Investigation of the Physical Mechanisms for the Formation and Maintenance of Microwave Hot Spots

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Abstract

Compared with traditional heating reactions, microwave heating reactions are characterized by faster reaction rates and higher yields. Phenomena in microwave reactions that differ from traditional heating are referred to as "microwave effects." Observed microwave effects include thermal phenomena, hot spot phenomena, selective heating, among others. Understanding and effectively controlling the microwave hot spot effect within microwave effects is crucial for the comprehension and application of microwave heating. Based on the quantum state identification master equation model for microwave reactions proposed by us in 2016, this study reveals that the emergence of the nonlinear phenomenon of microwave hot spots is macroscopically related to the non-uniform temperature distribution of the system and microwave intensity, and microscopically directly associated with the non-equilibrium behavior induced by microwave absorption. This paper proposes that microwave hot spots can be induced at specific points by preheating spatially localized points in the reaction vessel, and that intramolecular hot spots can also be induced by exciting local groups within specific molecules. Controllable microwave hot spot effects hold promise for applications in other fields, and the conclusions of this paper demonstrate that understanding the physical mechanisms of macroscopic non-equilibrium and nonlinear behavior from the quantum state level is essential.

Full Text

Preamble

Discussion on the Physical Mechanism of the Emergence and Maintenance of Microwave Hotspots

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Abstract

Microwave heating has been successfully applied in chemistry. Compared with traditional heating reactions, microwave heating reactions exhibit characteristics such as high reaction rates, high yields, and mild reaction conditions. Phenomena in microwave reactions that differ from traditional heating are termed "microwave effects." Observed microwave effects include thermal effects, superheating or hotspots, and selective heating. Understanding and effectively controlling microwave hotspot effects is crucial for comprehending and applying microwave heating. Based on the quantum state-specified master equation model for microwave reactions proposed in 2016, this study reveals that the emergence of microwave hotspots—a nonlinear phenomenon—is macroscopically related to non-uniform temperature distribution and microwave intensity, and microscopically directly associated with non-equilibrium behavior induced by microwave absorption. This paper proposes that microwave hotspots can be induced by preheating localized points in the reaction vessel, and that intramolecular hotspots can be formed by exciting specific local groups within molecules. Controllable microwave hotspot effects hold promise for applications in other fields, and our conclusions demonstrate the necessity of understanding the physical mechanisms of macroscopic non-equilibrium and nonlinear behavior from the quantum state level.

Keywords: microwave hotspots; nonequilibrium; master equation model; quantum state; nonthermal effect

Introduction

Microwave chemistry is a rapidly developing emerging field that offers unique advantages over conventional heating-based chemistry [?, ?]. Particularly in organic synthesis, microwave reactions demonstrate high yields, short reaction times, and mild reaction conditions. Researchers have even discovered reactions that cannot occur under conventional heating but proceed readily under microwave irradiation [?, ?]. In studies, phenomena in microwave reactions that differ from traditional heating are generally described as "microwave effects," which are further categorized into thermal and non-thermal effects to explain characteristics that cannot be achieved by heating alone. The existence of non-thermal microwave effects remains controversial [?]. Experimentally, due to different heating mechanisms, it is impossible to construct identical temperature fields using microwave and conventional heating, preventing the isolation of non-thermal effects from thermal effects for study. Theoretically, non-equilibrium molecular mechanics simulations also fail to provide a reasonable definition of non-thermal effects [?]. Meanwhile, numerous studies indicate that biological systems are more sensitive to microwave non-thermal effects—for example, at temperatures above 45°C, the mortality rate of *E. coli* exposed to microwave radiation is higher than that under conventional thermal sterilization at the same temperature [?]. Therefore, investigating and elucidating the complete mechanism of microwave reactions is essential for more effective utilization of this technology in organic synthesis and related applications.

Currently, commonly observed microwave effects include superheating, hotspot phenomena, and selective heating, none of which exist in traditional heating. Detailed investigation of the microscopic mechanisms of these phenomena contributes to a comprehensive understanding of microwave effects. Among them, the microwave hotspot effect is easily observed. Reports indicate that some hotspots are related to the size and concentration of activated carbon particles in solution, some are associated with other components, and some appear randomly [?]. Is there an intrinsic physical mechanism behind hotspot formation? What causes this nonlinear behavior [?]? It is well known that the energy of a single microwave photon is very small, yet many microwave hotspots are accompanied by visible light emission, indicating that microwaves can be continuously absorbed by hotspots to reach energy states capable of emitting light. Interestingly, although microwave hotspots emit visible light, their measured temperatures are not particularly high. These phenomena warrant thorough investigation.

