

Microwave Effect in Chemical Reactions

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Abstract

Time dependent perturbation theory predicts no change in the electronic state probability amplitudes of molecules unless the energy of the applied electromagnetic field matches an electronic energy level difference. Therefore, microwaves should have no non-thermal effect on chemical reactions. However, at low frequencies the oscillating potentials are essentially classical and the relevant question is whether the electronic molecular states evolve adiabatically or non-adiabatically. Time varying potentials can mix excited states into the instantaneous adiabatic ground state as the expectation of the energy changes in response to the potential. This mixing yields a non-zero excited state probability amplitudes $c_n(t)$. Measurements of these excited states, for example, by reactant collisions, may collapse the instantaneous ground state wave function onto the excited state with a probability $|c_n(t)|^2$. This non-adiabatic probability opens a new channel for chemical reactions in addition to the usual thermal Arrhenius probability. The temperature dependence of the reaction rate from these two channels will exhibit the microwave effects primarily at low temperatures. At high temperatures the Arrhenius probabilities will dominate and the microwave effects may be negligible. Most precise laboratory assessments of non-thermal microwave effects appear to have been at high temperatures. Several experiments are reviewed and one is found to have a wide enough temperature range to exhibit the predicted form. Our results also suggest that microwave couplings could induce reactions different from those weighted by the thermal probabilities.

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1. Introduction

Many chemists over the last several years have begun to use microwave ovens as a chemical reaction platform and frequently have reported¹⁻⁷ that several different reactions seem to run faster, with higher yields, or more completely than conventionally heated chemical reactions. These observations have led many to wonder if there is an effect of the microwaves in addition to the heating of the solvent than can enhance the reaction rate of the chemical reactions that are being studied. Recent new developments⁸⁻¹⁰ surrounding SiC reaction vessels and more accurate temperature measurements have reported that at generally higher temperatures there appears to be no non-thermal microwave effects. This paper is a theoretical exploration of the question of such a microwave effect.

A general assumption in chemical reactions is that there is a transition state from which the reaction will proceed if the transition state is occupied. The usual Arrhenius theory of reaction rates¹¹ assumes that the occupation of the transition state is determined by the thermodynamic probability $e^{-E/RT}$, where E is the difference between the ground state and the transition state, RT is the product of the gas constant and the absolute temperature. Increasing the temperature increases the thermodynamic probability that the transition state is occupied. The dielectric heating that accompanies microwaves will lead to increased reaction rates just as any other heating source. The important question: is there any effect beyond heating that can increase the reaction rate?

All of the considerations below will involve the quantum mechanical eigenstates Ψ_n with energy E_n of the unperturbed molecular Hamilton H_0 and the effect of a time dependent perturbation $V(t)$ on the state $|\Psi(t)\rangle$

$$|\Psi(t)\rangle = \sum_{n=1}^N c_n(t) e^{-iE_n t/\hbar} |\Psi_n\rangle, \quad (1)$$

where $c_n(t)$ is the probability amplitude for the Ψ_n . The probability $P_n(t)$ of finding the system in state Ψ_n at time t is given by the absolute value squared of the probability amplitude

$$P_n(t) = |c_n(t)|^2. \quad (2)$$

In section 2 comments about adiabatic evolution will be made, simple models will be examined, and the predicted form of the reaction rate will be presented. In section 3 we will, be examined rigorously examine the effects of a classical, externally driven, time-periodic vector potential. In section 4 the comparison with experiment and evaluation of fits to experiments will be discussed. Several studies will be discussed to seek evidence for the predicted signature for this effect. One paper¹² was found that appears to show the predicted behavior of the reaction rate. A discussion of the impact of non-adiabatic excitations is included in Section 5. The results of time dependent perturbation theory is discussed in Appendix A and the analysis of the temperature dependence of several microwave experiments is given in Appendix B.

2. Adiabatic and Non-Adiabatic Evolution

Quantum mechanical systems, for example, electrons in molecules, interact with electro- magnetic (EM) fields through the mechanism of the vector potential $\mathbf{A}(\mathbf{r}, \mathbf{t})$ ¹³, which will be discussed in more detail in the next section. The interaction of the quantum system with the EM field may be determined by replacing the momentum \mathbf{p} in the Hamiltonian by the sum $\mathbf{p} + e\mathbf{A}(\mathbf{r}, \mathbf{t})$ ¹⁴⁻¹⁶ where $-e$ is the electron charge. When this is done, the lowest order perturbation potential becomes

$$H_1 = \frac{e}{m} \mathbf{A}(\mathbf{r}, \mathbf{t}) \cdot \mathbf{p}. \quad (3)$$

If the vector potential depends on a single frequency ω , there are two broad ranges of frequency that need to be treated differently. One of these ranges is large frequencies, especially those in which Planck's constant \hbar times the frequency is near the energy differences between quantum energy levels $\Delta\epsilon$. The other frequency range is for very small values, almost near zero, where considerations of the adiabatic theorem and non-adiabatic processes can become important.

In the first range, when the frequencies and energy level differences are close to matching, it is necessary to write the vector potential as an operator that describes the absorption and emission of photons simultaneously with the changes in state occupation of the molecular quantum system.^{14,15}

In this range the photons and the electrons are strongly coupled and exchange energy in the form of photons and electron transitions between energy states. Time dependent perturbation theory (as discussed in Appendix A) calculates the change in the probability amplitudes for the excited states, assuming that the quantum system initially in the ground state ($c_s(t = -\infty) = 1$, and $c_n(t = -\infty) = 0$, for $n \neq s$). The well known result of this calculation is that unless the photon energy matches the energy level difference, there is no effect on the electron quantum system. In other words, the excited state probability amplitudes remain zero.

