Evidence for quantization of the transition state for *cis–trans* isomerization

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Cis–trans isomerization rates of *trans,trans*-1,3,5,7-octatetraene (OT) on the first excited singlet state ($2\ ^1A_g$) potential surface have been obtained as a function of vibrational energy by measuring the fluorescence lifetimes. A stepwise increase in the isomerization rate with increasing energy has been observed, which indicates quantization of the vibrational levels of the transition state for the *cis–trans* isomerization of a double bond. The energy spacing of $80\pm10\ \mathrm{cm}^{-1}$ between the first two steps tentatively is assigned to an in-plane bending vibration of the transition state.

Unimolecular reactions are an important type of elementary chemical reaction, in which an energized molecule dissociates to fragments or isomerizes. Many experimental and theoretical studies have been devoted to understanding this apparently simple chemical transformation.[1–3] The most frequently employed theory of unimolecular reactions is that formulated by Rice, Ramsperger, Kassel, and Marcus (RRKM).[4] The so-called RRKM theory is based upon several assumptions, one of which is that there exists a quantized transition state at the dynamical bottleneck separating the reactant from products and that the rate is given by the flux through vibrational levels of the transition state. Despite the frequent use of this theory, experimental evidence for quantization of the transition state was shown only recently. Moore and colleagues have demonstrated the quantization of the transition state in the unimolecular dissociation of ketene on the triplet surface.[5,6] More recently, Wittig and coworkers reported the stepwise variation of $k(E)$ with energy in the photoinitiated unimolecular decomposition of NO_2 and interpreted this as evidence for a quantized transition state.[7]

These recent observations suggest the general existence of quantized transition states in all unimolecular reactions. In order to confirm the generalization unambiguously, however, more experimental evidence is required not only for decomposition reactions but also for other types of unimolecular reactions. In this Communication, evidence for the quantization of the transition state is presented for an *isomerization* reaction. The *cis–trans* isomerization rate of *trans,trans*-1,3,5,7,-octatetraene (OT) on its first excited singlet state (S_1) potential energy surface is observed to increase in a stepwise manner with increasing energy as expected for quantized vibrational levels of the transition state.

The isomerization rate for OT in a supersonic jet expansion is deduced from the dependence of fluorescence lifetime on the vibronic energy. The experimental setup in this work is the same as reported previously.[8–10] Solid octatetraene maintained at 35 °C sublimes into the He carrier gas kept at 500–600 Torr, and the mixture is expanded through a pulsed valve with a 0.5 mm nozzle diameter. The output from a pulsed dye laser pumped with a XeCl excimer laser is frequency doubled with a KDP crystal using an autotracking system. The laser beam crosses the supersonic jet at 15 mm from the nozzle and is tuned to excite vibronic bands of the $S_1 \leftarrow S_0(2\ ^1A_g \leftarrow 1\ ^1A_g)$ transition state of OT. Fluorescence from the excited OT is collected with a 2 in. diam quartz lens, filtered with a color filter and an aperture, and then detected with a fast-response photomultiplier tube (PMT) (Hamamatsu H3284) with about a 300 ps risetime. The output signal of the PMT is directed to a 500 MHz digital oscilloscope. Each decay curve is averaged for 500 or 1000 decay profiles and stored for further analysis. At a given vibronic energy, measurements were repeated three times on different days to minimize systematic errors. The curves were transferred to a personal computer and fit with a least squares regression routine. This detection system allows accurate measurement of decays as short as 10 ns with the time resolution being limited mostly by the pulse duration of the excimer laser. The frequency of the dye laser was calibrated with a Ne optogalvanic cell with an accuracy of $\pm0.5\ \mathrm{cm}^{-1}$. The *trans,trans*-1,3,5,7-octatetraene sample was synthesized by dehydration of 2,4,8-octatrien-6-ol using pyridinium *p*-toluenesulfonate as a catalyst following the procedure described previously.[8] The alcohol was purchased from Sorl Laboratory and had a purity of 99.7% as determined by HPLC.

