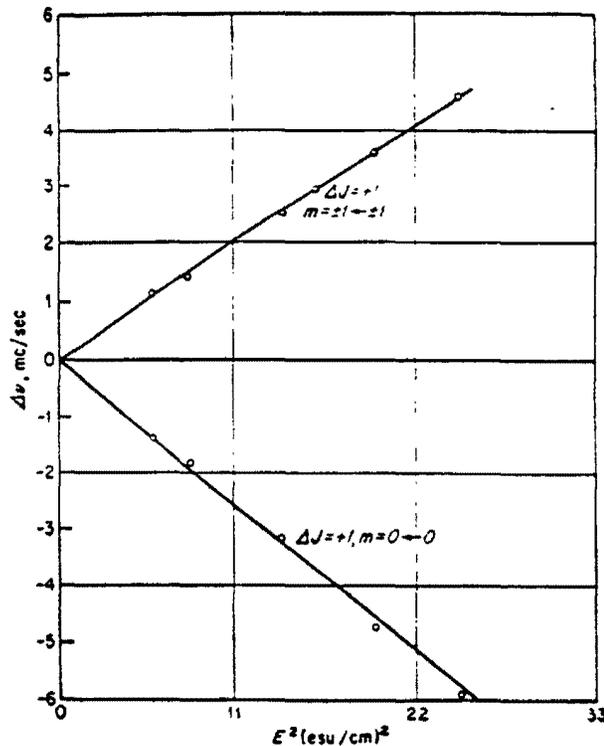
Figure 58[9]. - Theoretical and experimental measurements of Stark effects in the $J = 1 \rightarrow 2$ transition of the molecule OCS. The unaltered absolute rotational frequency is plotted at zero, and the frequency splitting and shifting is denoted as MHZ higher or lower than the original frequency.

Broadening and shifting of spectral lines occurs with the intermolecular Stark effect. The intermolecular Stark effect is produced by the electric field from surrounding atoms, ions, or molecules, affecting the spectral emissions of the species under study. In other words, the external electric field comes from *other* atoms and molecules. The other atoms and molecules are in constant motion, and so their electric fields are inhomogeneous in space and time. Instead of a frequency being split into several easily seen frequencies, the original frequency simply becomes much wider, encompassing all of what would have been the split frequencies. Remember our discussion on the effects of solvents and support materials? Many of those effects are the result of the intermolecular Stark effect.

The above examples demonstrated nicely how the Stark effect splits, shifts, and broadens spectral frequencies for atoms and molecules. The

intensities of the lines can also be affected. Some of these variations in intensity are shown in Figure 59[9]. The intensity variations depend on rotational transitions, molecular structure, and the electric field strength.
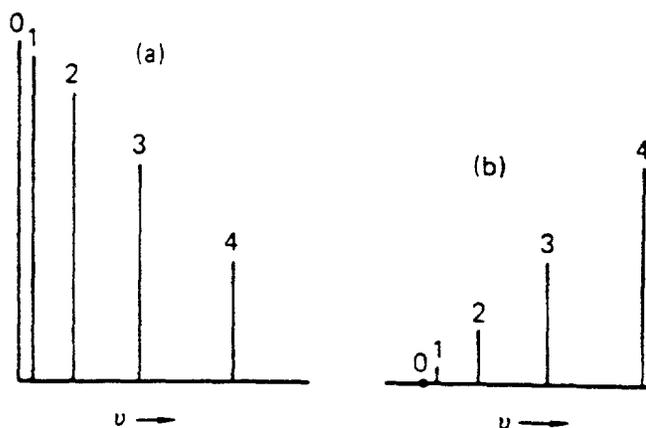
Figure 59[9]. - Patterns of Stark components for transitions in the rotation of an asymmetric top molecule. a) J = 4→5 transition; b) J = 4→4 transitions. The electric field is large enough for complete spectral resolution.

An interesting Stark effect is seen in a structure such as a molecule, which has hyperfine frequencies. Remember our rule of thumb - the hyperfine frequencies result from an interaction between the electron and the nucleus. This interaction can be affected by an external electric field. If the external electric field is weak, then the Stark energy is much less than the energy of the interaction between electron and nucleus, ie. the hyperfine energy.[9] The hyperfine lines are split into various new lines, and the separation between the lines is very small (low in frequency) compared to the original hyperfine splitting. This means that at low field strengths, the Stark effect produces Stark splitting at very low frequencies (radio and extra low frequencies).

If the external electric field is very strong, then the Stark energy is much larger than the hyperfine energy, and the molecule is tossed violently back and forth by the electric field. In this case the hyperfine structure is radically changed.[9] It is almost as though there is no hyperfine structure. The Stark splitting is identical to that which would have been observed if there were no hyperfine frequencies, and the hyperfine frequencies simply act as a small

perturbation to the Stark splitting frequencies.

If the external electric field is intermediate, then the Stark and hyperfine energies are equivalent. In this case, the calculations become very complex. Generally, the Stark splitting is around the same frequencies as the hyperfine splitting, but the relative intensities of the various components can vary rapidly with slight changes in the strength of the external electric field. Thus, at one electric field strength, a Stark frequency "A" could predominate in intensity, while at an electric field strength just 1% higher, a totally different Stark frequency "B" could predominate in intensity.

All of the preceding discussion on the Stark effect has concentrated on the effects due to a static electric field, such as one would find with a direct current. The Stark effects from a dynamic, or time-varying electric field produced by an alternating current are quite interesting and can be quite different. Just which of those affects appear, depends on the frequency of the electric field (alternating current) compared to the frequency of the atom or molecule in question. If the electric field is varying very slowly, such as with 60 Hz wall outlet electricity, then the normal or static type Stark effect occurs.

As the electrical frequency increases, the first frequency measurement it will begin to overtake is the line width (see Figure 16 for a diagram of line width). The line width of a curve is its' distance across, and the measurement is actually a very tiny heterodyned frequency measurement of one side of the curve minus the other side. Line width frequencies are around 100 KHz. In practical terms, line width represents a relaxation time for molecules, where the relaxation time is the time required for any transient phenomena to disappear. So if the electrical frequency is a lot less than the line width frequency, the molecule has plenty of time to adjust to the slowly changing electric field, and the normal or static type Stark effects occur.

If the electrical frequency is just a little less than the line width frequency the molecule changes its' frequencies, in rhythm with the frequency of the electric field. This is shown below in Figure 60[9]. As the electric field frequency starts to get into the KHz line width range, the Stark curves vary their frequencies with the electric field frequency and become broadened and blurred. When the electric frequency moves up and beyond the line width range to 1200 KHz, the normal Stark type curves again become crisp and distinguishable. In many respects, the molecule cannot keep up with the rapid electrical field variation and simply averages the Stark effect. In all three cases, the separation of the Stark frequencies is modulated with the electrical field frequency, or its' first harmonic (2 X the electrical field frequency).

Frequency (kilocycles)	Field strength (peak volts/cm)	
0 (D-c)	640	(a)
1	660	(b)
1200	910	(c)
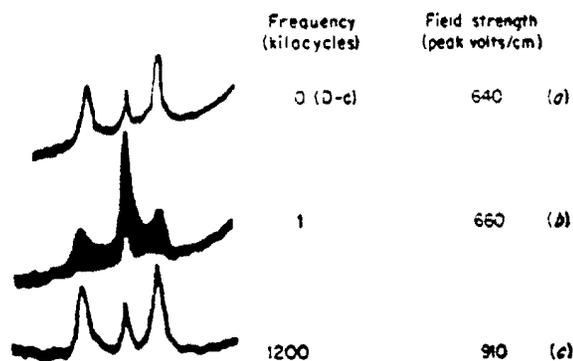
Figure 60[9]. - Stark effect for OCS on the J = 1→2 transition with applied electric fields at various frequencies. a) The Stark effect with a static DC electric field: b) Broadening and blurring of the Stark frequencies with a 1 KHz electric field: c) Normal Stark type effect with electric field of 1200 KHz.

