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ABSTRACT

Quantum mechanics and quantum chemistry have taught for more than 100 years that "photons" associated with microwaves cannot exert photochemical effects because their "photon energies" are smaller than chemical bond energies. Those quantum theories have been strongly contradicted within the last few decades by physical experiments demonstrating non-equilibrium, photochemical and photomaterial activity by microwaves. Reactions among scientists to these real physical models and proofs have varied from disbelief and denial, to acceptance of the real physical phenomena and demands for revisions to quantum theory.

At the previous "Nature of Light" meeting, an advance in the foundations of quantum mechanics was presented.[1,2] Those discoveries have revealed the source of these conflicts between quantum theory and microwave experiments.[3,4] Critical variables and constants were missing from quantum theory due to a minor mathematical inadvertence in Planck's original quantum work. As a result, erroneous concepts were formed nearly a century ago regarding the energetics and mechanisms of lower frequency light, such as in the microwave region.

The new discoveries have revealed that the traditional concept of "photons" mistakenly attributed elementary particle status to what is actually an arbitrarily time-based collection of sub-photonic, elementary particles.[5] In a mathematical dimensional sense, those time-based energy measurements cannot be mathematically equivalent to bond energies as historically believed. Only an *"isolated quantity of energy"*, as De Broglie referred to it, can be equivalent to bond energy. With the aid of the new variables and constants, the non-equilibrium mechanisms of light in the microwave region can now be described. They include resonant absorption, splitting frequency stimulation leading to electronic excitation, and resonant acoustic transduction. Numerous practical engineering applications can be envisioned for non-equilibrium microwaves.

Keywords: Microwave, non-equilibrium, photon, energy constant, oscillation, resonant

1. INTRODUCTION

Scientists have long held that light in only the visible and ultraviolet regions can be used to catalyze photochemical reactions. These "high energy photons" are believed to achieve non-equilibrium resonance with bond energies in reactants and materials, allowing dissociation and ionization of molecular components for subsequent reaction. Use of lower frequency light in the infrared, microwave, and radio regions has long been believed to exert effects on chemical reaction systems only through the transfer of heat and thermal energy. A dividing line between visible and infrared light thus served as a defining characteristic for the field of photochemistry. Above the line was ionizing radiation which could catalyze reaction systems, and below the line was nonionizing radiation which could do little more than serve as a source of heat.

The existence of that conceptual dividing line between visible (ioinizing) and infrared (nonionizing) light is due primarily to concepts developed by Einstein in relation to his work on the photoelectric effect, and later by Stark and Lewis. Einstein's 1905 Nobel prize-winning paper on the emission and transformation of light related to the photoelectric effect contains a section on the ionization of molecular gases by ultraviolet light,[6]

> *"We shall have to assume that, in ionization of a gas by ultraviolet light, an individual light energy quantum [photon] is used for the ionization of an individual gas molecule. From this it follows*

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immediately that the work of ionization (i.e., the work theoretically needed for ionization) of a molecule cannot be greater than the energy of an absorbed light quantum capable of producing this effect. If one denotes by J the (theoretical) work of ionization per gram equivalent, then it follows that:

$$R \, \beta v \geq J."$$

where *"R"* is the universal gas constant, *"β"* is a constant from Wien's earlier work,[*] and *"v"* is the frequency of electromagnetic radiation (light). In this paragraph Einstein introduced the concept of one absorbed quantum of light per molecule. He also essentially set bond energy equal to "photon" energy.

A few years later in 1909 Stark developed a similar theory on the quantum nature of light in the X-ray region.[7] He adopted Planck's quantum formula for light quanta with energy equal to *"hv"*, only to a limited extent, asserting the model was appropriate only in the X-ray region. In 1912 Einstein wrote another paper extending his earlier molecular ionization work to photochemical equivalence overall.[8] He enunciated the photochemical equivalence principle, namely that for every photon of electromagnetic radiation that is absorbed, one molecule of the substance reacts. Stark responded, pointing out the priority of his earlier paper. Einstein, in turn, answered curtly[9],

> *"J. Stark has written a note concerning a paper of mine, published recently, with the purpose of defending his intellectual property. I do not wish to comment on the question of priority implied in it, for it would hardly interest anyone, especially since the photochemical equivalence law must be regarded as a completely obvious consequence of the quantum hypothesis".*

Lewis later addressed Einstein's work and formally introduced the term "photon" to denote Einstein's light energy quantum as the carrier of electromagnetic light energy,[10]

> *"When the genius of Planck brought him to the first formulation of the quantum theory, a new kind of atomicity was suggested, and thus Einstein was led to the idea of a light quanta which has proved so fertile. ... **I therefore take the liberty of proposing… the name photon.** ... The energy of an isolated photon, divided by the Planck constant, gives the frequency of photons"* (Bold original)

Thus, it was Lewis who formalized ***photon*** energy as *"E = hv"*, based on Planck's quantum formula.[†] It was also Lewis who brought the dividing line between visible and infrared light into clear focus, writing in the same letter,

> *[I]t is necessary to assume that atoms are frequently changing their photon number by the exchange of photons of very small energy, corresponding to **thermal** radiation in the extreme infra-red."* (Emphasis added)

Further development in quantum chemistry took place in the 1920's. First Heisenberg,[11] and later Heisenberg, Born and Jordan published their matrix mechanics, using measureable parameters of electromagnetic frequency and amplitude rather than the unobservable position and period of revolution of the electron. The next year, in 1926, Schrödinger published his first of several articles on wave mechanics, modeling the electron as a real, physical wave.[12] By the end of that year, Burrau had performed a calculation of the H_2^+ ion in its ground state based on the Schrödinger equation. In 1927 Sidgwick wrote,[13]