Curve (a) of Fig. 1 shows the fluorescence decay rates (the inverse of fluorescence lifetimes) of the S_1 state of octatetraene excited in the vibrational energy range 2070–2270 cm^{-1}. At each vibrational energy three data points are shown. The decay rate increases very slowly from the origin of the S_1 state up to 2130 cm^{-1}. The data of curve (a) between 2070 and 2130 cm^{-1} shown in Fig. 1 are on the line of this smooth increase. The decay rate sharply increases at 2140 cm^{-1} by more than a factor of 2 and then stays almost constant up to an energy of 2190 cm^{-1} where it increases again. These two steps are distinctively noticeable in the energy range shown in this figure.

Understanding the features in curve (a) requires knowledge of the photochemistry and photophysics of the S_1 state of OT. Since the dynamics of electronically excited OT pro-

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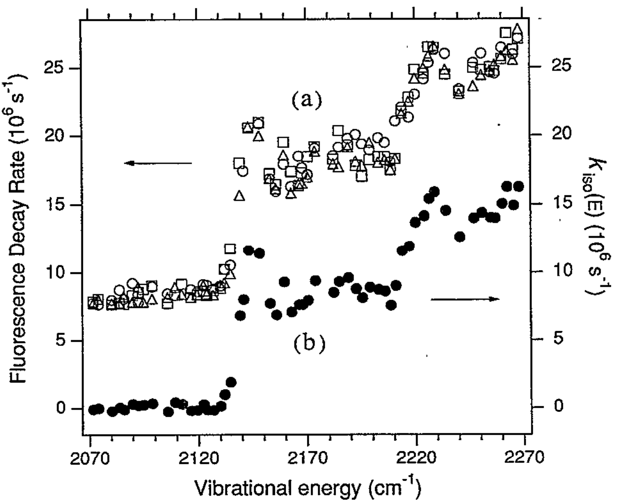

FIG. 1. Curve (a): Fluorescence decay rates of *trans,trans*-1,3,5,7-octatetraene (OT) excited to its first excited singlet state (S_1) with vibrational energies from 2070 to 2270 cm^{-1}. The decay rate varies in a stepwise manner with energy. Curve (b): Isomerization rate constants OT (S_1) obtained by subtracting the contribution of other decay channels (see the text for the procedure of calculation) in the same vibrational energy range as for curve (a). Two steps, one around 2140 cm^{-1} and the other around 2220 cm^{-1}, indicating quantization of the transition state for *cis–trans* isomerization of a double bond, are clearly noticeable.

vides the basis for understanding the photochemistry of natural polyenes which play important roles in biological processes such as vision and bacterial and plant photosynthesis,[11,12] it has been extensively studied both experimentally[8,13–15] and theoretically.[16] Below the threshold to isomerization, OT (S_1) relaxes to the ground electronic state through two competing channels, internal conversion and spontaneous emission. When the molecule is prepared with more energy than the barrier for *cis–trans* isomerization, this photochemical process also contributes to S_1 decay. The isomerization is nonadiabatic[8,15,17] and molecules isomerized over the barrier supposedly relax to the ground state without emitting fluorescence. Very similar behavior has been observed for *trans*-stilbene.[18–20] Thus, opening the isomerization channel drastically increases the decay rate of OT (S_1) and accounts for the break in the plot of decay rate as a function of energy, since the rate of isomerization increases much more rapidly than those of the other decay channels, internal conversion, and fluorescence.

The isomerization rate was approximately separated from the contributions of other decay channels. At the vibronic energies where isomerization occurs, the total decay rate of OT (S_1) is given by the sum of three processes, radiative decay, internal conversion, and isomerization; i.e., $k_{\rm total}(E)=1/\tau_r+k_{\rm ic}(E)+k_{\rm iso}(E)$. Petek *et al.* have reported that the decay rate $[1/\tau_r+k_{\rm ic}(E)]$ smoothly increases by a factor of 2 from ~1200 cm^{-1} up to ~2100 cm^{-1}.[8] Since the rate of the nonreactive decays is a weak function of energy, data points for decay rates below 2000 cm^{-1} were fit to a linear function of energy. The isomerization rate $[k_{\rm iso}(E)]$ is obtained by subtracting the calculated contribution of radiative decay and internal conversion, $1/\tau_r+k_{\rm ic}(E)$, from the total experimentally observed decay rate, $k_{\rm total}(E)$. Three experimental rate constants were averaged to yield one value at a given vibrational energy and plotted as curve (b) in Fig. 1. The rate constant suddenly increases from 0 to ~1.0×10^7 s^{-1} within a 10 cm^{-1} range around 2140 cm^{-1}. The rate constant then stays nearly constant until the 2220 cm^{-1} region where a second step shows up. The spacing between these two steps is 80±10 cm^{-1}. The first step corresponds to the threshold for isomerization, the lowest energy at which isomerization can take place. The sharpness of the step allows us to determine the threshold with a high accuracy and gives 2137±5 cm^{-1} for isomerization of OT on the S_1 surface.

