

Evidence for inhomogeneous broadening in vibrational overtone transitions: Formation of 1, 3-cyclohexadiene from *cis*-1, 3, 5-hexatriene

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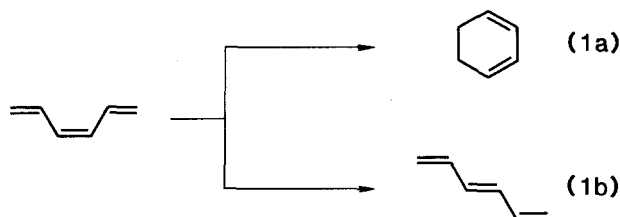
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By pumping the 4-0 and 5-0 C-H overtones of *cis*-1, 3, 5-hexatriene, the rates of 1, 3-cyclohexadiene formation are measured using a Stern-Volmer analysis. While the rate for 5-0 C-H excitation is faster than 4-0 C-H excitation, the latter is about one order of magnitude larger than that calculated from an RRKM treatment. Moreover, nonmonotonic variation in rates are found as a function of excitation wavelength within each overtone region. These observations cannot be explained by assuming pure homogeneous broadening of each overtone transition, but can be rationalized by including inhomogeneous contributions, which may originate from hot bonds in the initial state and/or from a rotational dependence of this electrocyclic reaction rate near threshold.

I. INTRODUCTION

Following the pioneering work of Reddy and Berry,¹⁻³ there have been several studies of unimolecular reactions induced by vibrational overtone pumping.⁴⁻¹⁴ These studies have been motivated by the belief that this form of photochemical activation is very specific, namely, the initial energy content and the initial vibrational motion of the activated molecule are both well known. The present study on the isomerization on *cis*-1, 3, 5-hexatriene presents evidence that the above description is oversimplified. Unimolecular processes induced by vibrational overtone pumping may lead to a much richer chemistry than previously suspected.

There are two isomerization reactions of *cis*-1, 3, 5-hexatriene in the wavelength region studied (700-880 nm),^{15,16}



The lower energy channel (1a) is a disrotatory electrocyclic reaction^{17,18} and the higher energy one (1b) is the *cis*-*trans* isomerization. The thermal reaction of (1a) was studied by Lewis and Steiner,¹⁹ while reaction (1b) was studied by Orchard and Thrush¹⁵ using UV excitation followed by internal conversion. The schematic potential energy curve of the two reactions and the energy levels associated with the vibrational overtones of *cis*-1, 3, 5-hexatriene are shown in Fig. 1, along with the reported Arrhenius parameters.^{15,19} In each overtone region, there are three distinct peaks indicating three different possible modes of initial excitation. For 4-0 and 5-0 excitation, only reaction (1a) is energetically allowed, while both channels are possible when 6-0 and 7-0 are pumped.

It is believed²⁰ that triplet states of *cis*-1, 3, 5-hexatriene occur around 607-350 nm which very efficiently cause *cis*-*trans* isomerization. We therefore confined our studies of the electrocyclic reaction to excitation via the third and the fourth overtones. We find that the rate of electrocyclic rearrangement as a function of laser wavelength across an over-

tone feature shows a strongly nonmonotonic variation. The exact origin of this behavior is presently unestablished, but arguments are presented that it arises from heterogeneous broadening of the overtone features.

II. EXPERIMENTAL

A. Sample preparation

1, 3, 5-Hexatriene was purchased as an approximately 3:7 mixture of *cis* and *trans* isomers from Aldrich or Columbia Organic. The procedure of isolating the *cis* isomer followed closely Hwa *et al.*²¹ with only slight modification. Briefly, 5 g of the mixture was placed in a 25 ml round bottom flask with ground joint. Then 9.3 g of maleic anhydride was added in several small portions over a 2 h period. A