The next frequency measurement that an ever increasing electrical frequency will overtake is the transitional frequency between two rotational levels. As the electric field frequency approaches a transitional frequency between two levels, the radiation of the transitional frequency in the molecule will induce transitions back and forth between the levels. The molecule oscillates back and forth between both levels, at the frequency of the electric field. When the electric field and transition level frequencies are exactly equal (in resonance), the molecule will be oscillating back and forth in both levels, and the spectral lines for both levels will appear simultaneously and at the same intensity. Normally, we would see only one level's frequency at a time, but a resonant electric field causes the molecule to be at both levels at essentially the same time, and so both transitional frequencies appear in its' spectrum.

As if this weren't incredible enough, for sufficiently large resonant electric fields, additional transition level frequencies can occur at regular spacings equal to the electric field frequency.[9] Also, splitting of the transition level frequencies can occur, at frequencies of the electric field frequency divided by odd numbers (electric field frequency - f_E - divided by 3, or 5, or 7, ie. f_E /3 or f_E /5.)

Next we get to the fun part. which is explaining what all this has to do with spectral catalysts. Electric fields cause the Stark effect. which is the splitting, shifting. broadening. or changing intensity of spectral frequencies

for atoms and molecules. As with many of the other mechanisms we have already discussed, changes in the spectral frequencies of reaction systems can affect the reaction rate and reaction path. Let's say we have a reaction system that looks like this:

$$A + B \xrightarrow{\text{C}} I_{\text{intermediates}} \xrightarrow{\text{C}} D + F$$

where A & B are reactants, C is a physical catalyst, I stands for the intermediates, and D & F are the products.

Now suppose that the reaction normally progresses at only a moderate rate, by virtue of the fact that the physical catalyst produces several frequencies that are merely *close* to harmonics of the intermediates. Suppose that when we add an electric field the catalyst frequencies are shifted so that now several of the catalyst frequencies are *exact* harmonics of the intermediates. This will catalyze the reaction at a faster rate. If we did not know about spectral catalysts and the Stark effect we would probably come up with all kinds of theories about the electric field promoting the catalyst and such, but what it all boils down to is the simple idea of more efficient energy transfer through matching resonant frequencies.

Now suppose that industrially it is known that the reaction normally progresses at only a moderate rate, and so the industrial solution has been to subject the reaction system to extremely high pressures. The high pressures cause broadening of the spectral patterns, which improves the transfer of energy through matching resonant frequencies. By understanding the underlying catalyst mechanisms of the reaction, we could do away with the high pressure system, and replace it with a simple electric field. Not only would this be less costly to the industrial producer, it would be much safer for the personnel to get rid of the high pressure equipment.

Some reactants when mixed together do not react very quickly at all, but when an electric field is added they react rather rapidly. Traditionally, we would say that the reaction is catalyzed by an electric field and the equations would look like this:

$$A + B \rightarrow D + F \qquad \text{And} \qquad A + B \xrightarrow{E} D + F$$
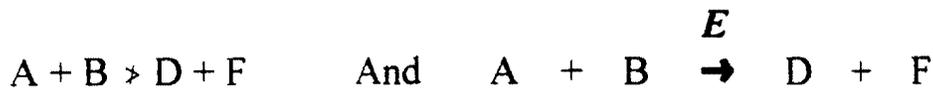
where E is the electric field. In this case, the physical catalyst "C" would have been replaced by the electric field "E". We might be tempted to say that instead of a spectral catalyst, we have an electrical catalyst. That would be a

bit short-sighted however, because in reality the electrical catalyst would work by changing the spectral frequencies of the chemical species in the reaction system so that the frequencies come into resonance, and the reaction can proceed. Understood this way, the electric field becomes just another tool to change spectral frequencies of atoms and molecules, and thereby affect reaction rates.

Now let's not forget the important aspect of reactions paths also. In the absence of an electrical field, a reaction will progress to one set of products:

$$A + B \xrightarrow{\quad C \quad} I_{ntermediates} \xrightarrow{\quad C \quad} D + F.$$
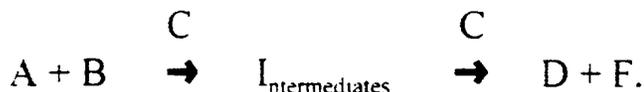
If we add an electrical field, at some particular strength of the field we will have changed the spectral frequencies so much, that a different intermediate is energized and the reaction proceeds down a different reaction path:

$$A + B \xrightarrow[\quad E \quad]{\quad C \quad} I_{ntermediates} \xrightarrow[\quad E \quad]{\quad C \quad} G + H.$$

This is very similar in concept to what we discussed in the beginning of this section, regarding the formation of different products depending on temperature. The changes in temperature caused changes in spectral frequencies, and hence different reaction paths were favored at different temperatures. Likewise, electric fields cause changes in spectral frequencies, and hence different reactions paths are favored by different electric fields. By tailoring an electric field to a particular reaction system, one can control not only the rate of the reaction but also the products produced.

The ability to tailor reactions, with or without a physical catalyst, by varying the strength of an electric field could be useful in certain manufacturing situations. It might be more cost effective to build only one physical set-up for a reaction system and to use an electric field to change the reaction dynamics and products, depending on which product is needed. This would save the expense of having a separate physical set-up for production of each group of products.

Besides varying the strength of an electric field, we can also vary the frequency. Suppose we know that our reaction will proceed at a much faster rate if we add a particular strength static electric field (direct current) as in:

$$A + B \quad \overset{C}{\underset{E}{\longrightarrow}} \quad I_{\text{ntermediates}} \quad \overset{C}{\underset{E}{\longrightarrow}} \quad D + F.$$
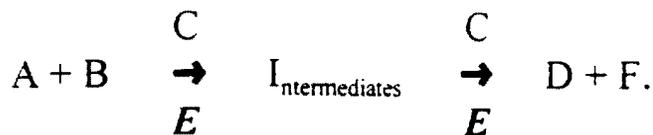
But suppose that because of our reactor design and location, it is much easier to deliver a time-varying electric field with alternating current. A very low frequency electric field, such as with wall outlet 60 Hz will produce the normal or static type Stark effects. We can adapt our reactor to the 60 Hz electric field and enjoy the same increase in reaction rate that we would have had with the static electric field.

Now suppose we know that a certain physical catalyst produces spectral frequencies that are *close* to intermediate frequencies, but are not *exact*. Let's say we have promoted the physical catalyst activity in the past by using high temperatures. We did not realize it at the time, but the high temperatures broadened the physical catalyst's spectral output to make it an exact match for the intermediates. Well now that we understand what is really going on, we can get rid of the high temperature boilers and use a moderate frequency electric field to broaden the spectral frequencies instead. We can use a frequency of around 100 KHz, equivalent to the line width frequencies, to broaden all of the curves and make the physical catalyst's spectral curves match those of the intermediates.

Moving right up the frequency scale, let's look at something higher - beyond the line width range, where the pattern returns to a normal Stark type effect. The separation of the Stark frequencies will be modulated with the electrical field frequency, or its' first harmonic (first-order Stark effects are modulated with the electrical field frequency, while second-order Stark effects are modulated by 2 X the electrical field frequency). Now let's say we are using a metallic platinum catalyst in a hydrogen reaction and we want to stimulate the 2.7 MHz hyperfine frequency of the hydrogen atoms. In the previous section we discussed using electromagnetic radiation to deliver the 2.7 MHz frequency. As you are probably beginning to guess, I am going to suggest using an alternating electric field at 2.7 MHz instead. Since platinum is a metal and conducts electricity well, we simply make the platinum a part of the alternating current circuit. The platinum will exhibit a Stark effect, with all the split **frequencies separated by 2.7 MHz.** There will be dozens of split frequencies in the platinum atoms that are heterodynes of 2.7 MHz. This massive heterodyned output will stimulate the hydrogen hyperfine frequency of 2.7 MHz. and direct our reaction.