Based on our quantum dynamics research, the quantum state-specified master equation model for microwave reactions holds promise for describing various microwave effects. This paper employs this theoretical framework to investigate the mechanisms of microwave hotspot formation and maintenance. First, we discuss the causes, conditions, and physical mechanisms of hotspot generation under microwave fields. Second, we explore how to controllably produce spatial hotspots and intramolecular hotspots. Finally, we address the generation and application of controllable non-equilibrium effects.

2.1 Theoretical Framework

The evolution of quantum state densities in the microwave reaction quantum state-specified master equation model is described by the master equation [?], where $N(S_i, t)$ represents the density distribution of molecules in the i-th region' s S state at time t, and Z denotes the molecular collision frequency. The equation includes collision energy transfer terms, microwave energy transfer terms, and chemical reaction terms. We assume that the microwave hotspot effects discussed in this paper do not involve reaction processes, so terms containing reaction rate constants can be neglected, and the quantum state index S can be converted to an energy index.

The model comprises collision energy transfer terms, microwave energy transfer terms, and chemical reaction terms, with the rules governing each term discussed extensively in the literature [?]. Collision energy transfer rates are influenced by temperature, density, and pressure, typically occurring on a timescale of 10^{-10} s. For simplicity, this paper adopts a collision frequency calculation, with the corresponding collision energy transfer function using the common double exponential form [**?**].

The microwave stimulated absorption and emission rate constants are given by a Lorentzian function, where ω_0 represents the microwave frequency, γ denotes the damping constant, and the rate is proportional to the density of final states. I corresponds to the microwave field intensity. Here, to simplify the model, we assume equal transition dipole moments between different energy levels. For actual systems, the variation of transition dipoles has been studied in our previous work; generally, increased anharmonicity and reduced symmetry at higher energy levels facilitate microwave absorption and emission [**?**]. Additionally, we assume that the intramolecular energy transfer rate is inversely proportional to the energy transfer distance.

We employ the kinetic Monte Carlo (KMC) method to solve the master equation [**?**, **?**, **?**]. In the Gillespie algorithm, the time step τ for each evolution is determined by a random number r_1 and the total rate k_{TOT} for that step. If there are M possible energy transfer pathways at a given moment, each with rate k_i, then the selection of energy transfer pathway m is determined by another random number r_2.

Parameters of the master equation model of microwave reaction (Energy in cm^{-1})

Parameter	Value
Collision frequency expression	$Z = Z_{0T}^{-1/2}$
Collision energy transfer	Double exponential
Absorption/emission rate	Lorentzian
Intramolecular energy transfer	$k_{ij} = k_0/(S_i - S_j + \Delta)$
Energy grid	Independent sampling
Z_0	1×10^9
C_1	100
C_2	0.015
T	100 K, 300 K, 500 K
I	0, 5×10^{10}, 5×10^{11}
ω_0	8 cm^{-1}
γ	0.12 cm^{-1}
k_{ij}	0, 10, 100
Δ	ΔS
Grid number	1500/2500
ΔS	10 cm^{-1}

In experiments, microwave hotspots exhibit higher temperatures than their surroundings and are often accompanied by luminescence. The relatively high temperature of microwave hotspots indicates that energy gain from microwave absorption exceeds energy loss from thermal conduction and radiation. The luminescence phenomenon suggests that some molecules in the hotspot region reach energy levels capable of emitting visible light [**?**]. To simplify the model, this paper assumes two types of microwave hotspots: spatial hotspots [**?**] ([Figure 1: see original paper]) and intramolecular hotspots ([Figure 2: see original paper]), corresponding to thermal conduction and luminous behavior, respectively. Microscopically, we assume that polar molecules, intramolecular polar groups, or polar clusters are the basic units for microwave absorption and emission, with the vibrational-rotational state distribution of these units being related to their apparent temperature.

Spatial hotspots, as shown in [Figure 1: see original paper], have temperatures significantly higher than their surroundings and can persist under microwave irradiation. Intramolecular hotspots, illustrated in [Figure 2: see original paper], behave in ways related to the rates of collisional energy transfer and intramolecular energy transfer. Within a large molecule, there exist groups with "temperatures" T_1, T_2, and T_3, with energy transfer rates k_{ij} between these three groups, and energy exchange with the environment through molecular collisions.