If the frequency of the EM field (vector potential \mathbf{A}) is much smaller than any electron energy level difference, the results discussed above would imply that there can be no effect on the probability amplitudes. Indeed, there have been a number of talks, books, and papers¹⁷⁻¹⁹ asserting this result and applying it to biological problems and other low frequency situations.

However, this conclusion may be premature because as the frequency decreases, the vector potential becomes more and more classical and then the relevant question is whether the electronic system is responding adiabatically or non-adiabatically to this classical vector potential. The classical vector potential does not contain photon creation and annihilation operators. It is necessary to explore the question of non-adiabatic excitations from adiabatic ground states at these small frequencies.

The adiabatic theorem,^{15,20,21} which is sometimes referred to as Ehrenfest's theorem^{22,23} essentially says that if a perturbation changes in time slowly enough, the probability amplitudes do not change even though the overall energy changes over time. In other words, if a system is in its ground state initially, it remains in the instantaneous ground state as the perturbation changes slowly in time. Quantum mechanically, the instantaneous ground state must be formed from a time dependent admixture of the original ground state and excited states. This time dependent admixture of states opens the system to the possibility of wave function collapse into an excited state if a measurement of the system occurs from outside of the system Hamiltonian. The probability of excited states in the instantaneous ground state has often been labeled the non-adiabatic probability of the excited states.¹⁶

A sizeable body of research is pursuing the questions of adiabaticity and non-adiabaticity in a variety of theoretical contexts. There are essentially two branches of such studies. One branch emphasizes the measurement induced wave function collapse of the adiabatic wave function to the excited state.

The other branch more directly examines the impact of including coupling terms between electrons and nuclei beyond the Born Oppenheimer approximation. Even in this second branch the impact of wave function collapse can be found in mixed states. Reviews by Matsika and Krause²⁴ and by Worth and Cederbaum²⁵ review the breakdown of the Born Oppenheimer approximation in a variety of contexts. They discuss the dynamical effects when two electronic potential energy surfaces are close together in energy and couple the electrons and ions via a conical intersection. These conical intersections induce a variety of phenomena called vibronic couplings (photochemical funnels) which can give rise to time varying probability amplitudes for different electronic states. These mixed states are believed to be responsible for unexpected bands in photoelectron spectral excitations of butadiene, benzenes, pyrozone, photochemistry of several organic molecules and radiationless relaxations of DNA and, of amino acids in proteins.

McEniry et al²⁶ report the coordinated efforts of a large research group studying the non-adiabatic transitions which must be considered when departing from the Born Oppenheimer approximation for condensed matter. They are attempting to carry on the earlier work of Ehrenfest^{22,23}, beginning with treating the electrons quantum mechanically for a given configuration of the nuclei and then treating the ionic motions classically. These schemes can all be treated as molecular dynamics calculations. The biggest challenge is the appropriate calculation of non-adiabatic processes which are required in order to describe correctly joule heating of the ions by the electrons, energy loss by energetic ions to the electron system and the inclusion of spontaneous emission by the electrons. Non-adiabatic transitions are also important for the understanding of photo-excitations of electrons in polymers and other solids.

Wodtke et al²⁷ review in detail the non-adiabatic electron excitations that appear to transpire at molecule/metal surface interactions. The role of large amplitude vibrations and non-adiabatic electron hole excitations in the metal are reviewed for several theoretical and experimental studies. The role of adiabatic mixed ground states between ions and neutrals as the molecule approaches the surface are analyzed in terms of non-adiabatic excitations involved in electron transfer and wave function collapse. Emphasis in their review was on searching for new theoretical approaches beyond the Born Oppenheimer approximation and on experiments probing details of non-adiabatic excitations and interactions.

Several explicit calculations have also found non-adiabatic excitations. One example, Smith et al²⁸ report on time-dependent Hartree Fock calculations of the instantaneous atomic charge distributions and dipole moments for three polyenes: ethylene, butadiene, and hexatriene. They observe non-adiabatic excitations where the frequency of the driving field is 30% to 50% of the excitation energy level differences to the lowest excited states. This non-adiabatic response increases with the length of the polyene molecules and with the corresponding decrease of the energy difference between the ground state and the excited state.

The other branch of models demonstrate that time-dependent mixed states can give rise to non-adiabatic excitations in the presence of wave function collapse induced by projective interactions from outside of the molecular model Hamiltonian itself.