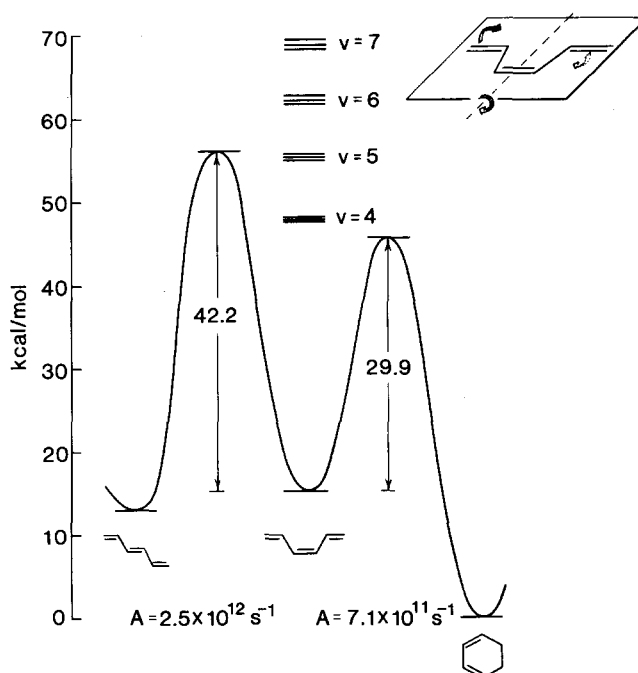


FIG. 1. Schematic diagram of the potential energy as a function of reaction coordinate for the isomerization of *cis*-1, 3, 5-hexatriene into either *trans*-1, 3, 5-hexatriene or 1, 3-cyclohexadiene, showing the energy levels of the C-H stretching overtones and the reported Arrhenius parameters for the formation of *trans*-1, 3, 5-hexatriene (Ref. 15) and 1, 3-cyclohexadiene (Ref. 7). The inset illustrates the possible coupling with external rotation of the reaction coordinate (a disrotatory motion) for electrocyclic isomerization.

vacuum stopcock with ground joint was attached to the round bottom flask and the air in the flask was evacuated when the reactants were trapped by liquid nitrogen. The reaction was then carried out in the dark for ~ 48 h at room temperature. Vacuum distillation yielded the *cis*-1, 3, 5-hexatriene with a purity of about 99%, as determined by gas chromatography. Major impurities were low-boiling-point hydrocarbons which did not interfere with the reaction or the analysis procedure. Samples used were always degassed by many freeze-pump-thaw cycles.

B. Optoacoustic spectroscopy

The overtone spectra were taken with an optoacoustic technique similar to that described before.^{5,6} A Knowles BT-1759 microphone was attached to an opening at the midpoint of a 15 cm long by 1.0 cm i.d. Pyrex cell with Torr Seal (Varian Associates). A 1.5 V battery was used to power the microphone. Both ends of the cell were cut at Brewster's angle and sealed with quartz windows also using Torr Seal. This cell, filled with typically 10–30 Torr of *cis*-1, 3, 5-hexatriene, was placed inside the cavity of a home-built cw dye laser pumped by suitable ion lasers. The pump laser and laser dye used for different wavelength regions and the overtones covered are listed in Table I. A variable speed chopper (PAR model 192) was inserted between the pump laser and the dye laser to amplitude modulate the intracavity power of the dye laser. The relative intracavity laser power was monitored by measuring the light reflected from one of the Brewster windows with an NRC 815 power meter. Both the optoacoustic signal and the laser power were processed by lock-in amplifiers (PAR 124A and 186A, respectively) and the outputs of the two were ratioed with a PAR model 193 ratiometer to give the normalized signal. The dye laser was tuned by rotating a two-plate birefringent filter placed at Brewster's angle inside the dye laser cavity. The resolution of this dye laser system is about 2 cm^{-1} . The output of the dye laser was split into two with a 4 mm thick quartz plate; one beam traveled through a solid etalon with $\text{FSR} = 17.4\text{ cm}^{-1}$ and was incident on another NRC 815 power meter sensor head; the other beam went into a calcium hollow cathode lamp filled with neon. The optogalvanic signals from the neon atomic transitions served as an absolute wavelength calibration while the fringes from the solid etalon served as a relative wavelength calibration. These signals along with the nor-

malized optoacoustic signal were monitored using a strip-chart recorder (Soltec 1242). The accuracy of the frequencies of the overtone absorptions is essentially determined by the resolution of the dye laser and is no worse than 3 cm^{-1} .

C. FTIR spectrum

The fundamental vibrational spectrum of the molecule is taken with a Nicolet 7199 FTIR. The spectrum is an average of 200 scans with 0.25 cm^{-1} resolution.