> *"It has been suggested that the development in the last few years of the theory of wave mechanics necessitates a fundamental change in our views of atomic structure. This theory, in the hands of de Broglie, Heisenberg, Schrödinger, and others, has had the most remarkable success in dealing with problems of atomic physics ... In developing a theory of valency there are two courses open to the chemist. He may use symbols with no definite physical connotation to express the reactivity of the atoms in a molecule, and may leave it to the subsequent progress of science to discover what realities these symbols represent: or he may adopt the concepts of atomic physics - electrons, nuclei, and orbits - and try to explain the chemical facts in terms of these."*

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[*] Einstein denoted a "photon" or quantum of energy as *"R βv"*. Planck formulated the same quantity of energy as *"hv"*, where *"h"* is Planck's constant, 6.626×10^{-34} J sec. Hence Einstein's product *"R β"* is equal to Planck's constant *"h"*.

[†] Planck assumed the quantum formula as a mathematical convenience in his original quantum work.

Heitler and London did the latter and adopted the concepts of atomic physics to explain concepts of chemistry. They suggested that if there could be a wave equation for a single electron, as described by Schrödinger, then there could also be a wave equation for two (2) electrons. Heitler and London thus extended Schrödinger's wave equation to the two electrons in the hydrogen molecule, publishing their work in 1927.[14] A fundamental assumption in their landmark work was the belief that a "photon" was an elementary particle of light which could couple resonantly with bond energies of molecules and thereby be absorbed, and that "photon" energies could thus be set equivalent to bond energies in mathematical descriptions of molecules.

An important new concept was introduced in 1931 by Maria Goeppert-Mayer,[15] who described the idea of two-photon absorption in her doctoral dissertation.[‡] By the 1960's the possibility of two-photon absorption had become a reality, and was described not only in the visible light region (in europium-doped crystals which emitted blue visible light after absorption of red visible light),[16] but also in the lower frequency infrared region. Two-photon absorption in which each infrared photon carries roughly half the energy needed to excite a fluorescent molecule, has found particular usefulness in biological microscopy. The idea of infrared two-photon photochemistry gradually came to be accepted, however it was believed to apply only to infrared photons and not to lower frequency light such as microwaves and radio waves.

Publications on the theory of microwaves in chemical and material reaction systems insisted (and still do) that even though traditionally "nonionizing" infrared photons can exert photochemical effects, microwave photons possess too little energy to do so and thus exert only thermal heating effects. The experimental evidence showed otherwise, however. In a letter to *Nature* in 1999, Rustum Roy wrote,[17]

> *"The use of microwaves to process absorbing materials was studied intensively in the 1970s and 1980s, and has now been applied to a wide variety of materials[1, 2, 3, 4]. Initially, success in microwave heating and sintering was confined mainly to oxide and some non-oxide ceramics[5, 6, 7, 8, 9, 10, 11]; but recently the technique has been extended to carbide semimetals[12, 13, 14] used in cutting tools. Here we describe the microwave sintering of powdered metals to full density. We are able to sinter a wide range of standard powdered metals from commercial sources using a 2.45-GHz microwave field, **yielding dense products with better mechanical properties than those obtained by conventional heating.** These findings are surprising in view of the reflectivity of bulk metals at microwave frequencies. The ability to sinter metals with microwaves should assist in the preparation of high-performance metal parts needed in many industries, for example, in the automotive industry." (Emphasis added)*

The non-equilibrium effects of the microwaves were clearly producing real, physical results which differed significantly from simple thermal heating effects. Other researchers such as M. Sato at the Japanese National Institute of Fusion Science found that microwaves could catalyze chemical and material reactions at substantially lower temperatures and in relaxation times shorter than those obtained by simple thermal relaxation.[18-24]
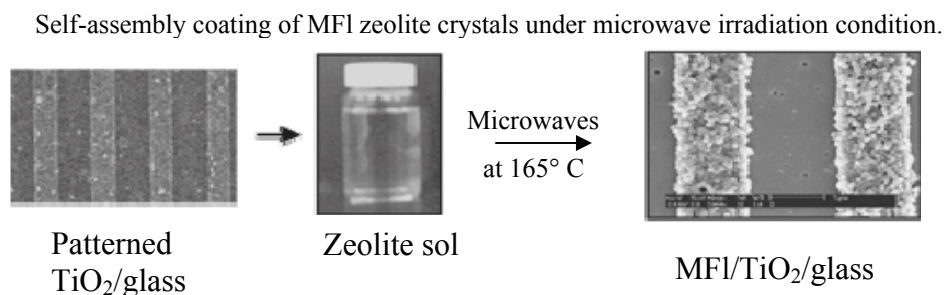
Self-assembly coating of MFl zeolite crystals under microwave irradiation condition.

Patterned TiO$_2$/glass → Zeolite sol → Microwaves at 165° C → MFl/TiO$_2$/glass

Figure. 1. Self-assembly coating of MFl zeolite crystals under microwave irradiation conditions, Sato et al.[ref]

Skeptics abounded however, due to the lack of explainable quantum mechanisms for these clearly non-equilibrium microwave effects. Fortuitously, advances within the last decade in the basic foundations of quantum mechanics have allowed the development of quantum descriptions of non-equilibrium microwave effects.

