ON THE DIRECT VIBRATIONAL SPECTROSCOPY OF TRANSITION STATES

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Received 10 February 1989

A technique for optically exciting and detecting vibrational resonances in transition state (TS) configurations of chemical reactions is described. By radiation-dressing the TS with tunable picosecond pulses under appropriate initial conditions, resonant TS interactions can become manifested by measurable changes in reaction rates and product rovibrational distributions. The essential features illustrating the TS spectral lineshapes and experimental conditions were modeled by adopting a radiation-dressed potential surface and evaluating the vibrational transition probability by an exact density-matrix solution. Results are presented describing (1) the conditions under which significant TS transition probability occurs, and (2) how a frequency-resolved vibrational spectrum can be interpreted in terms of the shape and dynamics of the reactive surface.

1. Introduction

The detection of transient molecular configurations, representing restructuring of chemical bonds, remains one of the foremost challenges in chemical physics. Until very recently, the most tangible information about the properties of these so-called "transition states" has come from indirect methods such as bimolecular reactive scattering [1,2] and state-to-state experiments [3]. For instance, Nieh and Valentini reported clear evidence of collisional resonances in the $H+H_2$ reaction, which they attribute to quasibound HHH vibrations [2].

The approaches used to date to directly detect transition states by optical means can roughly be generalized by two approaches: (1) collisionally perturbed product spectra manifested by "wing transitions", [4–8] and (2) optical Franck–Condon projection of transition state (TS) configurations onto stable structures by bound–free transitions [9–11]. Polyani [4], Brooks [5], and their coworkers relied on the former approach in their early seminal work on TS spectroscopy. Polanyi and co-workers [4] detected emission from the reaction complex $[FNaNa]^{\ddagger}$ at wavelengths that appear in the wings of the Na emission line. Brooks and co-workers [5] using a complementary scheme, detected absorption of the $[NaKCl]^{\ddagger}$ complex that occurs off-resonance from the Na D line, but which nonetheless correlates with dissociated Na D line emission. The idea of detecting wing absorptions due to reactive complexes was recently applied in the subpicosecond domain by Zewail and coworkers [7,8] for the photodissociation of ICN, CH_3I and NaI. These first examples of time-resolved TS spectroscopy used a pump–delay–probe sequence in which the probe frequency is tuned slightly off-resonance from a product absorption. In so doing they observed signals that rise and fall with delay time t representing a transition state geometry that "passes through" a resonance with the probe frequency.

The second strategy above involves the excitation of short-lived unbound states to long-lived bound states. Imre, Kinsey, and coworkers [9] recorded dispersed emission for dissociating CH_3I. Polanyi et al. [10] succeeded at multiphoton ionizing a transient $[HDD]^{\ddagger}$ configuration in the exchange reaction $H+D_2 \rightarrow HD+D$. Finally, Neumark and coworkers [11] have obtained vibrationally resolved TS spectra by photodetaching an electron from a stable $ClHCl^-$ anion and recording the photoelectron spectrum of the unbound ClHCl neutral complex.

We describe a new concept based on resonant vibrational excitation of transition state configurations. Electronic state excitation measures energy differences between two potential energy surfaces

(PESs); neither of which is likely to be known in the region of the transition state. Vibrational spectroscopy, on the other hand, can provide unambiguous identification of structures and force constants. The central idea here is that excitation of short-lived TS vibrations can become "imprinted" onto long-lived properties of the products that can be routinely detected (e.g. a change in product rovibrational distribution, reaction probability, and/or rate). It has been recognized theoretically [12–14] that intense laser fields can interact with transition states and alter the course of a chemical reaction. The reactive-complex absorption wings, observed by Brooks [5] and Zewail [7,8] and their co-workers for electronic states, are an example of this phenomenon, in the sense that these absorptions produce electronically excited product. The purpose of the present work is twofold: (1) to show that the conditions of a continuous-wave (cw) radiation-dressed TS can be realized for pulsed excitation, in a manner that is sensitive to the detection of *vibrational resonances* in the TS, and (2) present a formalism that exactly solves for the transition probability and lineshape for time-dependent PESs under strong field conditions.

2. Experimental concept

Tunable IR radiation ω is used to excite the TS vibrations. The experiment depends on constraining the entire reaction to occur within the duration of the ω laser pulse in order to achieve pseudo-cw excitation conditions. The requirement of intense IR radiation ($>\mathrm{GW/cm^2}$) is satisfied by using short (e.g. picosecond) high peak-power pulses. The reaction is initiated and product energy states detected using two other pulses, ω_r and ω_p. These are positioned within the longer duration ω pulse, as represented schematically in fig. 1. The presence of the ω pulse across the ω_r–t–ω_p short-pulse interval describes a reaction that evolves in the presence of an intense cw radiation field. The vibrational TS spectra are further enhanced by limiting the distribution of reactive trajectories so as to probe specific regions of transitional configuration space. This can be achieved by studying unimolecular reactions, or oriented bimolecular reactions initiated by dissociating a molecule in a suitably chosen van der Waals mixed dimer [15] (e.g. $\mathrm{XA{\cdot}BC \rightarrow {}_{-X}[A...B...C]^{\ddagger} \rightarrow AB+C}$).