D. Absorption cross sections

The absolute absorption cross section of the 5–0 C–H stretch overtone was calibrated in two ways. In the first method, a given mixture of *cis*-1, 3, 5-hexatriene (CHT) and neopentane (NP) was prepared and the optoacoustic spectrum was taken for this mixture. Another mixture of benzene (BZ) and neopentane was again prepared and its spectrum measured. The peak absorption cross section of *cis*-1, 3, 5-hexatriene was derived from the following equation:

$$\sigma_{\text{CHT}} = \sigma_{\text{BZ}} \cdot \frac{S_{\text{CHT}}}{S_{\text{NP}}} \cdot \frac{S'_{\text{NP}}}{S_{\text{BZ}}} \cdot \frac{P_{\text{NP}}}{P_{\text{CHT}}} \cdot \frac{P_{\text{BZ}}}{P'_{\text{NP}}}, \quad (2)$$

where S represents the peak optoacoustic signal, P the pressure, and σ the peak absorption cross section. Note that the pressures of neopentane in the two mixtures were not always the same and neither were the corresponding signals. The absorption cross sections of benzene were taken from Reddy, Heller, and Berry.²² This method can only be applied when the laser dye used covers a large wavelength range and the molecules in a mixture do not have overlapping absorptions.

In the second method, the overtone spectra of pure *cis*-1, 3, 5-hexatriene and benzene were taken separately at the same pressure under identical experimental conditions. Assuming ideal gas behavior, the peak absorption cross section of *cis*-1, 3, 5-hexatriene was derived from

$$\sigma_{\text{CHT}} = \sigma_{\text{BZ}} \cdot \frac{S_{\text{CHT}}}{S_{\text{BZ}}} \cdot \frac{(C_v)_{\text{CHT}}}{(C_v)_{\text{BZ}}}, \quad (3)$$

where the C_v 's are the heat capacities at constant volume.

The absorption cross sections of the fourth overtone derived from the two methods only differ by less than 10%. The absorption cross section of the third overtone could only be calibrated with the second method because of the limited tuning range of the laser dye.

TABLE I. Wavelength and overtone region covered by different dye laser systems.

λ (nm)		Pump laser	Dye	Overtone
840–940	Spectra Physics 171-01	Kr ⁺ All red lines	HITC	3rd
700–800	Spectra Physics 171-01	Kr ⁺ All red lines	LD-700	4th
560–655	Spectra Physics 165	Ar ⁺ All blue-green lines	Rhodamine-6G	5th
495–545	Spectra Physics 171-01	Kr ⁺ All violet lines	Coumarin-515	6th