[‡] Goeppert-Mayer later won the Nobel prize in physics for her discoveries regarding nuclear shell structure.

2. NEW DISCOVERIES IN QUANTUM MECHANICS

The new discoveries in quantum mechanics go back to the very origins of quantum concepts and Max Planck's famous paper[25] on black-body radiation published in early 1901. Planck was at the time a professor at the University of Berlin and had been pursuing two parallel lines of research in tandem: theoretical work on "resonant Hertzian radiation" (electromagnetic waves)[26] and theoretical work on black-body (thermal) radiation. In late 1900 Planck combined those two (2) lines of research into his derivation of the long sought after black-body equation, which described the thermal electromagnetic radiation emitted by an object based solely on its temperature. As Planck explained at the beginning of his paper, the starting point for his derivation was the classical Helmholtz equation for the internal energy of a system, "U = A + TS" ("U" is the internal energy, "A" is the Helmholtz work energy, "T" is temperature, and "S" entropy), summing the orderly work energy and random thermal energy.

Planck briefly described his resonance hypothesis, namely that resonant Hertzian waves are orderly and as such can be completely converted into work, "A". He next explained that the black-body experimental apparatus excluded all orderly work energy from its measurements, so that he could assume that the work energy in the black-body system was equal to zero. Therefore, according to Planck, in that particular experiment the internal energy was equal only to the thermal energy, "U = TS", and "*the entire problem is reduced to determining S as a function of U*". He borrowed some statistical methods from Boltzmann and the energy density method of Wien, and along the way adopted his quantum formula, "E = hv", as a mathematical assumption ("E" is energy, "h" Planck's action constant, and "v" frequency). This assumed formula was actually an abbreviated version of a mathematical relationship Planck used earlier in his electromagnetic theory,[26] namely:

$$\delta U \approx a \ \delta t_m \ v \tag{1}$$

where "a" was a generic constant and "t_m" was the measurement time for the electromagnetic ("EM") radiation.[§] Comparison of the two formulae, "U = a$t_m$$v$" versus "E = h$v$" suggests that his later constant "h" was actually the product of the generic constant "a" and the measurement time "t_m". Investigation of the mathematical procedures used in Planck's black-body derivation confirms that indeed, Planck's famous action constant "h", is really the product of a time variable and another constant.[**]

[§]-The energy of EM radiation is typically measured experimentally as a power value, e.g., Joules/sec, which is then multiplied by the measurement time, e.g., ten (10) seconds, to obtain the total amount of energy.

[**] Reproduced from Chapter 1., The Fundamental Physics of Electromagnetic Waves, in *Electromagnetic Waves*:[27]

"Proof of these facts are found in Planck's 1901 blackbody paper, in which he described the experimental data and mathematical methods he used:

"*§11. The values of both universal constants h and k may be calculated rather precisely with the aid of available measurement. F. Kurlbaum, designating the total energy radiating into air from 1 sq cm of a black body at temperature t˚ C in 1 sec, by S_t found that:*

$S_{100} - S_0 = 0.0731 \ watt/cm^2 = 7.31 \ x \ 105 \ erg/cm^2 sec$"   *(Underlines added)*

Instead of multiplying Kurlbaum's time-based power measurement by the measurement time to obtain total energy (as Planck had done in his earlier work), he converted the power measurement to energy density by dividing by the speed of light "c" (3 X 10^10 cm/sec), according to Wien's method:

"*From this one can obtain the energy density of the total radiation energy in air at the absolute temperature*

$$\frac{4 \cdot 7.31 \ x \ 10^5}{3 \ x \ 10^{10} \ (373^4 - 273^4)} = 7.061 \ x \ 10^{-15} \ erg/cm^3 \ deg^4$$"

The time variables in the numerator and denominator cancelled out and Planck was seemingly able to address energy independent of time. Dividing by the constant speed of light however, is the same as multiplying by time:

As to the identity of that generic constant, various mathematical and dimensional analyses have all lead to the same unrefuted conclusion – the previously hidden constant is an *energy* constant. [1-5, 27-32] To be precise, balancing the units reveals that the energy constant is the energy of a single wave or oscillation of EM radiation, i.e., 6.626 X 10^{-34} J/osc.[††]

Planck had adopted Wilhelm Wien's energy density calculation which caused the measurement time variable to be fixed at a value of one (1) second and simultaneously hidden. Because of the density calculation, when Planck later arrived at the point in his derivation where he calculated his constant "h", he unknowingly calculated it as the *product* of an energy constant, which will be denoted as "h̃", and the hidden and fixed time variable "t_m":

$$h = \tilde{h} \, t_m, \qquad \text{where } t_m = 1 \text{ second,} \qquad (2)$$

hence
$$h = 6.626 \times 10^{-34} \text{ J sec} = (6.626 \times 10^{-34} \text{ J}) (1 \text{ sec}). \qquad (3)$$

Distinguishing the separate energy constant and time variable provides the complete quantum formula:

$$E = \tilde{h} \, t_m \, \nu \qquad (4)$$

Analysis of the oscillation energy constant over time and space (e.g., frequency and wavelength) demonstrates that the energy of a single wave (oscillation) of electromagnetic energy is constant regardless of its frequency, time period, wavelength or wave number. When a parameter is constant over a shift in time or space it is a conserved and universal quantity. The energy constant is thus a universal constant for light, serving as an invariant parameter in the conservation of energy for light.[30]

