

# 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 ( $S_1$ ) potential surface have been obtained as a function of vibronic energy above the fluorescence maximum. A stepwise increase in the isomerization rate with increasing energy has been observed. The energy spacing of 50–10 cm<sup>-1</sup> 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 dis-

theoretical studies have been devoted to understanding this

quently employed theory of unimolecular reactions is that formulated by Rice, Ramsperger, Kassel, and Marcus (RRKM).<sup>4</sup> The so-called RRKM theory is based upon sev-

erized 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

on the triplet surface.<sup>5,6</sup> More recently, Wittig and co-

These recent observations suggest the general existence

order to confirm the generalization unambiguously, however,

( $S_1$ ) potential energy surface is observed to increase in a stepwise manner with increasing energy as expected for quantized vibrational levels of the transition state.

on the vibronic energy. The experimental setup in this work

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

the  $S_1$  ( $2^1A_g$ ) transition state of OT. Fluores-

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

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 data were transferred to a personal computer and fit with a

time resolution limit is about 100 ps. The laser beam

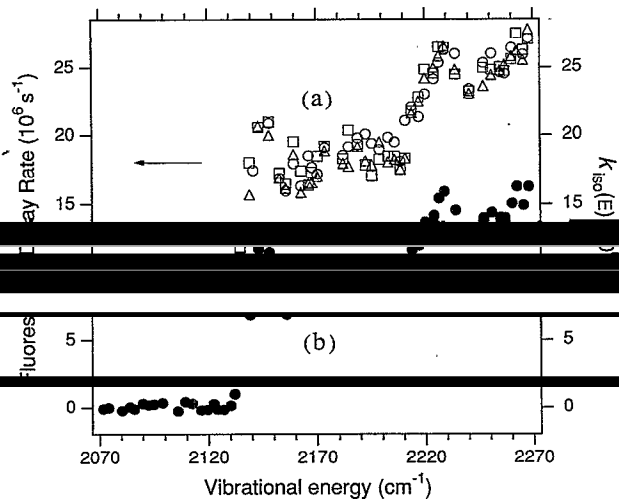
thesized by dehydration of 2,4,8-octatrien-6-ol using pyri-

ture described previously. The acronol was purchased from

shown. The decay rate increases very slowly from the origin of the  $S_1$  state up to 2130 cm<sup>-1</sup>. The data of curve (a) between 2070 and 2130 cm<sup>-1</sup> shown in Fig. 1 are on the line of

2170 cm<sup>-1</sup> by more than a factor of 2 and then stays almost constant up to an energy of 2190 cm<sup>-1</sup> where it increases

edge of the photochemistry and photophysics of the  $S_1$  state of OT. Since the dynamics of electronically excited OT pro-



perimental 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  $\sim 1.0 \times 10^7$  s<sup>-1</sup> within a 10 cm<sup>-1</sup> range around 2140 cm<sup>-1</sup>. The rate constant then stays nearly constant until the 2220 cm<sup>-1</sup> region where a second step shows up. The spacing between these two steps is  $80 \pm 10$  cm<sup>-1</sup>. The first step corresponds to

isomerization can take place. The absence of the step at 2140 cm<sup>-1</sup> gives  $2157 \pm 5$  cm<sup>-1</sup> for isomerization of OT on the S<sub>1</sub> surface.

The stepwise character of 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),<sup>1-3</sup>

$$k(E) = W^\ddagger(E - E_0) / h\rho(E) \quad (1)$$

for the procedure of calculation) in the same vibrational energy range as for

vibronal states, and  $h$  is Planck's constant. Usually  $\rho(E)$  is

vides the basis for understanding the photochemistry of natural processes such as vision and bacterial and plant

energies below the threshold. It equals one at the threshold, at the second excited vibrational level, and so on. Thus,  $k(E)$

experimentally and theoretically. Below the threshold for isomerization OT (S<sub>1</sub>) relaxes to the ground electronic state through the competing channels of fluorescence and spontaneous emission. When the molecule is prepared in an excited vibrational level, the isomerization process also contributes to S<sub>1</sub> decay.

increase by steps of  $\rho(E)$  as energy and therefore  $W^\ddagger(E - E_0)$  increases. The stepwise characteristics are most pronounced when 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

isomerized over the barrier supposedly relax to the ground state without emitting fluorescence. Very similar behavior has been observed for *trans* stilbene.<sup>18-20</sup> Thus, opening 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

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.

tization 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 isomerization rate was approximately separated from the contributions of other decay channels. At the vibrational energies where isomerization occurs, the total decay rate is the sum of radiative decay, internal conversion, and isomerization; i.e.,  $k_{\text{total}}(E) = 1/\tau_r + k_{\text{ic}}(E) + k_{\text{iso}}(E)$ . Petek *et al.* have reported

The position of the steps corresponds to vibrational levels of the transition state, which controls the flux of passage

first two steps,  $80 \pm 10$  cm<sup>-1</sup>, is the lowest frequency vibration of the transition state. Since OT is a relatively large

rate of the nonreactive decays is a weak function of energy, data points for decay rates below 2000 cm<sup>-1</sup> were fit to a linear function of energy. The isomerization rate [ $k_{\text{iso}}(E)$ ] is obtained by subtracting the calculated contribution of radiative decay and internal conversion,  $1/\tau_r + k_{\text{ic}}(E)$ , from the total experimentally observed decay rate,  $k_{\text{total}}(E)$ . Three ex-

which are perpendicular to the reaction coordinate or 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,  $\nu_{48}$ , which has a frequency of 76 cm<sup>-1</sup> in OT in the S<sub>1</sub> state.<sup>8</sup> A lower frequency vibra-

tion at  $\sim 49 \text{ cm}^{-1}$  is probably the reaction coordinate (tor-

<sup>1</sup>P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions* (Wiley, London, 1972).

agreement with the experimental value of  $6.0 \times 10^{-11} \text{ s}^{-1}$  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<sup>23</sup> by 10%.

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strated 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 col-

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<sup>21</sup>In the calculation, the degeneracy of the transition state is assumed to be 8. Ref. 8.

<sup>22</sup>The calculated and measured values are compared at  $2200 \text{ cm}^{-1}$  where the experimental values show smaller scattering than in other energy regions.

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