The first explicit theoretical model of non-adiabatic excitations can be found with a simple spin one-half in a rotating magnetic field. The dynamics of a spin in a rotating magnetic field was studied in 1937 by Schwinger²⁹ and the same problem has been included in the introductory quantum text by Griffiths.¹⁶ The problem involves a spin $1/2$ in a magnetic field that has magnitude B_0 , is canted from the z-axis by an angle α , and is rotating about the z-axis with an angular frequency ω . If the system starts in a spin up state along the field at time zero, the non-adiabatic probability of being found in the spin down state at a later time is non-zero and periodic in time.

$$P_{\downarrow}(t) = \omega^2 / \Omega^2 (\sin(\alpha))^2 (\sin(\frac{\Omega t}{2}))^2 \quad (4)$$

where $\Omega = \sqrt{\omega^2 + \omega_1^2 - 2\omega\omega_1 \cos(\alpha)}$ and $\omega_1 = eB_0/m$ the Larmor Frequency. This periodic probability represents the non-adiabatic transitions of this system that can occur every period $2\pi/\Omega$ when a measurement of the spin down state is made. In any period of the magnetic field rotation there is a chance that the system will be found in the higher energy state if the population of that state is measured. The instantaneous ground state of the spin is a mixture of the spin up and the spin down states. Any measurement of whether the spin down state is occupied will collapse the instantaneous ground state wave function to the spin down state or not depending on the results of the measurement. This effect vanishes as $\omega \rightarrow 0$. At finite frequency ω there will be non-adiabatic transitions in processes that measure the presence of the down spin state. This simple model has significant similarities to low frequency microwaves and chemical reactions.

The second simple two-state model of non-adiabatic behavior will further illustrate some of these ideas. The lower energy state, here chosen to have zero energy, will be called the bonding state (ground state). The higher energy state with an energy $\Delta\epsilon$ will be called the anti-bonding state (transition state). The application of this model will be to assume that if the system were to be found in the anti-bonding (transition) state, the system will break up or undergo a chemical reaction.

We now consider a time dependent, classical, potential matrix element that mixes these two levels together and makes the energy of the system time dependent. This potential is classical because its time development is determined by external sources and it is not effected by the quantum states of the molecule. We are particularly interested in these ideas when the frequency of the perturbation is small, $\hbar\omega < \Delta\epsilon$. The time dependent matrix element is

$$V_{01}(t) = ve^{i\omega t}. \quad (5)$$

The time dependent Schrodinger equation is ($\hbar = 1$)

$$i\frac{d}{dt} \begin{pmatrix} c_0(t) \\ c_1(t) \end{pmatrix} = \begin{pmatrix} 0 & ve^{i\omega t} \\ ve^{-i\omega t} & \Delta\epsilon \end{pmatrix} \begin{pmatrix} c_0(t) \\ c_1(t) \end{pmatrix} \quad (6)$$

with the initial condition that the molecule is initially in the bonding state ($|c_0(0)| = 1, c_1(0) = 0$). The exact solution is

$$c_0(t) = \cos(\lambda t) + i\frac{m}{\lambda} \sin(\lambda t), \quad (7)$$

and

$$c_1(t) = -i\frac{v}{\lambda} e^{-i\omega t} \sin(\lambda t), \quad (8)$$

where $m = (\Delta\epsilon - \omega)/2$ and $\lambda = \sqrt{v^2 + m^2}$.

If the molecule starts initially in the bonding state and the molecule is isolated from its surroundings, the instantaneous ground state of the system evolves adiabatically changing its energy in response to the time variation of the oscillating potential. However, for the ground state to change its energy, it must mix with other states of the system. For this simple two state model it means that the transition state must now become mixed into the new instantaneous ground state $|\Psi(t)\rangle$

$$|\Psi(t)\rangle = c_0(t)|bonding\rangle + c_1(t)|transition\rangle. \quad (9)$$

This mixing creates a new possibility. If there is a measurement of the presence of the transition state from the surroundings of the molecule, and the wave function collapses to the transition state, then the chemical reaction would proceed. In this context the measurement process could be as simple as the collision of the molecule with another reactant. If there is some probability that the transition state is occupied, then the reaction will proceed with essentially the probability $|c_1(t)|^2$. The probability of finding the transition state is given by

$$P_{trans} = \frac{v^2}{v^2 + ((\Delta\epsilon - \omega)/2)^2} \sin^2(\lambda t). \quad (10)$$

This probability of the transition state represents a non-adiabatic excitation process, and in the context of this paper, a new reaction pathway that has been opened up by the oscillating potential. Notice that the magnitude of this probability of this non-adiabatic process does not vanish as $\omega \rightarrow 0$. The strength of the reaction probability depends on the ratio $(v/\lambda)^2$. If that ratio is of order 10^{-6} , then the probability of the reaction per period is about 10^{-12} but at microwave frequencies this would mean an overall probability per second of 10^{-3} which can be detectable in a chemical synthesis.

The non-adiabatic aspect of this effect is the measurement of the existence of the transition state and the collapse of the instantaneous ground state. Between two instances within each period $2\pi/\lambda$ of the oscillations, the time dependent potential creates in the instantaneous ground state a maximal mixture including the transition state.

If collisions with reactants, for example, were to occur during a period when the mixing was larger and the system is found to be in the transition state, then the reaction could proceed. This collisional measurement of the presence of the transition state is fundamentally a probabilistic quantum mechanical effect.

If the excited state is the transition state for a chemical reaction, then an additional pathway for the chemical reaction has been opened up. If we write the averaged excited state probability of the transition state as $|c_1|^2$, the reaction rate for the reaction will have the following form

$$k_M = A(e^{-E/RT} + |c_1|^2). \quad (11)$$

where the first term is the product of the prefactor A and the thermal probability of the transition state is $e^{-E/RT}$. These non-adiabatic probabilities appear to be relatively small so this effect is quite different from the resonant interaction that changes both the number of photons present and the occupation of the excited states of the system.