The discovery of the hidden time variable and energy constant has many implications for practical applications of quantum mechanics. Einstein, and later Lewis, based their quantum "photon" concepts on the energy calculated by Planck's abbreviated quantum formula, unaware that his action constant was really the product of light's energy constant and a fixed, hidden time variable. If one changes the measurement time to half a second, the "photon" energy is halved. Likewise, if one doubles the measurement time to two (2) seconds, the "photon" energy doubles. To paraphrase Lewis, *The energy of an isolated photon, divided by the Planck constant, gives the frequency of photons **in a one second measurement interval**.*

An energy quantity such as "photon" energy, which depends on an arbitrarily fixed time period, cannot represent the fundamental particle of light, however. Such a construct produces a zoo of elementary particles, each with differing energies. This is in stark contrast to other universal constants that are actually constant, for example the constant charge of the electron. This variability in "photon" energy was the very problem that plagued early quantum pioneers and led de Broglie to bemoan the lack of an *"isolated quantity of energy"* for light.[33,34] One hundred years later the quantum riddle has been solved. De Broglie's isolated quantity of energy is the energy of a single oscillation of light, 6.626 X 10^{-34} J/osc. The photon is not the elementary particle of light, but rather is a collection of sub-photonic particles

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$$\frac{E/t \, s^2}{c} \quad = \quad \frac{E}{t \, s^2} \quad \text{x} \quad \frac{t}{s} \quad = \quad \frac{E}{s^3} \qquad 12.$$

where "s" is distance. In this case the time value by which the power measurement was multiplied was the constant "one second" unit time of the constant speed of light. Planck seems to have been unaware that by using Wien's energy density calculation he was actually causing the infinitely variable measurement time to be fixed at a constant value of one second. He also seems to have been unaware that the fixed time variable was subsequently hidden in the final calculations of his action constant "h":

$$h = 6.626 \times 10^{-34} \text{ Joules seconds} \qquad 13.$$

His action constant is actually the *product* of a true universal constant - "h̃" - and the fixed, hidden measurement time variable, "t_m".

$$h = \tilde{h} \, t_m, \qquad \text{where } t_m = 1 \text{ second} \qquad 14."$$

[††] Notably, the incomplete mathematical notation adopted by Planck - which omitted units for oscillations - is no longer necessary and the energy constant is given in proper and complete mathematical notation as energy per oscillation. See reference No. 27 for further discussion.

- individual light waves - each with the same constant energy regardless of their frequency or wavelength. Seen in this light, energetic and dynamic limitations attributed to microwave "photons" are actually artifacts of a mathematical inadvertence which took place many decades ago, at the dawn of the quantum era.

3. MICROWAVE MECHANISMS

3.1 Resonant Absorption

Absorption and transformation of electromagnetic waves by matter extends to all reaches of the spectrum. Visible and ultraviolet light are produced by electron motions, while infrared waves are produced by motions between atoms. Fine structure splitting frequencies result from the interactions of the electron's magnetic field with its electric field or from the rotational motions of molecules, and fall primarily in the infrared and microwave regions. Likewise, hyperfine structure splitting frequencies result from the interaction of the nucleus' magnetic field with the electric field of the electron, and fall in the microwave and radio wave regions. For example, the radio wave frequency used by astronomers to track clouds of hydrogen gas in the cosmos is the hydrogen hyperfine splitting frequency of 1420 MHz.

Fundamental to Planck's landmark quantum work was his recognition of the effects of resonant EM waves in his resonance hypothesis.[25] Namely, orderly resonant EM waves, once absorbed, are completely free to be transformed into work within a reaction system. Work involves the movement of mass through space over a period of time (mass X velocity^2). On the molecular or atomic level, work entails the breaking of bonds and the movement and rearrangement of atoms and sub-atomic components within a material or reaction system. Thus when one speaks of the transformation of light's energy into work energy in a chemical or materials sense, one is referring to the rearrangement of atoms and sub-atomic particles in chemical and material reactions. Inherent to the rearrangement of atoms and subatomic particles, are the motions of electrons, protons, and neutrons: components central to the fine and hyperfine splitting frequencies.

Planck's resonance hypothesis emphasized the existence of resonance or *"homogeneity"* between the frequency of the light energy and the frequency of the matter *"resonators"*. As Millikan stated in his 1916 vindication of Planck and Einstein,[35] *"absorption [of EM waves] is due to resonance (and we know of no other way in which to conceive it)"*. Energy distribution shapes for the classical electromagnetic theory of line widths, the quantum-mechanical theory of line widths, and Stark broadening are all resonance curves.[36] Significantly, Doppler broadening (which is due to the *random* heat motion of radiating atoms) follows a Gauss error distribution curve instead of a resonance curve. The ability of electromagnetic energy to be absorbed and converted into work depends not on its "photon" energy, but rather on its frequency and degree of resonance with the matter in question.