Another way to do it, of course, would be to leave the platinum out of the reaction altogether. The 2.7 MHZ field will have a resonant Stark effect on the hydrogen, separate and independent of the platinum catalyst. Copper is not normally catalytic for hydrogen, but we could use it to construct a reaction vessel like a Stark waveguide to energize the hydrogen. A Stark waveguide is used to perform Stark spectroscopy. It is shown below in Figure 61[9].
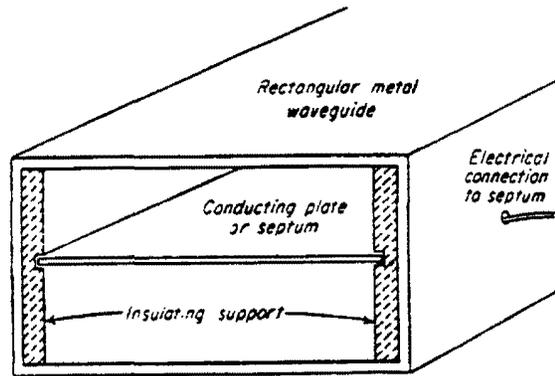
Construction of waveguide for producing Stark effects. Central metal plate is parallel to broad face of waveguide and is insulated from it. Electrical connection to this plate is made by a lead through a small hole in the center of the narrow face of the waveguide.

a)
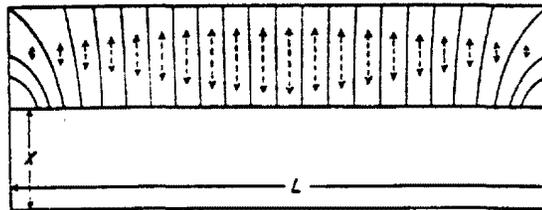
Distribution of electric fields in "Stark waveguide." Dielectric supports of central septum are assumed to be of negligible thickness. D-c or low-frequency field direction is shown with solid lines, the density of lines being proportional to the intensity. The microwave electric field is everywhere in the same direction as indicated by the dotted lines whose length is proportional to the field intensity. Identical fields which are not shown exist in the lower half of the waveguide. (From Shulman, Dailey, and Townes [528].)

b)

Figure 61[9]. - Stark waveguide. a) Construction of waveguide. b) Distribution of fields in Stark waveguide.

The electrical field is delivered through the conducting plate. We could make a reaction vessel for the flow through of gases and use an economical metal such as copper for the conducting plate. We deliver the 2.7 MHz alternating current through the electrical connection to the copper conducting plate. The copper spectral frequencies, none of which are particularly resonant with hydrogen, will exhibit a Stark effect with normal type splitting. The Stark frequencies will be split (heterodyned) apart by 2.7 MHz. Even though none of the actual copper frequencies matches the hydrogen frequencies. the Stark

splitting or heterodynes will match the hydrogen frequency. Dozens of the copper split frequencies will resonate indirectly with the hydrogen hyperfine frequency and direct our reaction.

If we have good enough equipment and a good enough understanding of our reaction system, we can use Stark resonance with a transition level frequency. Let's say that for a particular reaction path, we need to stimulate a molecule with a transition level frequency of 500 MHZ. We simply deliver the 500 MHZ electrical field to the molecule. This resonant electrical field causes the molecule to oscillate back and forth between the two levels at the rate of 500 MHZ. This creates the electrical conditions for light amplification (laser) and any added electromagnetic radiation at this frequency will be amplified by the molecule. In this way, an electrical field can substitute for the laser effects of physical catalysts.

In summary, by understanding the underlying spectral mechanism to chemical reactions, we can use electric fields as yet another tool to catalyze and modify those chemical reactions by modifying the spectral characteristics of the chemical species in the reaction system.

Magnetic Fields

In spectral terms, magnetic fields behave a lot like electric fields, only different. In the preceding section, we saw that spectral lines of atoms and molecules were split and shifted by the presence of an external electric field. Similarly, spectral frequency lines of atoms and molecules can be split and shifted by a magnetic field. In this case, the external magnetic field from *outside* the atom or molecule, interacts with the electric and magnetic fields already *inside* the atom or molecule.

This action of an external magnetic field on spectral lines is called the "Zeeman Effect", in honor of its' discovered, Dutch physicist Pieter Zeeman. In 1896 Zeeman discovered that the yellow flame spectroscopy "D" lines of sodium were broadened when the flame was held between strong magnetic poles. It was later discovered that the apparent broadening of the sodium spectral lines was actually due to their splitting and shifting. Zeeman's original observation has evolved into a separate branch of spectroscopy, relating to the study of atoms and molecules by measuring the changes in their spectral lines caused by a magnetic field. This in turn has evolved into the nuclear magnetic resonance spectroscopy and magnetic resonance imaging

used in medicine, as well as the laser magnetic resonance and electron spin resonance spectroscopy used in physics and chemistry.

<table>
<tr><td>(a)</td><td>(b)</td></tr>
</table>

Figure 62[6] - a) The Zeeman effect for the sodium "D" lines: b) Energy level diagram for the transitions in the Zeeman effect for the sodium "D" lines.

The Zeeman effect for the famous "D" lines of sodium is shown above in Figure 62[6]. The "D" lines are traditionally said to result from transitions between the $3p^2P$ and $3s^2S$ electron orbitals. As you can see, each of the single spectral frequencies is split into two or more slightly different frequencies, which center around the original unsplit frequency.

Now the interesting thing about the Zeeman effect is that the amount that the spectral frequencies are split apart depends on the strength of the magnetic field. See Figure 63[6] below. This diagram is for oxygen. When there is no magnetic field we see the two single frequencies at zero and 4.8. When the magnetic field is at low strength (0.2 Tesla) there is just slight splitting and shifting of the original two frequencies. As the magnetic field is increased, the frequencies are split and shifted farther and farther apart.

Figure 63[6]- Splitting of the ground term of the oxygen atom as a function of magnetic field[6].

The degree of splitting and shifting in the Zeeman effect, depending on magnetic field strength, is also shown below for the ^3P state of silicon.

Figure 64 - Dependence of the Zeeman effect on magnetic field strength for the ^3P state of silicon.

As with the Stark effect from an electric field, the Zeeman effect from a magnetic field is slightly different depending on whether we are talking about an atom or a molecule. We shall consider the case of atoms first. The Zeeman effect on atoms can be most easily divided into three magnetic field strengths - weak, moderate, and strong. If the magnetic field is weak, the amount that the spectral frequencies will be shifted and split apart will be very small. The shifting away from the original spectral frequency is so small in fact, that stimulation of the atom at the original spectral frequency will still stimulate the shifted frequencies. This is because they will be so close to the original spectral frequency that they will still be well within its resonance curve. As for the splitting, it is so small, that it is even *less* than the hyperfine splitting that normally occurs. This means that in a weak magnetic field, there will be only very slight splitting of spectral frequencies, translating into very low splitting frequencies in the lower regions of the radio spectrum and down into the very low frequency region. For example, the Zeeman splitting frequency for the hydrogen atom, which is caused by the earth's magnetic field is around 30 KHz. Larger atoms have even lower frequencies in the lower kilohertz and even hertz regions of the electromagnetic spectrum.

Without a magnetic field, we can stimulate an atom by using direct resonance with a spectral frequency or by using its fine or hyperfine splitting frequencies in the infrared through microwave, or microwave through radio regions, respectively. By merely adding a very weak magnetic field we can also stimulate the atom with an even lower radio or very low frequency

matching the Zeeman splitting frequency. Thus by simply using a weak magnetic field we can extend our range even lower in the radio frequency range than ever before possible. The weak magnetic field from the earth causes Zeeman splitting in atoms in the hertz and kilohertz ranges. This means that all atoms, including those in biological organisms, are sensitive to hertz and kilohertz EM frequencies, by virtue of being in the earth's magnetic field.