As will be discussed in the next section these non-adiabatic excited state probabilities will depend on certain matrix elements between the electronic states. This would imply that it may be possible to excite intermediate states that are quite different from the usual thermally excited states. This would mean that possibility different reaction products could be enhanced by the microwave non-adiabatic evolution.

3. Time Dependent Classical Vector Potential

Now we briefly discuss the theorem that has been used for more realistic models of molecules in the presence of a classical vector potential $\mathbf{A}(\mathbf{r}, \mathbf{t})$. For low frequency microwaves it is necessary first to realize that as the frequency ω becomes smaller the vector potential becomes more classical.³⁰⁻³² This classical vector potential will have a constant amplitude and a frequency that is determined by the microwave generator. The amplitude of the vector potential is completely independent of the molecular electron states. At these low frequencies the smaller energy photons become more numerous and the photon states become better approximated by coherent states with an average phonon number that is large.

In this classical limit the photon number is so large that spontaneous emission becomes negligible compared to the stimulated emission.³³

For simplicity, we consider a single component of the classical vector potential \mathbf{A} in the cavity of the microwave oven. The vector potential is

$$\mathbf{A} = A_y(x, t)\mathbf{j} = A_0 \sin(\omega t) \sin(kx)\mathbf{j} \quad (12)$$

where \mathbf{j} is a unit vector along the y axis and $\nabla \cdot \mathbf{A} = 0$. The frequency ω is determined by the microwave magnetron and the wave vector k is determined by a standing wave condition in the oven. The amplitude is a measure of the large photon number in the classical limit. The electric and magnetic fields are both standing wave

$$\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t} \quad (13)$$

$$E_y(x, t) = -\omega A_0 \sin(kx) \cos(\omega t), \quad (14)$$

$$\mathbf{B} = \nabla \times \mathbf{A}, \quad (15)$$

$$B_z(x, t) = kA_0 \cos(kx) \sin(\omega t). \quad (16)$$

The following is a clear application of the product rule of calculus. If Ψ is a wave function of the molecular system in the absence of a vector potential and satisfies the following Schrodinger equation,

$$i\hbar\Psi/\partial t = (p^2/2m + V)\Psi, \quad (17)$$

then the wave function Ψ_A defined by

$$\Psi_A = \exp\left(i\frac{eA_y(x,t)y}{\hbar}\right)\Psi, \quad (18)$$

can easily be shown to satisfy a Schrodinger's equation in the presence of the vector potential and the electric and magnetic fields as follows:

$$i\hbar \frac{\partial \Psi_A}{\partial t} = \left(\frac{p_x^2 + (p_y - eA_y)^2 + p_z^2}{2m} + V - eE_y y - \frac{e}{m} B_z L_z + e^2 B_z^2 y^2 + \frac{e\hbar}{2mi} k^2 A_y y \right) \Psi_A. \quad (19)$$

So Ψ_A is a solution of a Schrodinger equation in the presence of the vector potential.

In Equation (21) L_z is the z-component of the angular momentum. The next to the last term is the Harmonic oscillator potential that with a constant magnetic field gives rise to the Landau levels, and the last potential term arises from the fact that A_y varies with x .

We now expand the wave functions in Eqn. (20) relative to the eigenstates Ψ_n of the Hamiltonian without any EM fields by inserting a complete set of states,

$$c_n(t) = \langle \Psi_n | \Psi_A \rangle = \sum_{n'} \langle \Psi_n | \exp\left(i \frac{eA_y(x,t)y}{\hbar}\right) | \Psi_{n'} \rangle \langle \Psi_{n'} | \Psi \rangle e^{i\omega_{nn'}t}. \quad (20)$$

And if we chose $|\Psi\rangle = |\Psi_s\rangle$ to be the ground state and consider that $c_s(0)=1$ so that on the right side of Eqn. (16), we have $c_n(0)=\delta_{s,n}$

$$c_n(t) = \left\langle \Psi_n \left| \exp\left(i \frac{eA_y(x,t)y}{\hbar}\right) \right| \Psi_s \right\rangle e^{i\omega_{ns}t}. \quad (21)$$

The task now is to evaluate this matrix. This begins by examining the matrix element of the operator

$$M_{ns}(t) = \left\langle \Psi_n \left| \frac{eA_y(x,t)y}{\hbar} \right| \Psi_s \right\rangle = \frac{eA_0 \sin(\omega t)}{\hbar} \langle \Psi_n | \sin(kx)y | \Psi_s \rangle. \quad (22)$$

In this last equation we re-label the excited states Ψ_n so that the first excited state is now labeled by $n = 1$ and define

$$d_{1s} = \langle \Psi_1 | \sin(kx)y | \Psi_s \rangle, \quad (23)$$

which can be expanded about (x_0, y_0) , the center of mass location of the molecule.

We now define a ratio r_n and a new parameter α_{1s}

$$r_n = \frac{\langle \Psi_1 | \sin(kx)y | \Psi_s \rangle}{d_{1s}}, \quad (24)$$

$$\alpha_{1s} = \frac{eA_0 d_{1s}}{\hbar}, \quad (25)$$

and the matrix M can now be written as

$$M_{ns} = \alpha_{1s} \sin(\omega t) X_{ns}, \quad \text{where} \quad (26)$$

$$X = \begin{pmatrix} 0 & 1 & r_2 & r_3 & \cdots & r_n & \cdots \\ 1 & 0 & 0 & 0 & \cdots & 0 & \cdots \\ r_2 & 0 & 0 & 0 & \cdots & 0 & \cdots \\ r_3 & 0 & 0 & 0 & \cdots & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ r_n & 0 & 0 & 0 & \cdots & 0 & \cdots \\ \vdots & 0 & 0 & 0 & \vdots & 0 & \vdots \end{pmatrix}, \quad (27)$$

and where in the matrix we have explicitly written $r_1 = 1$. In the matrix X we have made the approximation of ignoring the matrix elements between the excited states and including only those matrix elements connecting the ground state to the excited states.