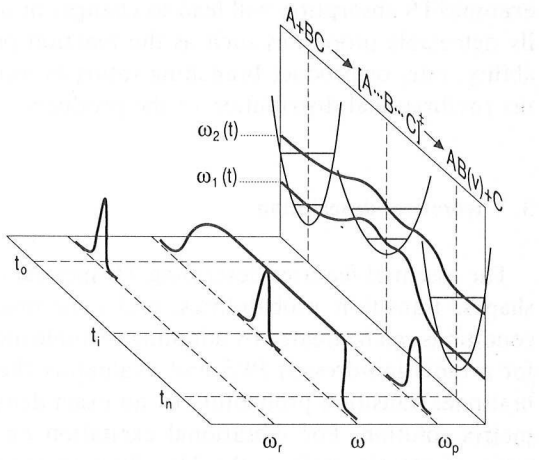

Fig. 1. Three-pulse sequence for detecting vibrational resonances in transition state configurations. The pulses ω_r, ω, and ω_p refer to excitation of reactant, transition state, and product, respectively. The temporally broad and narrow ω pulses shown are for continuous or discrete excitation of TS configurations. Idealized vibrationally adiabatic surfaces $\omega_1(t)$ and $\omega_2(t)$ are drawn to correlate with reactant and product vibrations.

The three-pulse sequence is experimentally achievable using commercial apparatus and standard techniques. The tunable IR pulse that spans the reaction period t can be generated by conventional optical parametric (OP) methods [16] involving the 1.06 μm output from a picosecond Nd:YAG laser that is also used to pump a dye laser (ω_r and ω_p). A standard pulse mode-locked Nd:YAG laser can produce a 25 ps pulse duration in excess of 50 mJ/pulse; the OP process in turn can conservatively generate 2 mJ of tunable IR in <20 ps pulses. Modest focusing to beam diameters less than 1 mm gives the necessary $>10\ \mathrm{GW/cm^2}$ pulse energies to vibrationally excite TS configurations. The duration of the Nd:YAG OP ω output is also conveniently longer than that of the typical dye laser pulses ($\approx$1–10 ps) used for ω_r and ω_p.

The present technique satisfies the following important experimental conditions: (i) high instantaneous number density of transition states, (ii) intense tunable IR radiation field, and (iii) well-defined reactant initial conditions (e.g. state-specific or isoenergetic excitation, and narrow temporal onset). The TS vibrational resonances may be detected as a function of ω and t in a number of ways. For

value over the τ_i interval. The general solution for $\Delta\rho = \rho_{11} - \rho_{22}$ is then given by

$$\Delta\rho(t_n) = r_{11}(t_n, t_0)\,\rho(t_0)\,, \qquad (6)$$

where $r_{11}(t_n, t_0)$ is obtained from the elements of the product matrix $\mathcal{Q}(t_n, t_0)$ by the expression

$$r_{11} = \tfrac{1}{2}[(q_{11}^2 + q_{22}^2) - (q_{12}^2 + q_{21}^2)]\,.$$

The piecewise rotation matrix solution has the advantages of (1) continuous validly over the range from weak to strong fields, thereby overcoming the limitations of perturbation theory, (2) complete generality for any time dependence of $\omega_1(t)$, $\omega_2(t)$, and $\mu(t)$ (as well as $\epsilon_0(t)$, if interest is on convolving over a temporal pulse shape), (3) proper accounting of coherence effects, which are important for changing potentials in strong fields, and (4) full solutions for intermediate time intervals.

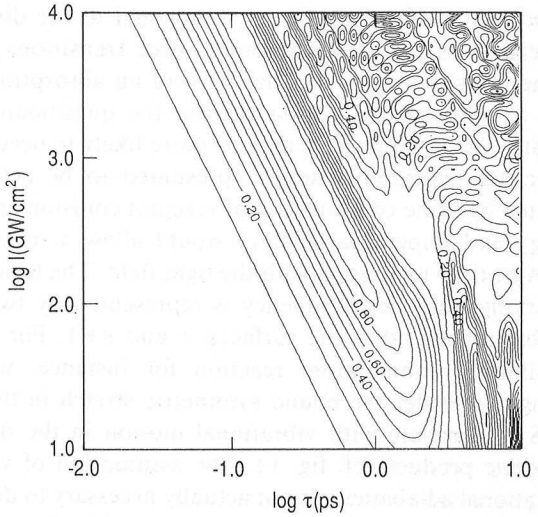

Fig. 2. Transition probability $P(v, v+1)$ for absorption ($\Delta\rho(t_0) = 1$) or stimulated emission ($\Delta\rho(t_0) = -1$) as a function of laser power density I and quasibound lifetime τ. Parameters used in the contour plot were $\mu = 0.2$ D, $\omega = 2020$ cm^{-1}, and $\omega_k(t) = a_k(2t/\tau - 1)^2 + b_k$, where $a_1 = 80$ cm^{-1}, $b_1 = 1000$ cm^{-1}, and $a_2 = 160$ cm^{-1}, $b_2 = 3000$ cm^{-1}.