At the other end of magnetic field strength, is the very strong magnetic field. In this case the splitting apart and shifting of the spectral frequencies will be very wide. With this wide shifting of frequencies, the difference between them (the splitting frequencies) will be much larger than the hyperfine splitting frequencies. This translates to Zeeman effect splitting frequencies at higher frequencies than the hyperfine splitting frequencies - somewhere around the microwave region. Although the addition of a strong magnetic field does not extend our reach in the electromagnetic spectrum at one extreme or the other, as a weak magnetic field does, it still provides us the option of several more frequencies to use in the microwave region.

The moderate magnetic field case is more complicated. The shifting and splitting caused by the Zeeman effect from a moderate magnetic field will be approximately equal to the hyperfine splitting. Although not widely discussed in the literature, it is possible to apply a moderate magnetic field to an atom, to produce Zeeman splitting equivalent to its' hyperfine splitting. This presents interesting possibilities. Earlier we discussed ways to guide atoms in chemical reactions by stimulating them with hyperfine splitting frequencies. The Zeeman effect provides a way to do that without introducing any spectral frequencies at all. By introducing a moderate magnetic field, we set up resonances within the atom itself, that stimulate and energize the atom.

The moderate magnetic field causes low frequency Zeeman splitting, that matches and hence energizes the low frequency hyperfine splitting in the atom. Now the low hyperfine splitting frequencies are actually the heterodyned difference between two electronic frequencies. When we stimulate the hyperfine splitting frequency, we will eventually stimulate the two electronic frequencies. This in turn causes the atom to be stimulated. The interesting thing about the Zeeman effect is that we can spectrally stimulate an atom by exposing it to a precise strength of magnetic field, and we don't need to use any spectral frequencies at all. The possibilities are quite interesting when one considers that an inert reaction system may suddenly spring to life upon the application of the proper moderate strength magnetic field.

Before we leave the subject of Zeeman effects on atoms, there is one more topic we should consider. That topic is the "normal" Zeeman effect versus the "anomalous" Zeeman effect. With the "normal" Zeeman effect, a spectral frequency is split by a magnetic field into three frequencies, with expected even spacing between them (see Fig. 65[25]). One of the new split frequencies is above the original frequency, and the other new split frequency is below the original frequency. Both new frequencies are split the same distance away from the original frequency. Thus the difference, between the upper and original, and the lower and original frequencies, is the same. This means that in terms of heterodyne differences, we have at most, two new heterodyned differences with the normal Zeeman effect. The first heterodyne or splitting difference is the difference between one of the new split frequencies and the original frequency. The other splitting difference is between the upper and lower new split frequencies. It is, of course, twice the frequency difference between either of the upper or lower frequencies and the original frequency.

In many instances the Zeeman splitting produced by a magnetic field results in more than three frequencies, or in splitting that is spaced differently than expected. This is called the "anomalous" Zeeman effect (Figs. 65 and 66).

no magnetic field

magnetic field present

expected splitting

(a)

no magnetic field

magnetic field present

expected splitting
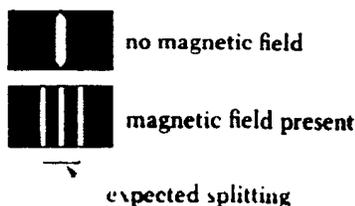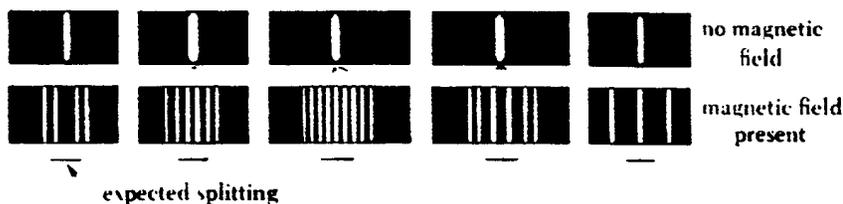
(b)

Figure 65[25] - The "normal" and "anomalous" Zeeman effects. a) normal; b) anomalous.

[25] Concepts of Modern Physics, 4 Edition. Beiser A. McGraw-Hill, 1987
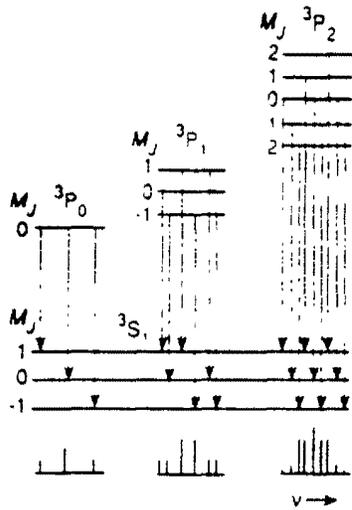
Figure 66[6] - Anomalous Zeeman effect for zinc $^3P \rightarrow {}^3S$.

If there are still just three frequencies, and the Zeeman effect is anomalous because the spacing is different than expected, the situation is similar to the normal effect. We still have, at most, two new splitting frequencies at our disposal. If, however, the effect is anomalous because more than three frequencies are produced, then we have a much more richly varied situation. Let's take the easy case where there are four Zeeman splitting frequencies (Fig. 67).

(a)

(b)
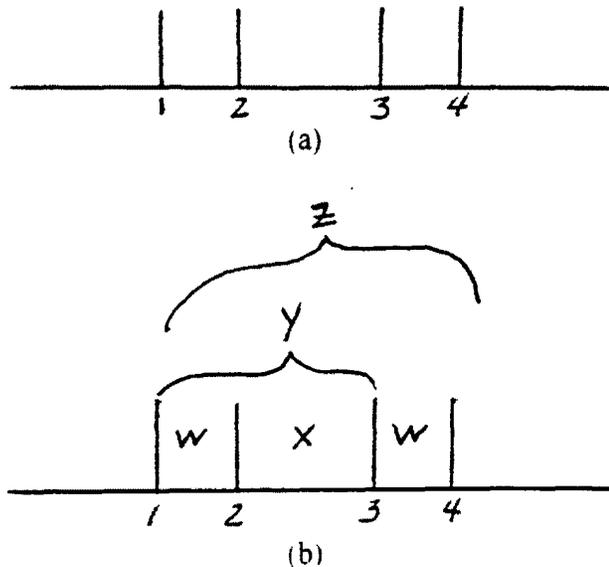
Figure 67 - The case of four (4) Zeeman splitting frequencies resulting in four (4) new heterodyned differences. a) the four (4) Zeeman splitting frequencies; b) the four (4) new heterodyned differences.

In this example of anomalous Zeeman splitting, there are a total of four frequencies, where once existed only one frequency. For simplicity's sake, we will call our new Zeeman frequencies 1, 2, 3, and 4. Frequencies 1 and 2 are split apart by an amount we will call "w". Frequencies 3 and 4 are also split apart by the same difference "w". Thus "w" is a heterodyned splitting frequency. Frequencies 2 and 3 are also split apart by a different amount, which we shall call "x". So far then we have two heterodyned splitting frequencies, as in the normal case.

There is more to come however with the anomalous case. Frequencies 1 and 3 are split apart by a third amount we will call "y". As you probably notice from looking at figure 67, "y" is really just the sum of "w" and "x". And frequencies 2 and 4 are also split apart by the same third amount "y". Finally, frequencies 1 and 4 are split even farther apart by an amount we will call "z". Once again, "z" is really just a summation amount from adding "w + x + w". So we end up with four heterodyned frequencies - w, x, y, and z - in the anomalous Zeeman effect with four frequencies.