The first column of the matrix $(\exp[iM])_{ns}$ will give us the probability amplitudes in the presence of this externally driven vector potential if the system is in its ground state whenever $\sin(\omega t) = 0$. Using *Mathematica* it is easy to see that

$$c_s(t) = \cos \left(\alpha_{1s} \sin(\omega t) \sqrt{\sum_{l=1} r_l^2} \right), \quad (28)$$

$$c_n(t) = \frac{r_n}{\sqrt{\sum_{l=1} r_l^2}} \sin \left(\alpha_{1s} \sin(\omega t) \sqrt{\sum_{l=1} r_l^2} \right) e^{i\omega_{ns}t}. \quad (29)$$

It is clear that the sum of the squares of the probability amplitudes add to one. The probability amplitudes are periodic functions of time with the microwave period. Note also at those moments when the vector potential is zero, the probability amplitudes reduce to $c_n'(0) = \delta_{s,n}$.

The probability of the excited state Ψ_n now varies with time and is

$$P_n(t) = \frac{r_n^2}{\sum_{l=1} r_l^2} \left(\sin \left(\alpha_{1s} \sin(\omega t) \sqrt{\sum_{l=1} r_l^2} \right) \right)^2. \quad (30)$$

It is well to point out here that the weighting of the excited state probabilities depends on the ratio of the matrix elements between the ground state and the excited states. This could mean that a particular intermediate state in a reaction could be excited in the presence of microwaves. Notice also that the strength of microwave fields is contained in the parameter α_{1s} .

Within every period of the microwave frequency the probability of an excited state passes from zero to a maximum value, possibly several times. Whether a given molecule actually achieves occupation of the excited state is probabilistic and dependent on wave function collapse.

The excitation probability now varies periodically with the period of the microwaves. This time variation makes it somewhat difficult to determine the effects of the excited state probabilities since they are continually changing from zero to a maximum value. Presumably, the best estimate of the probability is the average over the period of the microwave frequency. In this case the averaged probability per period is defined in terms of an integral $G(\alpha')$ where

$$G(\alpha'_{1s}) = \frac{1}{2\pi} \int_0^{2\pi} \sin^2(\alpha'_{1s} \sin(\theta)) d\theta. \quad (31)$$

The period averaged probability of an excited state is

$$\langle P_n(\alpha'_{1s}) \rangle = \frac{r_n^2}{\sum r_l^2} G(\alpha'_{1s}). \quad (32)$$

When α'_{1s} is very large the limit of $G(\alpha'_{1s})$ is $\frac{1}{2}$ and

$$\langle P_n(\alpha'_{1s}) \rangle \rightarrow \frac{1}{2} \frac{r_n^2}{\sum r_l^2}, \quad \alpha'_{1s} \rightarrow \infty. \quad (33)$$

For small α'_{1s} $G(\alpha'_{1s}) \rightarrow (\alpha'_{1s})^2 / 2$ and the average probability approaches zero

$$\langle P_n(\alpha'_{1s}) \rangle \rightarrow \frac{1}{2} \frac{r_n^2}{\sum r_l^2} \alpha'_{1s}{}^2, \quad \alpha'_{1s} \ll 1. \quad (34)$$

As can be seen from Figure 1, $G(x)$ has a maximum near $x = 2$ and oscillates with increasing x as it approaches the limit of one-half for large x .

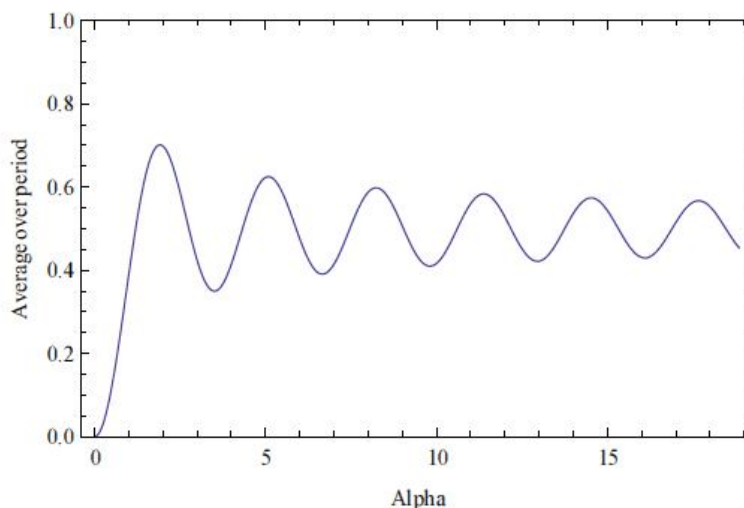


Figure 1. A Graph of the Factor $G(\alpha)$ as a Function of α .

The averaged probability amplitude for excitation now has a fairly complicated dependence on the magnitude of the microwave fields. From Figure 1 it can be seen that there are some optimal ranges for larger effects. At the same time, very small fields will lead to small excitation probabilities. In the next section we will explore some consequences of these results.