Planck's resonance hypothesis has been confirmed experimentally for microwaves. For example, in a study of fuel cell current discharge times, it was found that low intensity excitation of the fuel cell cathode with resonant microwave energy extended the current discharge time by 50%, in essence performing useful work on electrons transiting the fuel cell membrane. Excitation of the cathode with off-resonant microwaves of slightly higher frequency had no effect on the current discharge time and tracked with the control data.[37] In another example, mixed halide salt crystallization systems were irradiated with microwaves which were resonant with the rotational frequency for only one of the halide salts in the mixed salt system. Crystal axes, planes and shapes characteristic for the resonated salt were produced, rather than the crystal shapes normally obtained in the mixed salt system.[38] The work performed on the resonant molecules in the crystals grown under microwave irradiation caused them to move and arrange themselves in a particular order not present in the control crystals, which formed under purely thermal conditions. In studies performed at the Japanese National Institute of Fusion Science, the activation energy for nitridation of titanium-dioxide was reduced by 70% using non-equilibrium microwaves.[18] Similar findings were recently confirmed in a copper-based system as well. Likewise, research at the Toyota Central R&D Labs demonstrated biomass conversion into ethanol precursors in 1/50th the time with 50 X greater yields, using frequency specific microwaves. Off-resonant frequencies (2.45 GHz) did not work.[39]

Planck's incomplete quantum formula pointed early quantum pioneers in the wrong direction. Einstein and others were induced to conclude that the "photon" was the ultimate particle of light, when in fact it was simply a time-based collection of individual light oscillations (the true elementary particles of light). Scientists were drawn away from the essential beauty of Planck's resonance hypothesis, to the conclusion that photon energy was the crucial threshold for conversion of EM energy into work, rather than the frequency and resonance quality of the light waves. The conclusion that "photon energy" must be at least as large as the energy of a chemical bond and its accompanying photochemical equivalence concept, although logically based on the information then available, never-the-less introduced significant

limitations into concepts regarding the usefulness of lower frequency light waves in photochemical and photomaterial reaction systems.

Microwaves, when resonant with a component of a reaction system, can be absorbed and perform work on the system leading to chemical and materials transformations not found under simple thermal conditions.

3.2 Splitting Frequency Stimulation Leading to Electronic Excitation

Much useful information on the mechanisms of non-equilibrium microwaves can be gleaned from the microwave spectroscopy literature. In particular, fine and hyperfine splitting frequencies have been the subject of great interest and study by microwave spectroscopists.[40] One of the earliest microwave spectroscopy methods involved use of a microwave source of variable frequency and a microwave detector. Standard sweeping of the microwave spectrum was performed, looking for frequencies of increased amplitude emitted by the test material when irradiated by resonant microwaves. That arrangement had a major drawback related to the physical size of the waveguides and their propagation of the microwaves. An improvement to that method was developed that used a microwave source and a visible/UV detector. The excitation of the splitting frequencies by the microwaves caused subsequent excitation of the electronic frequencies with which the fine, hyperfine, and splitting frequencies are associated. The resulting electronic excitation was then detected by the visible/UV detector. In this manner, microwave spectroscopists were able to detect the various resonant microwave frequencies of a material.[‡‡]

The ability of EM light waves in the visible and ultraviolet regions to catalyze photochemical reactions by excitation of electronic frequencies is undisputed. It is the quintessential mechanism of photochemistry. It is also clear that the absorption of resonant fine and hyperfine splitting microwave frequencies can result in electronic excitation of a material. It is therefore reasonable to propose that irradiation of a reaction system with resonant splitting microwaves can result in electronic excitation of targeted reactants or intermediates, which in turn leads to catalysis of chemical and material reactions.

The use of splitting frequencies to catalyze reactions has been confirmed experimentally.   For example, the formation of water from stoichiometric quantities of hydrogen and oxygen gases has been catalyzed using the fine splitting alpha rotation-vibration microwave constant of the hydroxy intermediate, namely 21.4 GHz.[41]   Likewise, in a hydrogen peroxide dissociation model, oxygen gas production was increased 10-fold using a hyperfine splitting frequency of hydrogen (17.5 MHz), which is an atomic constituent of hydrogen peroxide.

Microwaves which stimulate fine or hyperfine splitting frequencies may produce electronic excitation in various reaction system species, leading to chemical and materials transformations not found under simple thermal conditions.

3.3 Resonant Acoustic Transduction

Acoustic waves are produced when longitudinal zones of high and low pressure (compression and rarefactions zones) propagate through a solid, liquid, gas or plasma. They differ from electromagnetic waves in that rather than electric and magnetic fields emitted by atoms or molecules moving through space, the atoms and molecules themselves move in space, oscillating around a central location.

Acoustic waves are traditionally produced by one of two (2) means. In the lower frequency regions below around 10 GHz, acoustic waves are produced by physical, mechanical transducers. The transducers come in direct contact with the test material or with a medium surrounding the test material such as liquid or gas. Electrical signals conveyed to the transducers are converted into oscillating mechanical motions. These mechanical motions first press the transducer surface against the material, creating a zone of high pressure, and then oscillate away from the material, creating a zone of rarefaction. The repeated mechanical motions create the alternating zones of compression and rarefaction typical of longitudinal acoustic waves.

[‡‡] This energy transformation pathway functions in reverse as well. Irradiation of a material with one of its resonant electronic frequencies in the visible/UV region can lead to emission of splitting frequencies in the microwave region which can be measured with a microwave detector.

There are certain limitations to this transducer technology, and above the threshold of about 10 GHz, current fabrication technologies are unable to produce effective transducers. Thus, when studying phenomena in the ultrahigh region of the acoustic spectrum, traditional transducers cannot be used. Instead, electromagnetic waves are used as the driving force, producing compression and rarefaction zones in the material as wave after wave of light impacts upon the surface of the material. This ultrahigh acoustic method is made possible by the phenomenon of momentum associated with light. This phenomenon was theorized by de Broglie in his doctoral thesis, and has been confirmed[42,43] many times throughout the recent century in numerous and varied experimental systems.[§§]

These various aspects of acoustic wave production evolved into technology concepts in which transducers were used for low frequency applications, electromagnetic waves were used for ultrahigh applications, and never the twain could meet. Traditionally, electromagnetic waves were thus not used at lower frequencies where transducers were available, and numerous acoustic texts taught that EM waves *could not* be used to produce lower frequency acoustic waves. While it was true that transducers simply could not be fabricated for the ultrahigh acoustic frequency region, there appeared to be no such limitations in the production of lower frequency electromagnetic waves.