4. Model calculations

The above model will serve to demonstrate the experimental technique represented in fig. 1 by addressing two important questions: (1) under what conditions will significant TS transition probability occur, and (2) can a vibrationally resolved spectrum be interpreted in terms of the detailed shape and dynamics of the reactive PES? These points are examined in figs. 2 and 3, respectively. Although a general strong-field solution has been presented, we adopt a simple model for the reactive trajectory in that we assume localized trajectories, no decay or relaxation processes over the TS lifetime other than reaction, and a constant transition dipole moment μ.

We consider transitions between unbound dissociative motion and optically active quasibound vi-

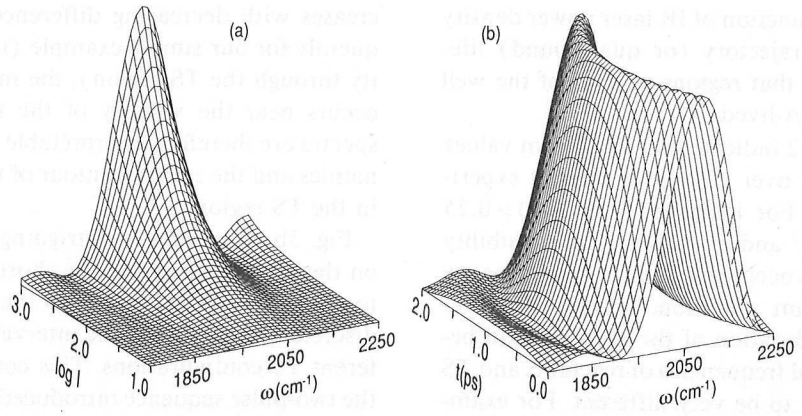

Fig. 3. Calculated transition state vibrational lineshapes: (a) Continuous excitation over a trajectory lifetime of $\tau = 200$ fs. Peak transition probability is $P = 0.71$. (b) Discrete excitation over 200 fs intervals for $\tau = 2$ ps and $I = 100$ GW/cm^2. Peak probability is $P = 0.10$. Other conditions are given in the caption to fig. 2.

the reactive PES the excitation takes place. The two-dimensional (ω, t) vibrational spectrum in fig. 3b, consequently, portrays the change in vibrational frequency that occurs during the reactive trajectory.

We close by noting that resonant interactions in the transition state are most easily detected by monitoring the reaction probability or rate, which will be enhanced for absorption and suppressed for stimulated emission. However, a more informative dimension of detection is available by monitoring changes in the product rovibrational distribution. This is because a strong correlation exists between the transition state and product vibrations, due to vibrational adiabaticity. Vibrational correlation, which has been demonstrated for reactants and products in full-collision bimolecular reactive scattering [3], is considerably greater in the half-collision dissociation of the TS to product due to better geometric overlap and to less time available for energy redistribution. If modeled after a unimolecular dissociation, the half-collision state-to-state reaction probability depends primarily on Franck–Condon overlap factors and final-state interactions [18]. Correlating TS excitation to specific product vibrational states, therefore represents a very powerful state-to-state detection capability.

5. Summary and conclusions

An experimental and theoretical basis has been presented for directly recording and analyzing vibrational spectra of rapidly evolving transient configurations in a chemical reaction. The experimental approach makes use of strong field conditions and is modeled as a radiation-dressed time-dependent PES. The present work, however, departs from previous treatments in that we show that pseudo-cw intense field conditions can be met in a pulsed experiment. Furthermore, we provide a functionally exact solution for calculating transition probabilities and lineshapes that is non-perturbative, continuously valid for all field strengths, and which properly accounts for the important role of coherence under these conditions.

We have demonstrated that detectable TS absorption probabilities are possible for routine short-pulse (e.g. picosecond) excitation conditions. Distinct vibrational bandshapes can be recorded that are interpretable in terms of the PES contour for bound motions that exist orthogonal to the reaction coordinate (e.g. the symmetric stretch in an atom–diatom reaction). In summary, the technique described here provides state-to-state analysis, where state excitation occurs directly in the transition state.

Acknowledgement

This work was supported by the Aerospace Sponsored Research program.

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