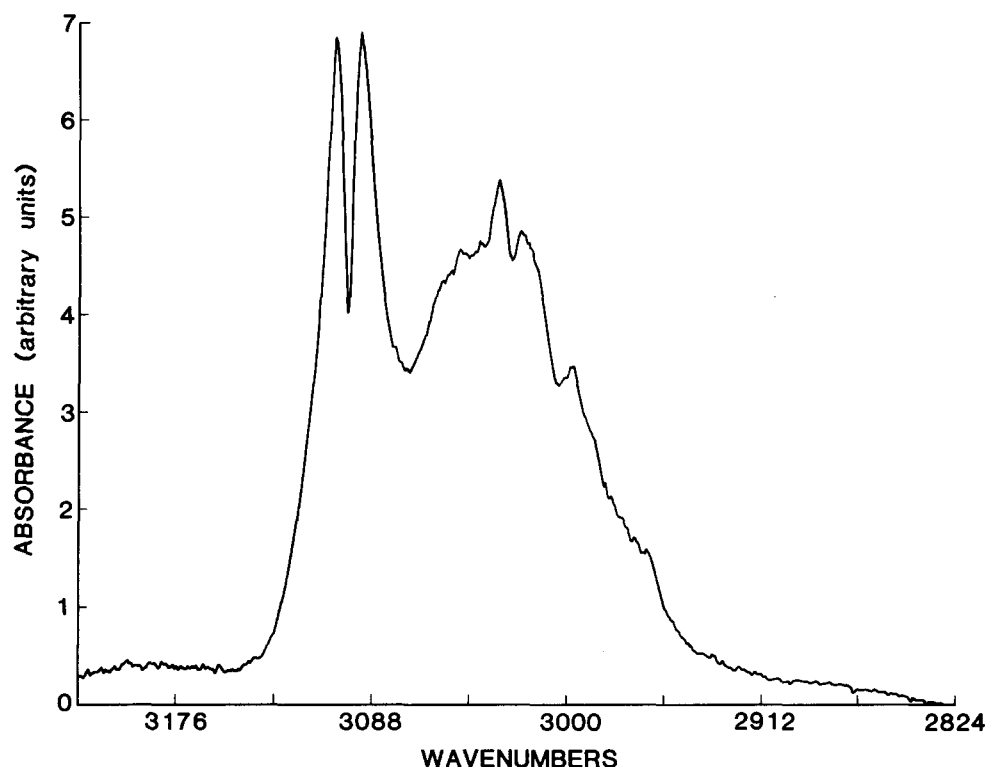


FIG. 2. Fundamental C-H stretching of *cis*-1, 3, 5-hexatriene. Eight different C-H vibrations contribute to the fundamental absorption band; the assignments are given in Ref. 24.

E. Kinetic measurements

The photolyses were performed in a 1 cm i.d. and 26 cm long Pyrex cell sealed by a greaseless Teflon stopcock. Quartz windows were attached at Brewster's angles on both ends of the photolysis cell by Torr Seal. The photolyses were carried out inside the cavity of the cw dye laser with room lights all blocked. The illumination from the fluorescent lights in the laboratory was found to induce *cis-trans* isomerization of the hexatriene but did not affect the electrocyclic

reaction. The mechanism for the *cis-trans* isomerization induced by room lights seems to be a photon initiated, surface catalyzed chain reaction and should be an interesting research topic in itself. Heating the photolysis cell with a heat gun at a nozzle temperature of 350 °C between each photolysis run further suppressed the *cis-trans* isomerization. For electrocyclic reaction, surface effects appear to be absent, because the rates for this process were unaffected by changing the surface to volume ratio in the thermal kinetic study.¹⁹ Furthermore, neither blocking the room lights nor heating the cell between runs affected the rates in the present study.

Typical photolysis times varied from 50 min to 2 h, depending on the rates of product yield. The percentage of product yield was always kept to less than 2% so that the amount of reactant could be assumed constant. The laser power was monitored during the photolysis with a NRC 815 power meter.

The quantitative analysis of both the reactant and the product was carried out by gas chromatography, using a Perkin-Elmer 3920 GC with FID detector and Valco gas sampling valve. A 10 ft. × 1/8 in. stainless steel column packed with 33% β , β' -oxidipropionitrile on 100/120 gas chrom-RZ (from Altech Associates) performed a complete separation of *cis*-1, 3, 5-hexatriene and 1, 3-cyclohexadiene when the oven temperature was maintained at 32 °C and the He carrier gas flow rate was set at 26 ml/min. Absolute quantitative analysis was performed using a calibration curve (a straight line) of chromatogram peak height in mV vs the amount of authentic sample injected (in mTorr). The standard is injected as a known mixture of *cis*-1, 3, 5-hexatriene and 1, 3-cyclohexadiene to mimic closely the real experimental conditions.

There was no systematic order of carrying out the photolyses at the wavelengths studied. After all the data were