It was thus theorized that since lower frequency EM waves in the microwave and radio wave regions carry momentum just as do their higher frequency counterparts in the ultrahigh acoustic region, these lower frequency EM waves would produce acoustic waves in an irradiated material. The concept that low frequency electromagnetic waves could produce acoustic waves, was first verified by the instant author in the late 1990's in the radio region at 1.7 MHz.[44] Briefly, the ability of resonant acoustic waves, at controlled amplitude levels, to enhance growth rates of biologics had been identified and was under active investigation. In the sugar snap pea model, delivery of the resonant acoustic frequency of 1.7 MHz via an acoustic transducer accelerated sprout growth and increased germination levels. Subsequent delivery of the resonant acoustic frequency via 1.7 MHz EM waves (without the use of a transducer) produced similar results. Thus the biologic matter functioned as a living tranducer, transforming the momentum of the electromagnetic waves into acoustic waves, just as in the ultrahigh frequency acoustic methods.

The fact that lower frequency EM waves produce acoustic waves in an irradiated material was subsequently confirmed independently by Guilliorit et al in the microwave region.[45] These researchers found that microwaves transmitted to a specimen produced acoustic waves in the specimen, which reached maximal acoustic wave amplitudes when the microwave frequency matched a resonant acoustic frequency of the specimen.
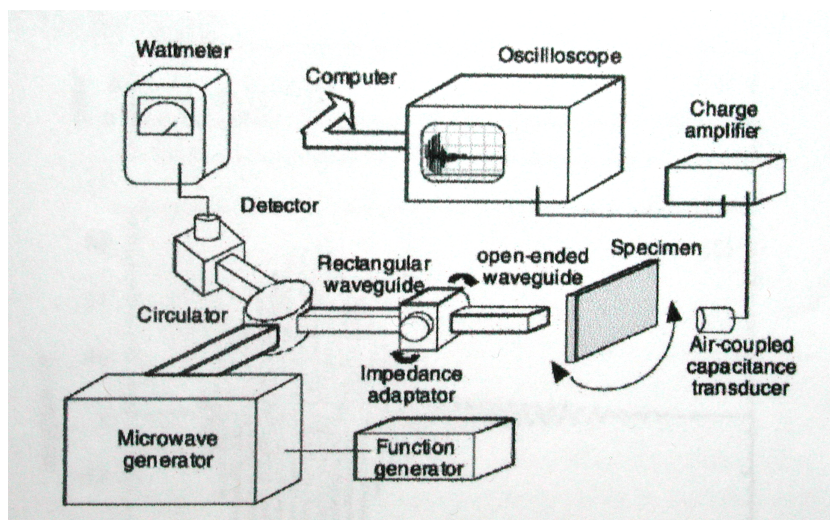

Figure 2. The experimental design employed by Guilliorit et al. The specimen was a graphite-fiber reinforced composite plate. Microwaves emerged from the end of the open-ended waveguide and irradiated the specimen. An air-coupled capacitance transducer detected the acoustic waves in the specimen. Guilliorit confirmed this effect in numerous other specimens and materials.

[§§] The energy/mass/momentum aspects of light are addressed in greater detail in the paper **"The Conservation of Light's Energy, Mass and Momentum"**, which accompanies this paper in this same program, *The Nature of Light: What are Photons? IV.*

In the resonant acoustic transduction mechanism of microwaves, therefore, when a chemical or material reaction system is irradiated with microwaves of frequency equal to a resonant acoustic frequency for the system, acoustic waves will be produced and the effects of that acoustic resonance will be seen in the system. The microwaves will be transduced and transformed into resonant acoustic energy, which in turn is free to be converted into work in the system. At lower amplitudes of acoustic resonance the work may result in stimulation and enhancement of processes, while at higher acoustic energy amplitudes, disruption of bonds, macromolecules, and material planes and axes may result. Resonant acoustic waves also possess great utility in spectroscopy, identification and diagnostic technologies. The mechanisms by which acoustic waves exert their effects on chemical and material reaction systems include the acoustoelectric, magnetoacoustic, and acousto-EM effects,[44] in addition to the commonly recognized mechanisms such as cavitation and mechanical effects.[***]

Microwaves can produce acoustic oscillations and waves in matter, and when delivered particularly at resonant acoustic frequencies, can have dramatic non-equilibrium effects in reaction systems.