3 Results and Discussion

Using the quantum state-specified master equation model combined with the microwave model described above, we investigate microwave hotspot effects, seeking to clarify two questions: how hotspots are generated and how they are maintained.

The time evolution of vibrational-rotational energy levels for molecules at 300 K under microwave irradiation is shown in [Figure 3: see original paper]. Red scatter points represent energy level changes under strong microwave fields, while blue points show behavior under pure thermal collisions. Subgraphs (b) and (c) display magnified views of the equilibrium oscillation period and strong absorption period, respectively. [FIGURE:3(a)] reveals that molecules experience both microwave and thermal collision effects. When the interaction time is less than 1.5 s, collisional energy transfer dominates, causing chaotic oscillations in molecular energy states. [FIGURE:3(b)] shows that during this period, the evolution under combined microwave and thermal collisions is similar to that under pure thermal collisions. After 1.5 s of microwave exposure, the molecular internal energy suddenly increases rapidly. The detailed view in [FIGURE:3(c)] demonstrates that while energy levels fluctuate due to thermal collisions, the dominant trend is rapid internal energy elevation caused by microwave absorption.

We also simulated the evolution of vibrational-rotational energy levels for molecules in a strong microwave field at 500 K, with results shown in [Figure 4: see original paper]. Numerous vertical line-like scatter points appear in the figure, characterizing the rapid microwave absorption process. Since the simulation energy limit was set to 15000 cm^{-1}, energy levels reaching this limit subsequently release energy through microwave emission and molecular collisions. Notably, the applied microwave intensity at 500 K was 10 times weaker than that at 300 K. However, comparing [Figure 3: see original paper] and [Figure 4: see original paper] reveals that molecules at 500 K have a much higher probability of rapid energy increase through microwave absorption than at 300 K. Simulations at 100 K under strong microwave fields showed no rapid absorption phenomena even after extended simulation times. These findings indicate that although the timing of microwave hotspot appearance is random, elevated temperatures facilitate microwave absorption, and the system has a higher probability of developing microwave hotspots.

The vertical lines representing rapid energy level increase in [Figure 4: see original paper] also demonstrate that strong microwave fields can significantly alter the population distribution of molecular internal states, causing the system to deviate from conventional thermal equilibrium distributions. However, since these vertical lines appear for relatively short durations, whether they fundamentally affect the molecular energy state distribution requires examination of the temporal distribution of molecular states.

[Figure 5: see original paper] shows the temporal distribution probabilities of molecular vibrational-rotational states under microwave irradiation at environmental temperatures of 100 K (a) and 300 K (b). Black points indicate no microwave effect; red points indicate microwave intensity $I = 5 \times 10^{11}$ with initial energy level $S = 1000$ cm^{-1}; blue points indicate the same microwave intensity with initial energy level $S = 10000$ cm^{-1}. At 100 K, with an initial level of $S = 1000$ cm^{-1}, no significant difference in energy level temporal distribution is observed after 500 sampling averages, regardless of microwave presence. When the initial level is $S = 10000$ cm^{-1}, microwave effects dominate completely, and all sampled states remain in high-energy regions during the sampling period. At 300 K, the energy level distribution remains in thermal equilibrium without microwave irradiation or with weak microwave fields ($I = 1 \times 10^5$). Under strong microwave fields, the distribution deviates from thermal equilibrium, with significantly increased population in high-energy regions, exhibiting strong non-equilibrium characteristics. At 300 K, the influence of initial energy level on population distribution is relatively small.

Different polarities of groups within large molecules lead to varying efficiencies in microwave absorption, and heat transfer rates between different groups also differ. Studies show that intramolecular energy transfer timescales range from milliseconds to picoseconds [**?**, **?**], indicating that intramolecular hotspots are plausible. Based on the intramolecular energy transfer model shown in [Figure 2: see original paper], we simulated the evolution of energy levels in various polar groups under different temperatures, microwave intensities, and intramolecular energy transfer rates. When intramolecular energy transfer rates are large, the energy state distributions of the three groups converge. When these rates are small, significant differences emerge between the groups' energy distributions. [Figure 6: see original paper] depicts the vibrational state distributions of three different groups in multi-hotspot molecules at 100 K (a) and 300 K (b) under microwave irradiation, where one group has an initial energy level of $S = 10000$ cm^{-1} while the others start at $S = 1000$ cm^{-1}.