4. Experimental

Heating water in our microwave oven allowed us to determine the value of the electric field in the microwave cavity. Initially, when the temperatures are low and the cooling due to radiation and conduction is negligible, the time rate of change of the temperature is given by

$$C_V \frac{dT}{dt} = \frac{1}{2} \omega \epsilon'' E^2, \quad (35)$$

where C_V is the heat capacity for the volume of water, ω is the angular frequency corresponding to 2.45 GHz, ϵ'' is the imaginary part of the complex dielectric function³⁴ and E is the electric field. From our measurements at 1000 watts we found that $E = 1.22 \times 10^3$ N/C which is equivalent to an amplitude for the vector potential of $A_0 = 7.92 \times 10^{-8}$ Vs.

Using this amplitude for the vector potential we want to estimate the parameter

$$\alpha'_{1s} = \alpha_{1s} \left(\sum r_l^2 \right)^{1/2} = \frac{3eA_0 d_{1s}}{\hbar} \left(\sum r_l^2 \right)^{1/2}, \quad (36)$$

where the factor of 3 is included to approximately account for the fact that the microwaves in the cavity are actually standing waves in each direction. As a somewhat crude estimate of the transition matrix element for a molecule, we calculate the $2s \rightarrow 3p$ transition between hydrogenic states and find $y_{sp} = 1.8a_0$ where a_0 is the Bohr radius. This gives

$$\alpha'_{1s} = 0.031 \left(\sum r_l^2 \right)^{1/2}. \quad (37)$$

Let us now examine two different limits for estimating the occupation probabilities of the first excited state. First, let us assume that $\alpha'_{1s} = \pi/2$, so that the Sine squared achieves the value of 1 at least twice a period. In this case we must have $(\Sigma r^2)^{1/2} = 50.7$ and the probability of occupation of the first excited state becomes

$$P_n(t) = 1/(50.7)^2 \sin^2 \left(\frac{\pi}{2} \sin(\omega t) \right) = 0.00039 \sin^2 \left(\frac{\pi}{2} \sin(\omega t) \right). \quad (38)$$

The probability averaged over a period will be 1.95×10^{-4} .

For the other limit, assume that there are only two levels, then α'_{1s} is small the average probability will be 4.8×10^{-4} . Both of these estimates seem to very small, but it is important to compare these probabilities to the relevant thermodynamic excitation probabilities.

Kappe and colleagues^{8,9,35} have carried out an important series of experiments comparing microwave heated and conventionally heated reactions. They have observed that it is critical for reaction temperatures to be measured accurately. They have found that optical fiber probes give reproducible results and that stirring is often required to ensure homogeneity. For many reactions they have been able to compare reaction rates with and without microwaves and have reported that few, if any reactions, yield different reaction rates if the temperatures are measured carefully.

We have studied a number of papers (discussed in Appendix B) and found that for all of those which measured rates for at least two different temperatures it appears that the behavior in that range was clearly dominated by Arrhenius behavior and it would be predicted that reactions with and without microwaves should have the same rates. None of these reviewed papers appeared to have made measurements over a large enough range of temperatures to verify our predictions.

However, there is one paper by Kurfürstová and Hajek¹² with a very wide range of temperatures. In this paper they studied the microwave induced catalytic transformation of 2-tert-butylphenol over a temperature range from -176°C to $+75^{\circ}\text{C}$.

When the reaction rates were plotted in an Arrhenius plot ($\text{Log}(k_M)$ versus the inverse absolute temperature) it was found that the measured rate constant temperature was well described by the formula described in this paper.

$$k_M = A(e^{-E/RT} + |c_1|^2). \quad (39)$$

There are two very different temperature ranges from this equation. At high temperatures the thermal probability $e^{-E/RT}$ will be dominant and the behavior will be Arrhenius-like. In this range there should be no difference between the reaction rate with and without microwaves. At low temperatures the thermal probability will be negligible and the reaction rate will be constant as a function of temperature. The crossover temperature T_0 will depend on the ratio of the activation energy E and the log of the excited state probability $\log(|c_1(t)|^2)$ and will be different for each different reaction. The crossover temperature T_0 is defined by

$$T_0 = \frac{E}{-R \ln(|c_1|^2)}. \quad (40)$$

For temperatures higher than T_0 ($T > T_0$), the reaction rate with or without microwaves will be almost the same. If $T < T_0$, there will be a difference in the reaction rate with or without microwaves.

The points in Figure 2 are from Kurfürstová and Hájek and the solid line and the dashed line been chosen to give a reasonably accurate graph to the data. For the dashed line the parameters are $A = 0.15$, $E = 13.3 \text{ KJ/mol}$, and $|c_1|^2 = 0.00018$. These values are close to the same range as the estimates made above.

Overall the shape of the theory curve and the experimental data are moderately convincing. It would be much better if there had been more low temperature measurements in the gap between the lowest and next lowest temperatures. The current fit does rely very much on the lowest temperature data point. Also, there was an anomalous value of the reaction rate at $+24^\circ\text{C}$ which was much smaller than at the -7°C measurement. The anomalous data point at $+24^\circ\text{C}$ was ignored in making the fit.