4. DISCUSSION

The non-equilibrium state is typically spoken of in regard to non-equilibrium *thermodynamics*. Considering recent discoveries in the foundations of quantum mechanics, this designation appears too narrow for the full range of processes and phenomena displayed by nature. After all, the classical Helmholtz equation for the internal energy of a system,

$$U = A + TS,\qquad(5)$$

considers not only the thermal energy of a system but also its work energy. Planck's brilliant resonance hypothesis extended Helmholtz's concept of work energy to include resonant electromagnetic light waves as well. Given Planck's extensive education by Helmholtz on resonance phenomena, he was undoubtedly aware of the effects of resonant mechanical waves on a system. When a system is in a steady state of oscillatory motion and it is exposed to oscillatory forces of the same frequency, the energy absorbed by the system is transformed into energy of motion in the system itself. The system experiences an acceleration in its oscillatory motion allowing the system's oscillations to travel greater and greater distances within the same time period. Mathematically, a system with resonant frequency "ν_r" exposed to an outside force of frequency "ν_o", experiences an acceleration "a". In the resonance equation derived from Newton's second law of motion, if the outside frequency is very close to the resonant frequency, the denominator will be very small and the amplitude "A" of the system's oscillations will become very large:

$$A = \frac{a}{\left| \nu_r{}^2 - \nu_o{}^2 \right|}\qquad(6)$$

Planck recognized that the emission and absorption of electromagnetic waves was "*a resonance phenomenon in that the above-named oscillators [e.g., atoms] not only emit waves, but also are excited into oscillation by the incoming waves… These oscillators would emit waves because of their oscillations, and thus emit energy, but in turn would absorb selectively incident waves through resonance, thus <u>amplifying their oscillation energy.</u>*"[26] (underline added). Planck understood that resonant waves could lead to exceedingly large amplitudes of oscillations in a mechanical system (Figure 3., below). He applied this same logic to electromagnetic waves on the microscale. Light waves absorbed through resonance would amplify an absorbing system's atomic or molecular oscillations. The electromagnetic energy is transformed into work energy – work is the motion of mass in space and time - and these pre-existing *motions* on the microscale were amplified and increased. This is Planck's resonance hypothesis.[5]

[***] A full discussion of these acoustic mechanisms is beyond the scope of this paper on microwaves, and the reader is directed to reference No. 44 for further information.
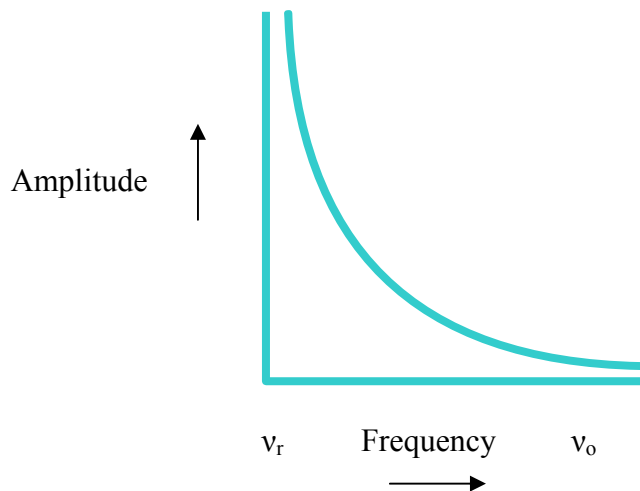
Figure 3. Amplitude plotted as a function of an applied resonant force. As the outside frequency "ν_o" approaches the resonant frequency "ν_r", the amplitude of the system's oscillations increases dramatically.

This distinction between resonant work energy and entropic thermal energy was reinforced by Millikan a decade later when he stated, "[T]*he phenomena of absorption and of emission show that…oscillators possess natural frequencies…and the characteristic waves which they emit are of these frequencies … [I]f any particular frequency is incident upon such a substance the oscillators in it which are in tune with the impressed waves may be assumed to absorb the incident waves"*.[35] Millikan's own meticulous experimental findings on the photoelectric effect showed that, *"emission of [electrons] from the atom…takes place especially copiously when the impressed frequency coincides with a 'natural frequency' "*. Millikan made it clear that the photoelectric effect upon which Einstein had based his quantum concepts was a resonant work phenomenon and not a thermal process. The resonant photoelectric effect, said Millikan, *"furnishes a proof which is quite independent of the facts of black-body radiation, of the correctness of the fundamental assumption of the quantum theory, namely, the assumption of a discontinuous… [EM]energy absorbed by the electronic constituents of atoms from [light] waves"*.

Thus, although the term non-equilibrium is most commonly heard in reference to thermodynamics, it may well be more appropriate to refer to *non-equilibrium energy dynamics*, encompassing both resonance work energy and thermal energy.

Particular emphasis has been placed on the maximization of entropy in engineering applications. Far less emphasis is placed on maximizing resonant work energy in technology processes. This imbalance in focus between the fundamental energies comprising the internal energy of a system may be due in part to Planck's statement of the black-body puzzle as being solved when resonant work energy is omitted and *"the entire problem is reduced to determining [entropy] S as a function of [energy] U"*. Early quantum pioneers were aware of resonance phenomena, as indicated above by Millikan's statements above, however Planck himself focused almost exclusively on thermal/entropic processes rather than on resonant work processes in his later more influential years. Both Heisenberg and Schrödinger attempted unsuccessfully to include resonance energy dynamics in their work, and struggled with what they termed the "*resonance catastrophe*". Schrödinger wrote, *"I do not wish, however, to attempt to work out the calculation of the resonance case"*. (For more information on recent developments in resonance energy dynamics, the reader is referred to reference No. 29.)