If there were six (6) frequencies from the anomalous Zeeman effect, there would be even more heterodyned differences. This is what makes the anomalous Zeeman effect so much fun. It gives us far greater flexibility in choice of frequencies than the normal Zeeman effect gives us. In the normal Zeeman effect the original frequency is split into three evenly spaced frequencies, with a total of just two heterodyned frequencies. In the anomalous Zeeman effect the original frequency is split into four or more unevenly spaced frequencies, with at least four or more heterodyned frequencies. The anomalous Zeeman effect creates a virtual smorgasbord of frequencies to choose from.

Now that we have discussed the Zeeman effect for atoms, it is time to move on to the Zeeman effect in molecules. Molecules come in three basic varieties - ferromagnetic, paramagnetic, and diamagnetic[26]. Ferromagnetic molecules are what we think of as typical magnets. The materials hold a strong magnetic field and are composed of magnetic elements such as iron, cobalt, and nickel. Bar magnets and magnets like the ones we put on the refrigerator door are made of ferromagnetic elements and molecules.

Paramagnetic molecules[26] hold only a weak magnetic field. If a paramagnetic material is put into an external magnetic field, the magnetic moment of the material's molecules are lined up in the same direction as the

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[26]Magnetism, An Introductory Survey, Lee EW, Dover Publ, New York, 1970.

external magnetic field's. Now, the magnetic moment of the molecules is the direction in which the molecule's own magnetic field is weighted. It is a lot like a teeter-totter on a playground. If children of exactly equal weight sit on either end of the teeter-totter, the weight will be evenly distributed and the teeter-totter will not tip more to one side than the other. But if one of the children is light, and the other child is heavy, the teeter-totter will tip naturally towards the heavy child. Similarly, the magnetic moment of a molecule will tip to whichever side of the molecule is more heavily weighted in terms of its' own magnetic field. Paramagnetic molecules then, tip in the *same direction* as an externally applied magnetic field. Because paramagnetic materials line up with an external magnetic field, they are also weakly attracted to sources of magnetic fields.

Common paramagnetic *elements* include oxygen, aluminum, sodium, magnesium, calcium, and potassium[26]. *Stable molecules* such as oxygen (O_2) and nitric oxide (NO) are also paramagnetic. Molecular oxygen makes up approximately 20% of our planet's atmosphere. Both molecules play important roles in biologic organisms. In addition, *unstable molecules*, more commonly known as free radicals or chemical reaction intermediates, are also paramagnetic. Paramagnetic *ions* include hydrogen, manganese, chromium, iron, cobalt, and nickel. Many paramagnetic substances occur in biological organisms. For instance the blood flowing in our veins is an ionic solution containing red blood cells. The red blood cells contain hemoglobin, which in turn contains ionized iron. The hemoglobin, and hence the red blood cells are paramagnetic. In addition, hydrogen ions can be found in a multitude of organic compounds and reactions. For instance, the hydrochloric acid in our stomachs contains hydrogen ions. Adenosine triphosphate (ATP), the energy system of nearly all biological organisms, requires hydrogen and manganese ions to function properly. Thus the very existence of life itself depends on paramagnetic materials.

Diamagnetic molecules[26], on the other hand, are repelled by a magnetic field, and line up what little magnetic moments they may have *away* from the direction of an external magnetic field. Diamagnetic substances do not hold a magnetic field. Examples of diamagnetic *elements* include hydrogen, helium, neon, argon, carbon, nitrogen, phosphorus, chlorine, copper, zinc, silver, gold, lead, and mercury. Diamagnetic *molecules* include water, most gases, organic compounds, and salts such as sodium chloride. Salts are really just crystals of diamagnetic ions. Diamagnetic *ions* include lithium, sodium, potassium, rubidium, caesium, fluorine, chlorine, bromine, iodine, ammonium, and

sulphate. Ionic crystals usually dissolve easily in water, and as such the ionic water solution is also diamagnetic. Biologic organisms are filled with diamagnetic materials, because they are carbon based lifeforms. In addition, the blood flowing in our veins is an ionic solution containing blood cells. The ionic solution (plasma) is made of water molecules, sodium ions, potassium ions, chlorine ions, and organic protein compounds. Hence our blood is a diamagnetic solution carrying paramagnetic blood cells.

In regards to the Zeeman effect, we will first consider the case of paramagnetic molecules. As with atoms, the effects can be categorized on the basis of magnetic field strength. If the external magnetic field applied to a paramagnetic molecule is weak, the Zeeman effect will produce splitting into equally spaced levels[9]. In most cases, the amount of splitting will be directly proportional to the strength of the magnetic field, as in "first-order" Stark effects. A general rule of thumb is that a field of one (1) oersted (slightly larger than the earth's magnetic field) will produce Zeeman splittings of approximately 1.4 MHz in paramagnetic molecules. Weaker magnetic fields will produce narrower splittings, at lower frequencies. Stronger magnetic fields will produce wider splittings, at higher frequencies. In these first order Zeeman effects, there is usually only splitting, with no shifting of the original or center frequency as we saw with Zeeman effects on atoms.

In many paramagnetic molecules there are also second-order effects where the Zeeman splitting is proportional to the square of the magnetic field strength[9]. In these cases, the splitting is much smaller and of much lower frequencies. In addition to splitting, the original or center frequencies shift as they do in atoms, proportional to the magnetic field strength.

Sometimes the direction of the magnetic field in relation to the orientation of the molecule makes a difference. For instance, π frequencies are associated with a magnetic field parallel to an exciting electromagnetic field, while σ frequencies are found when it is perpendicular. Both π and σ frequencies are present with a circularly polarized electromagnetic field. Typical Zeeman patterns for a paramagnetic molecule are shown below in Figure 68[9]. The π frequencies are seen when $\Delta M = 0$, and are above the long horizontal line. The σ frequencies are seen when $\Delta M = \pm 1$, and are below the long horizontal line. If a paramagnetic molecule were placed in a weak magnetic field, circularly polarized light would excite both sets of frequencies in the molecule. If we wanted to, we could control which set of frequencies a molecule was excited by, by controlling its orientation with respect to the magnetic field.
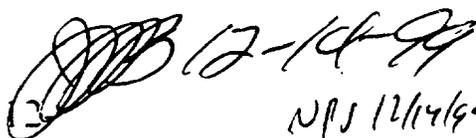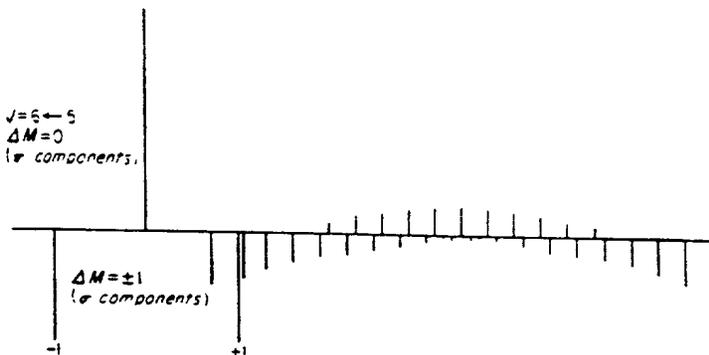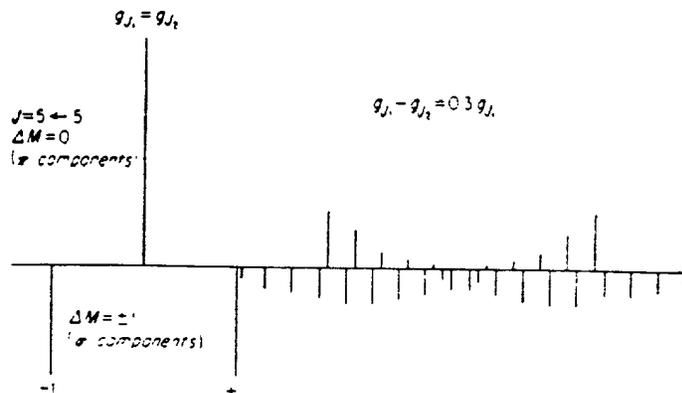
Figure 68⁹ - Typical Zeeman splitting patterns for two different transitions in a parmagnetic molecule.