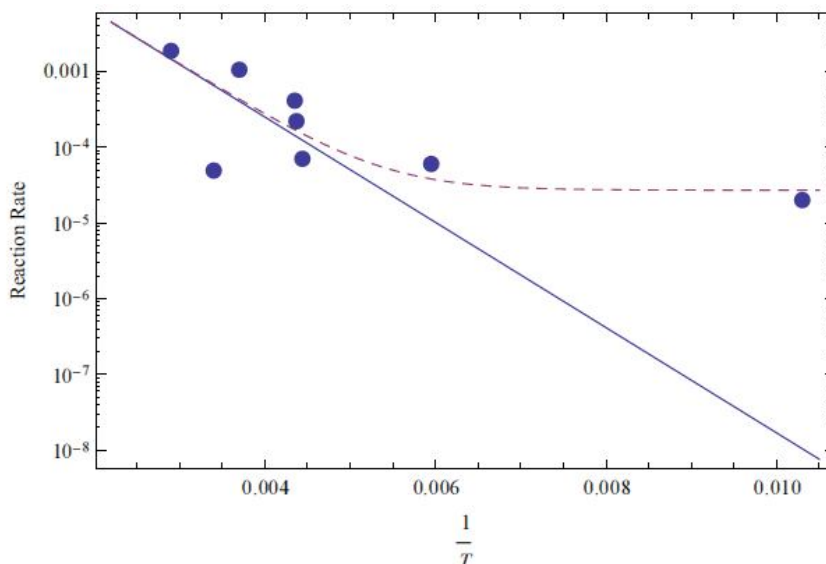


Figure 2: A graph of the reaction rate versus inverse absolute temperature along with data measured by Kurfürstová and Hájek for the catalytic transformation of 2-tertbutylphenol. The transition state energy $E = 13.3\text{kJ/mol}$, prefactor 0.15 and microwave induced average probability of 0.00018. The log linear plot without microwaves is plotted as a solid line, and the other plot with microwaves and parameters as discussed in the text is shown as a dashed line.

5. Discussion

This paper has explored the low frequency behavior of molecular systems to classical oscillatory potentials. The instantaneous response of a quantum system to a time dependent potential is to adiabatically form a mixed instantaneous ground state so that the energy can vary with the potential. Measurements of the existence of excited states in this mixed instantaneous ground state by interactions with other molecules can give rise to a non-adiabatic second route to chemical reactions. The probability of this reaction rate will depend on the excited state probability $|c_n(t)|^2$ within the instantaneous ground state. The widely held belief (based on TDPT) that there cannot be off-resonant effects ignores the adiabatic response of quantum systems and the concomitant non-adiabatic collapse of the instantaneous ground state to the transition state.

Because these effects depend on the excited state probability amplitudes, the effect is likely to be small, but not necessarily zero as is widely believed. The probability amplitudes found in this study are periodic in time, sometimes equal to zero, and so the reaction rate is assumed to depend on the probability averaged over a period.

The matrix elements connecting the ground state to excited states in the presence of the vector potential can weigh the excited states differently than their thermal weighting. This would mean that microwave chemistry should allow products to be produced which would not be favored by heating alone. The amplitude of the microwave fields, the power, will have an effect on the probabilities, but there should be little or no temperature effects due to the microwaves.

The temperature dependent reaction rate should be a sum of the Arrhenius effects and the microwave induced reactions. That means there will be a crossover temperature above which the Arrhenius effects will dominate and below which the microwave effects will dominate. Because of the relatively small size of the microwave probabilities the microwave enhancement will not be easily detectable at high temperatures.

The experiment by Kurfürstová and Hájek¹² is well described by our predicted reaction rate. Most other experiments comparing microwave and non-microwave heating reaction rates appear to be at high temperatures where the microwave effect is small.

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Appendix A: Time Dependent Perturbation Theory (TDPT)

For the general states Ψ_n and $\Psi_{n'}$ the equations of motion¹⁴ for the probability amplitude are given by

$$i\hbar \frac{\partial}{\partial t} c_n(t) = \sum_{n'} V_{nn'} c_{n'}(t) e^{i\omega_{nn'}t} \quad (\text{A1})$$

where $\hbar\omega_{nn'} = E_n - E_{n'}$ and the potential matrix elements $V_{nn'} = \langle \Psi_n | V | \Psi_{n'} \rangle$ are also functions of time.

If we label the ground state with s and the excited states with n , then we can write the initial conditions (at the time $t \rightarrow -\infty$)

$$c_s(-\infty) = 1, c_n(-\infty) = 0, \text{ for all } n. \quad (\text{A2})$$

If we write out the equation of motion for an initially unoccupied state at very short times in which none of the amplitudes have changed from their initial values, we find

$$i\hbar \frac{\partial}{\partial t} c_n(t) = V_{ns}(t) c_s(t) e^{i\omega_{ns}t} = V_{ns}(t) e^{i\omega_{ns}t}, \quad (\text{A3})$$

where in the second equality we have assumed that the ground state amplitude as well as the excited state amplitudes have not changed from their initial values. Since the right side does not contain any unknowns, it can be integrated immediately

$$c_n(t) = \frac{1}{i\hbar} \int_{-\infty}^t V_{ns}(t') e^{i\omega_{ns}t'} dt'. \quad (\text{A4})$$

This equation has been obtained by assuming that $c_S(t) = 1$ for all of the time in the interval $(-\infty, t)$.