Previous difficulties in development of resonance dynamics can be attributed in large part to misconceptions regarding "photons" and the elementary particle of light. Einstein's light quantum theory and photochemical equivalence concepts relied heavily on the understanding that the photon was an indivisible particle of light. Planck's abbreviated quantum formula led early investigators to conclude that the energy of the photon and energy level terms were paramount, rather than the frequency and resonance characteristics of the EM light waves and absorbing/emitting matter. Schrödinger described this state of affairs in his final paper on wave mechanics stating, *"[A]s soon as the conception of the 'terms' as discrete energy levels had been introduced, we were obliged to see a corroboration of that conception in every new [energy] exchange phenomenon discovered, even if there is really nothing present in nature beyond the resonance phenomenon…I do question whether it is not very much more to the point to push the idea of the frequency …instead of that of the 'kinetic energy of the single electron'."*[12]

The photon is not an indivisible particle however, and its energy is merely the summation of individual wave energies in a one second interval of time. One sees from consideration of the complete quantum formula, "$E = \tilde{h}\, t_m\, \nu$", that the energy constant "$\tilde{h}$" provides the energy of a single oscillation of light, while the product of the measurement time and frequency "$t_m\, \nu$", provides the number of waves to be summed. Given the importance of frequency and resonance to the absorption of EM light waves by matter, it does seem that Schrödinger's sense of the importance of "*the idea of the frequency*" was correct. Nowhere is this idea more important than in the application of microwaves to reaction processes.

Calculated "photon" energies in the microwave region are considerably less than chemical bond energies. Scientists quite naturally concluded that as a consequence of the quantum theory those low energy microwave "photons" would not provide enough energy to affect reaction system dynamics in any appreciable manner. In light of the new quantum discoveries, it is no longer tenable to assume that light must be absorbed in units equivalent to one second measurement intervals, however. Recent advances in spectroscopy and laser technology have demonstrated that most reaction system dynamics take place on time scales much smaller than one second. The mere fact that microwave "photon" energies are less than bond energies is no longer a limiting condition when considering the effects of microwaves on chemical and material systems.

New degrees of freedom are now available for elucidating the mechanisms of microwaves on matter. The Helmholtz relationship designates two (2) broad categories of energy which are summed to provide the total internal energy of a system:

$$U = A + TS$$

namely work energy "A" and thermal energy "TS". If one desires to increase the internal energy of a system, there are but three choices – increase work energy, temperature or entropy. Planck's derivation of the black-body equation assumed the work energy was zero, and thus the original foundational work in quantum mechanics focused on entropy and temperature:

$$U = TS \tag{7}$$

Widespread adoption of this limited construct in statistical renditions contributed to the current focus on increasing entropy, which is well entrenched in industrial and engineering processes. This limiting approach is no longer necessary. It is perhaps time to focus on increasing work energy rather than temperature or entropy[†††]. Microwaves promise to be the perfect vehicle for this. For example, as previously described, non-equilibrium microwaves reduced activation energy by 70% in a titanium-oxide nitridation system, and a biomass conversion time/yield ratio was decreased 2,500 times.

Embracing equilibrium and maximal entropy leads to only small fluctuations which quickly return to stable stationary states.[46] This hardly seems the most efficient manner in which to bring about significant chemical and material ***changes***. Non-equilibrium systems undergo significant fluctuations and in dissipation of those fluctuations useful work can be done and important change accomplished. As Prigogine noted in his 1977 Nobel lecture, "*non-equilibrium may be a source of order. Irreversible processes may lead to a new type of dynamic states of matter*".[47] Although referring to non-equilibrium thermodynamic processes, his concepts can be applied to resonant work processes and non-equilibrium microwaves.

A fundamental aspect of Helmholtz's internal energy relationship was his distinction between work energy and thermal energy.[2] According to Helmholtz, the transformation arising from the *orderly, uniform* motion of atoms is work energy. Energy transformations that make use of the *random, chaotic* motion of atoms constitute heat energy and are unavailable to do work. Planck maintained this distinction in his famous black-body paper, *"Entropy depends on disorder and this disorder…depends on the irregularity with which it constantly changes its amplitude and phase… If amplitude and phase both remained absolutely constant, which means completely homogeneous vibrations, no entropy could exist and the vibrational energy would have to be completely free to be converted into work."* To the extent that microwaves are both constant, orderly, and homogeneous (i.e., resonant) with an irradiated material, the non-equilibrium state caused by the microwaves serves as a source of order and leads to a new type of dynamic state of matter through the dissipation of work energy in the material.

[†††] Observation of M. Sato, of the Japanese National Institute of Fusion Science.

Where the absorption of EM light waves causes fluctuation, instability, or non-equilibrium in the stationary state of the system, a rapid and dramatic change may be triggered away from the unstable stationary state to a new state. These are precisely the changes described throughout the 1970's - 1990's using microwaves to process materials. *"[S]ymmetry breaking instabilities are of special interest as they lead to a spontaneous 'self-organization' of the system both from the point of view of its space order and its function."[48]*

Lagrange summarized the underlying processes most eloquently in his famous work on analytical mechanics.[49] The energy of a system at constant velocity *"results solely from the inertia forces of the bodies"*, while the moment of force *"Fδs"* causes an acceleration of the body. *"The sum of these two quantities, when equated to zero, constitutes the general formula of dynamics…these forces equilibrate each other and the system is in equilibrium, but when the equilibrium does not hold, the bodies must necessarily move due to all or some of the forces which act on them."*

The absorption of microwaves by chemical or material reaction systems – whether by mechanisms of resonant absorption, electronic excitation caused by splitting frequency stimulation, or transformation to resonant acoustic waves - introduces forces into the system that disrupt the equilibrium of the already existing thermal/entropic equilibrium forces. These new EM work forces create a state in which the equilibrium does not hold, and the system components must necessarily move due to the microwave forces which act on them. In the case of uniform, orderly microwave oscillations, there can be – as Planck suggested - no entropy and the microwave energy is completely free to be converted into work.

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