When the magnetic field strength is intermediate, the interaction between the paramagnetic molecule's magnetic moments and the externally applied magnetic field produces Zeeman effects equivalent to other frequencies and energies in the molecule. For instance, the Zeeman splitting may be near a rotational frequency and disturb the end-over-end rotational motion of the molecule[9]. The Zeeman splitting and energy may be particular or large enough to uncouple the molecule's spin form its' molecular axis.

If the magnetic field is very strong, the nuclear magnetic moment spin will uncouple from the molecular angular momentum. In this case the Zeeman effects overwhelm the hyperfine structure, and are of much higher energies at much higher frequencies. In spectra of molecules exposed to strong magnetic fields, the hyperfine splitting appears as a small perturbation

of the Zeeman splitting.

Next we will consider Zeeman effects in so called "ordinary molecules" or diamagnetic molecules. Most molecules are of the diamagnetic variety, hence the designation "ordinary". This includes of course most organic molecules found in biologic organisms. Diamagnetic molecules have rotational magnetic moments from rotation of the positively charged nucleus, and this magnetic moment of the nucleus is only about 1/1000 of that from the paramagnetic molecules. This means that the energy from Zeeman splitting in diamagnetic molecules is much smaller than the energy from Zeeman splitting in paramagnetic molecules. The equation for the Zeeman energy in diamagnetic molecules is:

$$\mathcal{H}_Z = -(g_J J + g_I I)\cdot\beta H_0$$

where J is the molecular rotational angular momentum, I is the nuclear-spin angular momentum, g_J is the rotational g factor, and g_I is the nuclear-spin g factor. This Zeeman energy is much less, and of much lower frequency, than the paramagnetic Zeeman energy. In terms of frequency it falls in the hertz and kilohertz regions of the electromagnetic spectrum.

Last but not least, we get to the end of this magnetic section where we consider the implications of all this Zeeman splitting for catalysts and chemical reactions. A weak magnetic field will produce hertz and kilohertz Zeeman splitting in atoms and second order effect paramagnetic molecules. Virtually any kind of magnetic field will produce hertz and kilohertz Zeeman splitting in diamagnetic molecules. All these atoms and molecules will then become sensitive to radio and very low frequency (VLF) electromagnetic waves. The atoms and molecules will absorb the radio or VLF energy and become stimulated to a greater or lesser degree. We could use this catalytically to add energy to a particular molecule or intermediate in a chemical reaction system. For instance, in our old friend hydrogen and oxygen gas turning into water over a platinum catalyst, the hydrogen atom radical is important for maintaining the reaction. In the earth's weak magnetic field, Zeeman splitting for hydrogen is around 30 KHz. We could energize the hydrogen atoms in our reaction system by applying the Zeeman splitting frequency for hydrogen (30 KHz) to it. Energizing the hydrogen atoms in the reaction system will duplicate the mechanism of action of platinum, and catalyze the reaction. Of course, if we took our reaction into space, away from the earth's weak magnetic field, hydrogen would no longer have a 30

KHz Zeeman splitting frequency, and the 30 KHz would no longer catalyze the reaction.

The vast majority of materials on this planet, by virtue of existing within the earth's weak magnetic field, will exhibit Zeeman splitting in the hertz or kilohertz regions. This applies to biologics and organics as well as inorganic or inanimate materials. Humans are composed of a wide variety of atoms, diamagnetic molecules, and second order effect paramagnetic molecules. These atoms and molecules all exist in the earth's weak magnetic field. These atoms and molecules in humans all have Zeeman splitting in the hertz and kilohertz regions, because they are in the earth's magnetic field. Biochemical and biocatalytic process in humans are thus sensitive to hertz and kilohertz electromagnetic radiation, by virtue of the fact that they are in the earth's weak magnetic field. As long as humans continue to exist on this planet, they will be subject to spectral catalyst effects from hertz and kilohertz EM waves because of the Zeeman effect. This has significant implications for low frequency communications, as well as chemical and biochemical reactions, diagnostics, and treatment of diseases.

A strong magnetic field will produce splitting greater than the hyperfine frequencies, in the microwave and infrared regions of the EM spectrum in atoms and paramagnetic molecules. In our hydrogen/oxygen reaction, we could add a strong magnetic field to the reaction system and transmit MHZ and/or GHz frequencies into it to energize the hydroxy and hydrogen reaction intermediates. If we were using physical platinum to catalyze our reaction, we might find that at a particular magnetic field strength, both the platinum and the reaction intermediate spectra had frequencies that were split and shifted in such a way that *even more frequencies matched* than without the magnetic field. In this way, we would be using Zeeman splitting to improve the effectiveness of our physical catalyst, by copying its mechanism of action.

A moderate magnetic field will produce Zeeman splitting in atoms and paramagnetic molecules at frequencies on par with the hyperfine and rotational splitting frequencies. This means that a reaction system can be energized without even adding electromagnetic energy. Put the reaction system in a moderate magnetic field that produces Zeeman splitting equal to the hyperfine or rotational splitting. For instance, we might use a magnetic field that causes hyperfine or rotational splitting in hydrogen and oxygen gas, that matches the Zeeman splitting in hydrogen atom or hydroxy radicals. The hydrogen or hydroxy intermediates would be energized and they would proceed through the reaction cascade to produce water. By using the

appropriately tuned moderate magnetic field, we could use the magnetic field to turn the reactants in to catalysts for their own reaction, without the addition of physical catalyst platinum or spectral platinum. Although the magnetic field would simply be copying the mechanism of action of platinum, the reaction would have the *appearance* of being catalyzed solely by a magnetic field.

Finally, the last thing we will consider in this section is the direction of the magnetic field in relation to the orientation of the molecule. You will recall that when the magnetic field is parallel to an exciting electromagnetic field, π frequencies are produced. When the magnetic field is perpendicular to an exciting electromagnetic field, σ frequencies are found. Let's say we have an industrial reaction system with the same starting reactants, but we want to be able to produce different products at will. We can use our know-ledge of magnetic fields and catalysts to preferentially guide the reaction to one set of products or another. For the first set of products we orient the electromagnetic excitation parallel to the magnetic field, producing one set of π frequencies, which leads
to a first set of products. When we want a different product, we change the direction of the magnetic field so that it is perpendi-cular to the exciting electromagnetic field. This produces a different set of σ frequencies, and a different reaction pathway is energized, producing a differ-ent set of products. In this way, we can use our knowledge of Zeeman splitting and spectral catalysts to fine tune the specificity of our reaction systems.

In summary, by understanding the underlying spectral mechanism to chemical reactions, we can use magnetic fields as yet another tool to catalyze and modify those chemical reactions by modifying the spectral characteristics of the chemical species in the reaction system.

In future sections, we will detail how acoustic frequencies interact with chemical systems, and also how reactor vessel size and shape affect reaction systems.

Complex pattern laser design will be discussed (producing multiple non-resonant frequencies from the same laser system to duplicate part or all of an atomic or molecular spectral pattern with a single laser.)

Design of superconducting and/or supermagnetic materials will be discussed based on spectral catalyst theory. If electric field or magnetic field can affect spectral frequencies, then frequencies can affect E/B field. Also, solvents & supports can affect frequencies of individual components. Hence, combination of particular elements in certain ratios,to form molecules & crystals, creates resonances between atoms which allow superconductivity and supermagnetism. Should be able to use catalyst theory to design room temperature superconducting and/or supermagnetic materials.