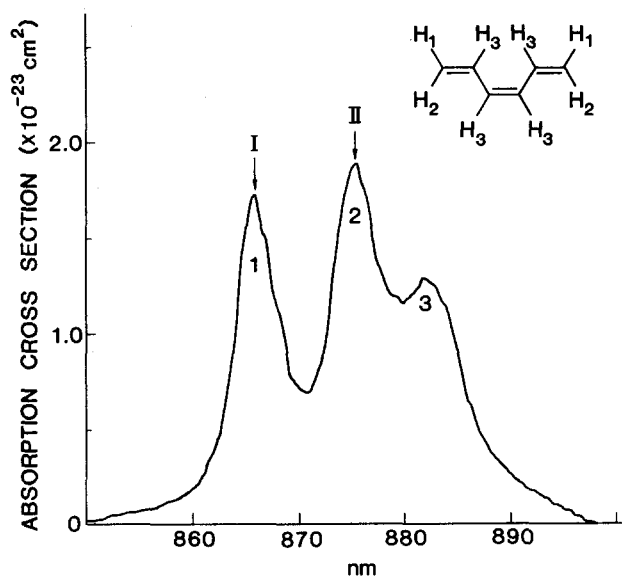


FIG. 3. 4-0 C-H overtone absorption of *cis*-1, 3, 5-hexatriene. Peaks 1, 2, and 3 correspond to the absorptions from the three types of H atoms labeled on the structure shown. The arrows point to photolysis wavelengths studied. The Roman numerals match with those presented in the corresponding reduced Stern-Volmer plot (Fig. 9).

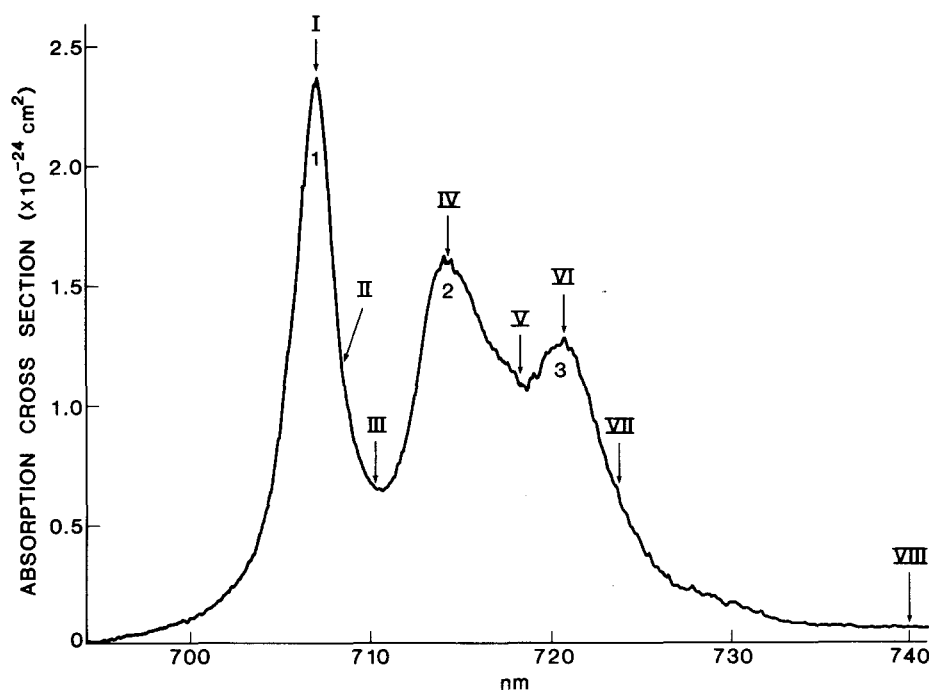


FIG. 4. 5-0 C-H overtone absorption of *cis*-1, 3, 5-hexatriene. The meaning of the Arabic and Roman numbering is the same as in Fig. 3.

collected, the first data point of the whole study was repeated. The measured value fell within the error of the original studies. Therefore, no significant instrumental drift occurred over a 3 month period of the study.

The transmittances of the end mirrors (usually $\leq 10^{-3}$) of the dye laser are quantities crucial for the absolute intracavity power measurement. They were measured with a Varian 2300 spectrophotometer with a capability of measuring o.d. = 4. The transmittances from 707 to 730 nm were also measured by placing the end mirror into the laser beam coming from the output coupler of the dye laser. Laser powers measured with and without the end mirror in front were thus used to calculate the transmittance. Again, both methods gave excellent agreement.

III. RESULTS

A. Spectroscopic measurements

The spectra of the 1-0, 4-0, 5-0, 6-0, and 7-0 C-H stretch of *cis*-1, 3, 5-hexatriene are shown in Figs. 2-6, and the Birge-Sponer plot of the system is shown in Fig. 7. It is clear from Fig. 7 that the four overtone absorptions show "localized" behavior, while the fundamental transition does not. From the slope and the intercept of the best fit line through the points representing the corresponding peaks of only the overtone absorptions, we determined ω_e and $\omega_e x_e$ (see Table II).