As shown in [FIGURE:6(a)], similar to spatial hotspot behavior, at 100 K the initial energy level largely determines each group' s energy distribution. When the initial level is $S = 10000$ cm^{-1}, some samples return to low-energy states through stimulated emission and collisional energy transfer, while others absorb microwaves to reach higher energy levels, leading to intramolecular microwave hotspots. At 300 K, all three polar groups have a certain probability of rapid microwave absorption that increases high-energy level population. The probability of rapid microwave absorption to reach high energy levels is approximately 10 times higher when the initial state is $S = 10000$ cm^{-1} compared to $S = 1000$ cm^{-1}.

These simulation results demonstrate that the difference between microwave energy transfer and collisional energy transfer mechanisms underlies microwave hotspot effects. Strong microwave fields can drive molecular energy states to elevate through rapid microwave energy absorption, significantly deviating from thermal equilibrium distributions. The internal energy state distribution of molecules becomes non-equilibrium, rendering the temperature concept inadequate. Studying differences between microwave and conventional thermal reactions by constructing identical temperature fields has inherent limitations. Although the simulation results using the master equation model are consistent with existing experimental phenomena, the reliability of these theoretical predictions still requires experimental verification.

Several features of microwave energy transfer differ significantly from conventional heating, leading to various microwave effects. The property that higher molecular energy levels facilitate easier microwave absorption constitutes the physical mechanism for microwave hotspot generation and maintenance. The microscopic basis for this property is illustrated in [Figure 7: see original paper]. When molecules are at low energy levels, the energy gap between adjacent levels exceeds microwave photon energy, preventing microwave absorption and making collisional energy transfer dominant. For typical molecules, anharmonicity becomes increasingly significant with rising energy levels, and transition dipole moments between adjacent levels increase. For nearly all molecules, the density of quantum states increases with molecular energy. These two characteristics indicate that higher energy levels favor microwave absorption or emission. Phenomena such as microwave heating of metals and microwave-induced plasma generation demonstrate that under certain conditions, microwave absorption rates far exceed energy loss rates.

Based on this microscopic mechanism, exciting molecules or molecular groups with high-energy light during microwave irradiation can significantly increase the probability of microwave hotspot occurrence and enable some control over hotspot generation. The luminescence characteristics of materials under microwave fields can also be used to monitor hotspot formation. The physical mechanism shown in [Figure 7: see original paper] suggests that combining different frequencies and intensities of light can manipulate molecular internal energy evolution to some extent, providing possibilities for controllable utilization of non-equilibrium behavior.

Conclusion

This study employs the quantum state-specified master equation model proposed by the authors in 2016 to investigate the possible mechanisms of microwave hotspot formation and maintenance, addressing how hotspots are generated and sustained, and presenting the microscopic mechanism of microwave energy transfer [**?**, **?**]. The research demonstrates that: at room temperature (300 K), strong microwave fields have a certain probability of inducing rapid microwave energy absorption and energy level elevation; at low temperature (100 K), the probability of inducing microwave hotspots is nearly zero; pre-exciting molecules can increase the probability of microwave hotspot occurrence; and the probability of molecules absorbing microwaves to maintain or elevate their energy increases with temperature. The conclusions support the controllable generation of both spatial and intramolecular microwave hotspots.

Theoretically, when intramolecular and intermolecular energy transfer rates are low, intramolecular microwave hotspots can be induced through excitation of local functional group vibrational or electronic states. This study provides a potential method for site-specific activation of particular chemical bonds. Additionally, microwave hotspot effects can be utilized to construct non-uniform temperature fields, optimizing chemical synthesis through coupling between different temperature distributions and reactant distributions. Controllable microwave hotspots and non-equilibrium effects will also find important applications in other fields, and the conclusions of this paper are not limited to microwave energy transfer [**?**]. In industrial production, the random nature of microwave hotspot generation reduces controllability for large-scale manufacturing. Monitoring luminescence behavior can help determine hotspot formation. In communications, the extensive application of microwave and millimeter-wave radiation raises concerns about potential health effects from high-intensity high-frequency radiation. The non-uniformity of radiation heating, particularly hotspot effects, represents the primary factor for potential biological damage, as local temperature increases may harm organisms. Considering that hotspot generation depends on temperature distribution, radiation intensity, and exposure time, these characteristics can be manipulated to reduce hotspot occurrence. In medicine, controllable hotspot effects can be exploited to deliberately induce hotspots at specific biological locations to inactivate pathological tissues. Related theories and applications will be developed in subsequent studies.

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164.
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