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In addition, crystallization (e.g. growth of single and/or multiple crystals from single and/or multiple solutions) is a special type of spectral catalysis, namely autocatalysis. In autocatalysis, the end product catalyzes the original reaction. This is what happens in crystallization. A solution with molecules could rest as a solution for years. But if you introduce a "seed crystal" the solution will crystalize into solid form. Without wishing to be bound by any particular theory or explanation, in this case, the seed crystal that has been introduced, emits its spectral frequencies into the solution. Those spectral frequencies of the crystalized form, catalyze formation of more crystal. Thus spectral catalyst mechanisms can be applied to the processes of crystallization. These same processes are also applicable to solid state crystallization.
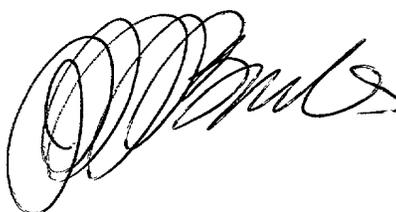
APPENDIX A

Hydrogen & Platinum Frequency Matrix

Horizontal - Hydrogen Frequencies (Thz)
Vertical - Platinum Frequencies (Thz)

100	7.7144	10.756	15.732	24.2382	40.1985	54.4367	74.0016	114.2	138.438	159.881	233.882	274.081	298.3.9	314.55	456.3
364.501	0	0	0	0	0	0	0	0	0	0	0	0	0		
421.428	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
438.127	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
443.127	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
443.479	0	0	0	0	0	0	5.39293	0	0	0	0	0	0	0	
449.757	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
459.561	0	0	0	0	0	0	0	0	0	0	0	0	0	0	305..
473.862	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
474.478	0	43.9902	0	0	0	0	0	0	0	0	0	0	0	0	
497.495	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
512.918	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
513.333	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
520.151	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
547.216	0	0	0	0	0	0	0	0	0	0	0	1.99655	0	0	
547.489	0	0	0	0	0	0	0	0	0	0	0	1.3954	0	0	
556.12	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
558.379	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
565.537	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
572.474	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
592.536	0	0	0	0	0	0	8.00707	0	0	0	0	0	0	0	
594.35	0	0	0	0	0	0	0	0	0	0	0	0	1.99200	0	
614.388	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
658.534	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
563.126	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
666.389	0	0	0	0	0	0	9.00506	0	0	0	0	0	0	0	
674.365	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
674.821	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
682.614	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
692.932	0	0	0	0	0	0	0	0	5.00464	0	0	0	0	0	
715.081	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
719.366	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
727.883	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
750.124	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
755.838	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
759.276	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
764.2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
768.555	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
785.066	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
808.823	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
810.27	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
815.975	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
816.431	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
818.412	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
822.889	0	0	0	0	0	0	0	0	0	0	0	3.00236	0	0	0
823.88	0	0	0	33.991	0	0	0	0	0	0	0	3.00597	0	0	
826.305	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
860.17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
860.624	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
874.558	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
879.639	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
901.957	0	0	0	0	0	13.9976	0	0	0	0	0	0	0	0	0
904.338	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
907.95	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
911.162	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.9946
913.453	0	0	0	0	0	0	0	7.99871	0	0	0	0	0	0	1.99963
917.24	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2.00792
920.761	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
921.877	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
922.336	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
927.168	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
928.067	0	0	58.9923	0	0	0	0	0	0	0	0	0	0	0	0
935.67	0	0	0	0	0	0	0	0	0	0	0	4.00061	0	0	0
936.644	0	0	0	0	0	0	0	0	0	0	0	4.00477	0	0	0
949.744	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
954.939	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
967.06	0	0	0	0	0	15.0079	0	0	0	0	0	0	0	0	0
975.906	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
978.208	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
985.304	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
987.312	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
993.388	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
998.553	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
999.985	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
1012.56	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
1013.12	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
1018.06	0	0	0	42.0023	0	0	0	0	0	0	0	0	0	0	

A1

	100	7.7144	10.786	15.732	24.2382	40.1985	64.4367	74.0016	114.2	138.438	159.881	233.882	274.081	298.319	314.051	456.811
1018.75	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1023.26	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1026.2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1026.92	0	0	0	0	0	0	0	5.39229	0	0	0	0	0	0	0	0
1028.96	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1029.42	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1031.67	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1034.53	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1035.36	0	0	0	0	0	0	0	2.9992	0	0	0	0	0	0	0	0
1036.19	0	0	0	0	0	0	0	4.0023	0	0	0	0	0	0	0	0
1037.99	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1050.76	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1057.58	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1059.23	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1063.75	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1067.44	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1069.45	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1073.27	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1080.72	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1081.02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1081.63	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1082.35	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1088.21	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1088.63	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1091.11	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1094.74	0	0	0	0	0	0	0	0	0	0	0	0	3.99422	0	0	0
1096.55	0	0	0	0	0	0	0	0	0	0	0	0	4.00082	0	0	0
1098.17	0	0	0	0	0	0	0	0	0	0	0	0	4.00674	0	0	0
1102.57	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1104.97	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1107.93	0	0	0	0	0	0	0	0	0	8.00308	0	0	0	0	0	0
1109.36	0	0	0	0	0	0	0	14.991	0	0	0	0	0	0	0	0
1110.99	0	103.003	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1119.82	0	0	0	0	0	0	0	0	0	0	7.00408	0	0	0	0	0
1120.9	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1127.27	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1127.82	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1130.93	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1132.62	0	105.008	71.9947	0	0	0	0	0	0	0	0	0	0	0	0	0
1135.86	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1140.75	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1144.43	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1151.66	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1154.82	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1174.62	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1175.91	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1180.66	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1181.92	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1185.23	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1187.63	0	0	0	48.9983	0	0	0	0	0	0	0	0	0	0	0	0
1191.74	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3.99485	0
1192	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3.99572	0
1192.46	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3.99726	0
1195.11	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4.00615	0
1196.33	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1199.89	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1201.18	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1203.93	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1205.36	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1213.24	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1214.99	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1223.16	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1228.63	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1230.33	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1234.17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1234.63	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1234.71	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1239.81	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1247.53	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1248.16	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1251.13	0	115.996	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1254.61	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3.99492	0
1256.04	0	0	0	0	0	0	0	0	10.9986	0	0	0	0	0	3.99948	0
1257.71	0	0	0	0	0	0	16.3957	0	0	0	0	0	0	0	4.0048	0
1265.87	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1271.87	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

A2

100	7.7144	10.756	15.732	24.2382	40.1985	64.4367	74.0016	114.2	138.438	159.881	233.882	274.081	298.319	314.05	456.9
1281.07	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
1288.82	0	0	0	0	0	20.0013	0	0	0	0	0	0	0	0	
1293.16	0	0	0	0	0	0	0	0	0	0	0	0	0		
1294.72	0	0	0	0	0	0	0	0	0	0	0	0	0		
1298.91	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
1307.77	0	0	0	0	0	0	0	0	0	0	0	0	0		
1309.56	0	0	0	0	0	0	0	0	0	0	0	0	0		
1318.13	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
1321.35	0	0	83.9912	0	0	0	0	0	0	0	0	0	0		
1332.83	0	0	0	0	0	0	0	0	0	0	0	0	0		
1348.83	0	0	0	0	0	0	0	0	0	0	0	0	0		
1361.32	0	0	0	0	0	0	0	0	0	0	0	0	0		
1378.57	0	0	0	0	0	0	0	0	0	0	0	0	0		
1384.61	0	0	0	0	0	0	0	0	10.0017	0	0	0	0		
1398.14	0	0	0	0	0	0	0	0	0	0	0	0	0		
1408.04	0	0	0	0	0	0	0	0	0	0	0	0	0		
1425.32	0	0	0	0	0	0	0	0	0	0	0	0	0		
1438.14	0	0	0	0	0	0	0	0	0	8.39507	0	0	0		
1450.02	0	0	0	0	0	0	0	0	0	0	0	0	0		
1462.85	0	0	0	0	0	0	0	0	0	0	0	0	0		
1475.06	0	0	0	0	0	0	0	0	0	0	0	0	0		
1476.35	0	0	0	0	0	0	0	0	0	0	0	0	0		