If the interaction is quite localized in time and if the amplitudes do not change much in time, this integral could be a good approximation. If the interaction is restricted to be present for a finite time interval, the value of the integrand for positive times up to ∞ should be zero. If we extend the range of integration to the remaining interval (t, ∞) , which should not contribute to the value of the integral, the value of this integral becomes the Fourier transform of the time-dependent potential evaluated at the frequency of the energy difference between the ground state and the excited state $\hbar\omega_{ns} = E_n - E_S$,

$$c_n(\infty) = \frac{1}{i\hbar} \int_{-\infty}^{\infty} V_{ns}(t') e^{i\omega_{ns}t'} dt' = \frac{1}{i\hbar} \hat{V}_{ns}(\omega_{ns}). \quad (\text{A5})$$

At this point, it is clear what the standard argument concludes. If we designate, (for the next few sentences only), the microwave frequency as ω_0 and the standing wave has the time dependence

$$V_{ns}(t) = V_0 \cos(\omega_0 t), \quad (\text{A6})$$

then the Fourier Transform is

$$\hat{V}_{ns}(\omega) = \pi V_0 (\delta(\omega - \omega_0) + \delta(\omega + \omega_0)). \quad (\text{A7})$$

The frequency of the microwave is orders of magnitude smaller than the typical energy difference between molecular bonding and anti-bonding levels and so this Fourier transform is zero when evaluated at ω_{ns} . Thus, time-dependent perturbation theory predicts that the microwaves make no change in the excited state occupation, or in any probability amplitudes.

Appendix B: Evaluation of Experimental Reaction Studies

In this appendix the results of a number of careful studies¹ comparing microwave heating and conventional heating are listed and evaluated as to whether the data were taken in the Arrhenius dominated temperature range, if it is possible to determine this.

Most of these studies were conducted at one or a few temperatures. Where possible an estimate of the activation energy E has been made and if that activation energy was large ($E > 5\text{kJ/Mol}$) it is likely that the measurements were taken in the Arrhenius dominant region where the thermal probability is larger than the microwave induced reaction rate.

Most of the studies in this compilation were found to be in the Arrhenius dominated range, though there is barely enough data to completely support this conclusion.

Arvela and Leadbeater³⁶ studied the coupling of 4-chlorotoluene with Phenylboronic acid at four different temperatures with and without cooling. Without cooling the reaction rate gave a linear Arrhenius plot with an activation energy of $E = 13\text{kJ/mole}$. Cooling at the same temperatures did not give a straight Arrhenius plot.

Bacsa, Desai, Dibo, and Kappe³⁷ did a very thorough study of nonapeptide syntheses with microwave and conventional heating. Using the limited temperature data the activation energy is estimated to be 10.5kJ/Mol . The study contains a wealth of data including cooling between short microwave exposures, but these were too complicated for carrying out a comparison of the reaction amounts from integrating the reaction rate of the treatments.

The study by Hosseine, Stiasni, Barbieri, Kappe³⁵ examined five different reactions of "organocatalysis". The Mannich type reaction of acetone with ethyl glyoxylate did not yield Arrhenius behavior and seemed to be beset with significant decomposition of its end products. The study of α -Imino ethyl glyoxylate and s-proline reaction in acetone/DMSO was carried out at two temperatures. The estimated activation energy was 17kJ/Mole which suggests this was in the Arrhenius dominated temperature range. The Mannich- type reaction of protected Dihydroxyacetone with α -Imino ethyl glyoxylate was conducted at 60°C only.

The 3-component Mannich reaction of cyclo-hexanone, formaldehyde, and aniline also gave data only for 65^o C and found no difference between microwave heating and conventional heating. The Hajos-Parrish-Eder-Sauer-Weichert reaction was studied at two temperatures and gave an activation energy of 46kJ/Mol.

The Herrero, Kremsner, Kappe⁸ study is probably the most detailed and careful study for delineating the problems of temperature measurement and temperature homogeneity. Several different reactions were studied all showing little or no difference between microwave heating and conventional heating.

The Diels-Alder cycloaddition of 5-Methoxycarbonyl-2- pyrone and phenylacetylene was carried out at only one temperature and we could not identify the temperature range of the reaction rate. The microwave heated samples all had a slightly higher product than the conventionally heated reactions. This difference did not depend on the reaction time and thus is inconsistent with our predictions. The authors attributed this difference to different heating profiles.

The nucleophilic substitution of benzyl chloride with triphenylphosphine did not give rise to a simple Arrhenius behavior and was not consistent with our model. The effective activation energy was smaller at high temperatures and larger at low temperatures which would be the opposite of our simple model. The alkylation of Triazole with 2, 2',4'-trichloroacetophenone was carried out at three different temperatures (140^o C, 170^o C, 200^o C). When the reaction rate was plotted for these three points it gave a good straight line with an activation energy of 7.4kJ/Mol. The study of the reaction of Methacrylic acid with (R)-1-phenylethylamine was also carried out at three temperatures. These gave a good linear Arrhenius plot with an activation energy of 20.5kJ/Mol.

The remarkable studies using the SiC microwave shield and heating source carried by Obermayer, Guttman, and Kappe¹⁰ reported no difference between microwave and non-microwave heating for a large number of reactions. It appears that these were measured at only a single temperature.

While not definitive, it does appear that most studies with good temperature measurement appear to have been carried out in the high temperature range where the microwave enhancement of the reaction is not observable. The only data which covers both the high and low temperature ranges is that of Kurfürstová and Hájek as discussed in the main text.