Although there are three possible conformations of *cis*-1, 3, 5-hexatriene:

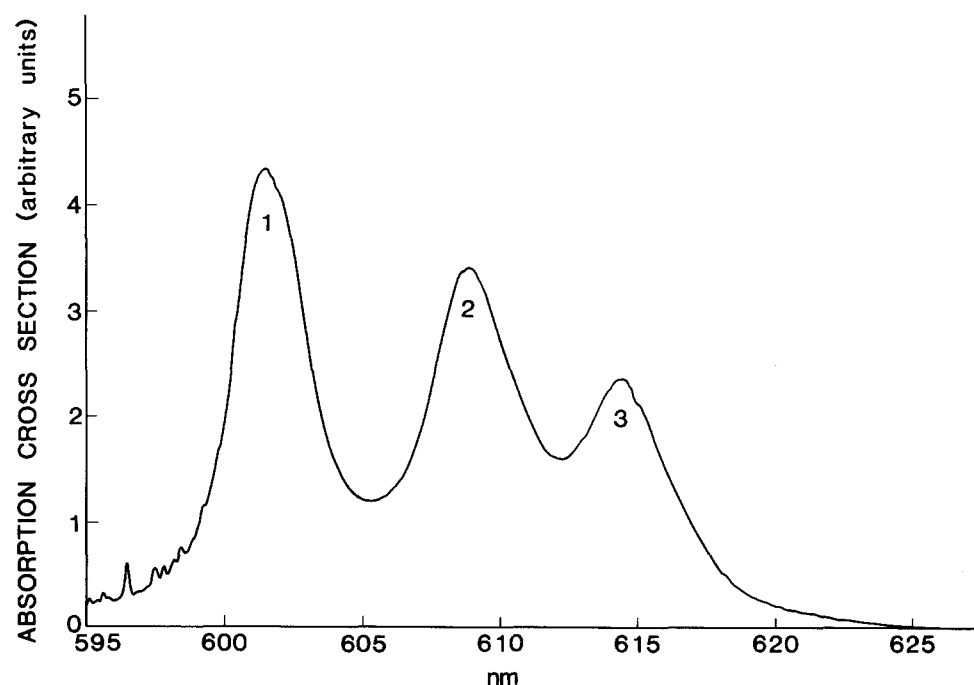


FIG. 5. 6-0 C-H overtone absorption of *cis*-1, 3, 5-hexatriene. The meaning of the Arabic numbering is the same as in Fig. 3. The sharp structure at shorter wavelengths is due to water vapor overtone transitions.

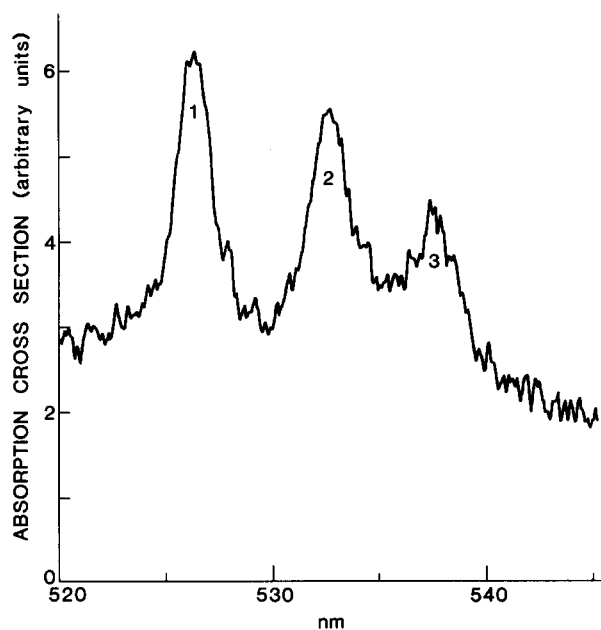


FIG. 6. 7-0 C-H overtone absorption of *cis*-1, 3, 5-hexatriene. The meaning of the Arabic numberings is the same as in Fig. 3. A background continuum is prominent in this region.