A3

12-14-99

NJ 12/17/99

100	456 816	516 588	690 591	730 591	755 131	770 563	781 549	2466	2923	3083	3157	3137	3221	3236 7	9 5004	39 9702	58 4706
364 501	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
421 428	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
438 127	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
443 127	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
443 479	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
449 757	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
459 561	1 00601	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
473 862	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
474 478	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
497 495	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
512 918	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
513 333	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
520 151	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
547 216	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
547 489	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
556 12	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
558 378	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
565 537	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
573 474	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	30 9979	0
592 536	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
594 35	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
514 388	0 99627	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
658 534	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
663 126	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
666 389	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
674 365	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
674 821	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
682 614	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
692 832	0	0	1 0031	0	0	0	0	0	0	0	0	0	0	0	0	0	0
715 081	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
719 866	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
727 883	0	0	0	0 99588	0	0	0	0	0	0	0	0	0	0	0	0	0
750.124	0	0	0	0	0 99337	0	0	0	0	0	0	0	0	0	0	0	0
755 838	0	0	0	0	1 00094	0	0	0	0	0	0	0	0	0	0	0	0
759.276	0	0	0	0	1 00549	0	0	0	0	0	0	0	0	0	0	18 9961	0
764 2	0	0	0	0	0	0 99136	0	0	0	0	0	0	0	0	0	0	0
768.555	0	0	0	0	0	0 99701	0	0	0	0	0	0	0	0	0	0	0
785 066	0	0	0	0	0	0	1 00437	0	0	0	0	0	0	0	0	0	0
808 923	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
810 27	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
815 975	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
816.431	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
818.412	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	13 997
822.889	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
823.88	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
826.305	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
860 17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
860 624	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
874 558	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
879 639	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	22 0074	0
901 957	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
904 338	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
907 95	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
911.162	1 99459	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
913 453	1 99961	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
917.24	2.0079	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
920.761	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
921.877	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
922.336	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
927.168	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
928.087	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
935.67	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	16.0024
936.644	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
949.744	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
954.939	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
967.06	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
975.906	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
978 208	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
985.304	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
987.312	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
993 388	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
998 553	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
999 985	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1012 56	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1013 12	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1013 06	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

A4

100	456 816	616 688	690 691	730 591	755 131	770 863	781 649	2466	2923	3083	3157	3197	3221	3236 7	18 5004	39 9 02	58 4
1018 75	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1023 26	0	0	0	0	0	0	0	0	0	0	0	0	0			
1026 2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		0
1026 92	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1028 36	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1029 42	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1031 87	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1034 53	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1035 96	0	0	0	0	0	0	0	0	0	0	0	0	0	0	55 9966		
1036 19	0	0	0	0	0	0	0	0	0	0	0	0	0	0	56 0091		
1037 99	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1050 76	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1057 58	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1059 23	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1063 75	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1067 44	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1069 45	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1073 27	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1080 72	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1081 02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1081 63	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1082 35	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1088 21	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1088 63	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1091 1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1094 74	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1096 55	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1098 17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1102 57	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
1104 97	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
1107 93	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1109 36	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1110 99	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	9 0008
1119 82	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
1120 9	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1127 27	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
1127 82	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
1130 93	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
1132 62	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1135 86	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1140 75	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1144 43	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1151 66	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1154 82	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1174 62	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1175 91	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1180 66	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1181 92	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1185 23	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1187 63	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1191 74	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1192	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1192.46	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1195 11	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1196.33	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1199 89	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1201.18	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1203 93	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1205.36	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1213.24	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1214.99	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1223 16	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1228 63	0	1 9923	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1230 33	0	1 99506	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1234 17	0	2 00129	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1234 63	0	2 00203	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1234.71	0	2.00216	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1239 81	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1247.53	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1248 16	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1251 13	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1254 61	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1256 04	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1257 71	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1265 67	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1271 87	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

A5

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100	456 816	616 688	690 691	730 891	755 131	770 563	781 649	2466	2923	3083	3157	3197	3221	3236 7	18 5004	39 9732	58 4706
1281 07	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1298 82	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1293 16	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1294 72	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1298 91	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1307 77	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1309 56	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1318 13	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1321 35	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1332 83	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1348 83	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1361 32	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1378 57	0	0	1 99593	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1384 61	0	0	2 00467	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1398 14	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1408 04	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1425 32	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1438 14	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1450 02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1462 85	0	0	0	2 00146	0	0	0	0	0	0	0	0	0	0	0	0	0
1475 06	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1476 35	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Appendix B.

The idea that all electromagnetic waves have the same amount of energy, no matter what the frequency, is not at all intuitive for most people. To the contrary, so many scientific phenomena are explained in terms of "high" energy photons vs. "low" energy photons, that it seems contradictory and paradoxical. Therefore, I will demonstrate this remarkable concept with simple algebraic equations.

1. Consider a first "photon" of 400 Thz frequency. We calculate its' total energy according to the Planck equation:

$$E = hf,$$

where E is the energy of the photon, h is Planck's constant (6.626×10^{-34} J·s), and f is the frequency in Hz. Thus, for frequency #1,

$$E_1 = (6.626 \times 10^{-34} \text{ J·s}) \times (400 \times 10^{12} \text{ Hz}),$$

$$E_1 = 2650.4 \times 10^{-22} \text{ J},$$

$$E_1 = 2.6504 \times 10^{-19} \text{ J}.$$

2. Consider a second "photon" of 573 Thz frequency. We calculate its' total energy according to the Planck equation:

$$E = hf,$$

where E is the energy of the photon, h is Planck's constant (6.626×10^{-34} J·s), and f is the frequency in Hz. Thus, for frequency #2,

$$E_2 = (6.626 \times 10^{-34} \text{ J·s}) \times (573 \times 10^{12} \text{ Hz}),$$

$$E_2 = 3796.7 \times 10^{-22} \text{ J},$$

$$E_2 = 3.7967 \times 10^{-19} \text{ J}.$$
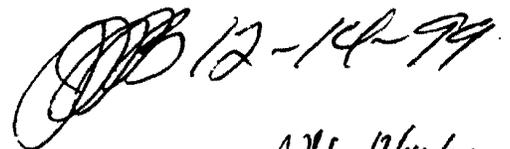
3. Therefore, we have obtained the following information:

Frequency		**Energy**
1.	400 Thz	2.6504×10^{-19} J
2.	573 Thz	3.7967×10^{-19} J.

4. Next we must calculate the amount of energy in one wave for each frequency.

A. In our first frequency, there are 400×10^{12} waves per second. Therefore, we take our total energy, and divide it by the number of waves, to obtain the energy in one wave at this frequency:

Energy per wave (E_w) = Total energy (E) ÷ Number of waves.

$$E_{w1} = (2.6504 \times 10^{-19} \text{ J}) \div (400 \times 10^{12} \text{ waves}),$$

$$E_{w1} = 0.006626 \times 10^{-31} \text{ J/wave},$$

$$E_{w1} = 6.626 \times 10^{-34} \text{ J/wave}.$$

B. In our second frequency, there are 573×10^{12} waves per second. Therefore, we take our total energy, and divide it by the number of waves, to obtain the energy in one wave at this other frequency:

Energy per wave (E_w) = Total energy (E) ÷ Number of waves,

$$E_{w2} = (3.7967 \times 10^{-19} \text{ J}) \div (573 \times 10^{12} \text{ waves}),$$

$$E_{w2} = 0.006626 \times 10^{-31} \text{ J/wave},$$

$$E_{w2} = 6.626 \times 10^{-34} \text{ J/wave}.$$

5. No matter what frequency you use, you will always arive at the same answer. All waves of electromagnetic energy, no matter what the frequency, have exactly 6.626×10^{-34} J of energy per wave. As you have probably noticed by now, this is the same as Planck's number, 6.626×10^{-34} J·s. Planck's number is really the amount of energy per wave. We just are not taught to think of it that way.