The stepwise change in the isomerization rate is predicted by RRKM theory. According to the theory, the unimolecular rate constant $k(E)$ of molecules with vibrational energy E is given by Eq. (1),[1–3]

$$k(E)=W^{\ddagger}(E-E_0)/h\rho(E), \tag{1}$$

where $W^{\ddagger}(E-E_0)$ is the number of vibrational levels of the transition state with energy less than $E-E_0$, E_0 is the threshold energy for reaction, $\rho(E)$ is the density of vibrational states, and h is Planck's constant. Usually $\rho(E)$ is almost a smooth function of vibrational energy in the energy region around the threshold except for relatively small molecules such as triatomic molecules.[1–3] $W^{\ddagger}(E-E_0)$, however, is a step function of vibrational energy, i.e., it is zero at energies below the threshold. It equals one at the threshold, two at the energy of the first excited vibrational level, three at the second excited vibrational level, and so on. Thus, $k(E)$ should change from 0 to $1/h\rho(E_0)$ at the threshold and increase by steps of $1/h\rho(E)$ as energy and therefore $W^{\ddagger}(E-E_0)$ increases. The stepwise characteristics are most pronounced just above the threshold where the spacings between vibrational levels in the transition state are the largest. It becomes less pronounced with increasing energy since the spacings between levels become increasingly smaller and the size of step, $1/h\rho(E)$, decreases simultaneously due to the increase of $\rho(E)$. Since $W^{\ddagger}(E-E_0)$, which gives a stepwise increase of RRKM rate constant with energy, is based on the implicit assumption that the vibrational levels of transition state are quantized, experimental observation of a stepwise variation of rate constant provides strong evidence for quantization of the transition state. The isomerization rate of OT obtained in this work thus follows the prediction of RRKM theory; it increases in a stepwise manner with increasing energy.

The position of the steps corresponds to vibrational levels of the transition state, which controls the flux of passage from reactant to product. The energy spacing between the first two steps, 80±10 cm^{-1}, is the lowest frequency vibration of the transition state. Since OT is a relatively large molecule with 48 vibrational modes, it is not unreasonable to expect that frequencies of most vibrations in the reactant, which are perpendicular to the reaction coordinate of torsional motion, should be similar to those of the transition state. Based upon this optimistic expectation, the lowest frequency vibration of the transition state is tentatively assigned to the in-plane bending motion, ν_{48}, which has a frequency of 76 cm^{-1} in OT in the S_1 state.[8] A lower frequency vibration at ~49 cm^{-1} is probably the reaction coordinate (torsion). A preliminary RRKM calculation[21] gives a rate constant of $3.4\times10^6\ \mathrm{s}^{-1}$ at 2200 cm^{-1}.[22] This is in reasonable agreement with the experimental value of $8.0\times10^6\ \mathrm{s}^{-1}$ at the same energy, considering the fact that the vibrational frequencies of approximately half of the vibrational modes are used by arbitrarily decreasing the *ab initio* values[23] by 10%.

Moore and colleagues[5] and Wittig's group[7] have demonstrated the quantization of the transition state for unimolecular bond-breaking reactions. The present work involves an isomerization in which a bound molecule rearranges into another stable geometry. Our results not only provide additional evidence for quantization of the transition state but also extends the previous work to a different class of unimolecular reactions. Also, it is interesting that quantization is observed in a molecule with 48 degrees of freedom. Other large molecules might reveal similar effects. Extensive collection and analyses of the data for a broader range of energies are underway. A complete description of various features of the isomerization of OT and the quantitative comparison with RRKM theory will be presented in a full paper with detailed discussion on the implication of these observations for unimolecular reaction dynamics.

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