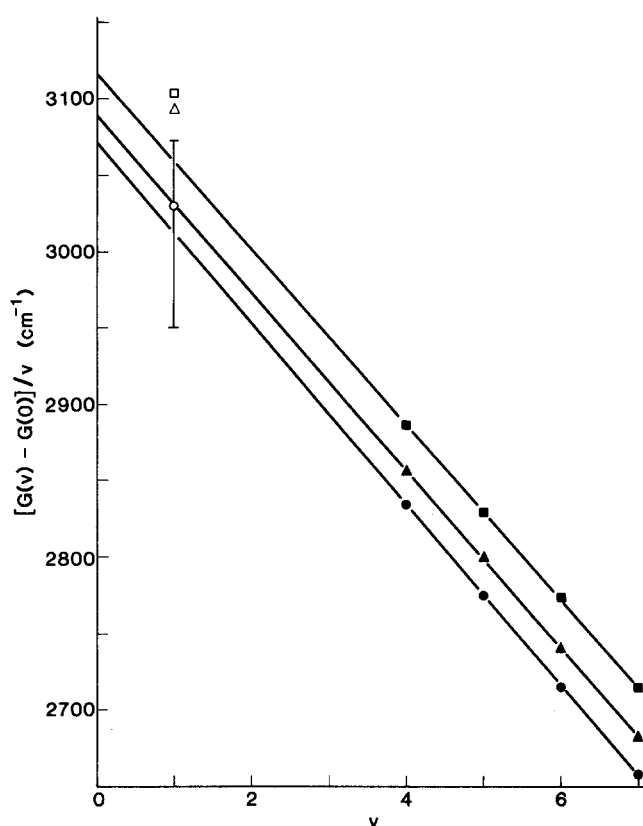
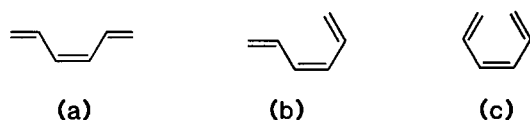


FIG. 7. Birge-Spinner plot for different C-H oscillators of *cis*-1, 3, 5-hexatriene. The peaks in the overtones labeled 1 are denoted by ■, those labeled 2 by ▲, and those labeled 3 by ●. The solid lines are the best straight line fits to the overtones. The open symbols represent the three most distinct peaks in the fundamental region. According to Ref. 25, there are six vibrational modes overlapping in the region spanned by the error bar on the open circle ○.

only the most stable conformer (a) exists in the gas phase at room temperature. This conclusion is based on the structure deduced from electron diffraction studies,²³ which is consistent with the C_{2v} symmetry that rationalizes the observed IR and Raman data. Thus, it is believed that the observed overtone transitions come from the same conformer (a) as well.

By comparing the fifth overtone spectrum of *cis*-1, 3, 5-hexatriene with those of propene and *cis*-2-butene,²⁴ the following tentative assignments are made: the four nonterminal vinylic C-H's are assigned to the lowest frequency peak because terminal vinylic C-H's always absorb at higher frequencies. The two terminal C-H's at the positions *trans* to the C-C bonds are assigned to the highest frequency peak as in the case of propene. The remaining two C-H's contribute to the middle peak. Without isotope substitution, these assignments are not established with certainty. The assignments of the IR and Raman spectra in the fundamental transition region were made by Lippincott and Kennedy.²⁵

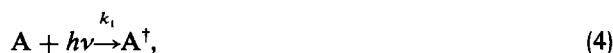
Not shown in Figs. 2-6 are some very weak (less than 10% of the strongest peak at the higher overtone band) featureless "bumps" between 750-820 and 625-695 nm. These weak absorptions might come from combinations of low frequency motions, such as C=C-H bending or C=C stretching with C-H stretching overtones, or might be some other more complicated interactions, such as Fermi resonances.^{26,27}

The peak absorption cross sections of the strongest features of the third and the fourth overtones are 2.0×10^{-23} and 2.4×10^{-24} cm², respectively. The errors of the relative absorption cross section within an overtone band are around

$\pm 2\%$, while the errors of the absolute absorption cross sections are estimated to be $\pm 15\%$.

B. Isomerization kinetics

A simple Stern-Volmer mechanism



combined with a steady state assumption leads to the following rate equation:

TABLE II. Spectroscopic constants obtained from Birge-Spinner plots of the C-H stretching overtones.

Peak ^a	ω_e/cm^{-1}	$\omega_e x_e/\text{cm}^{-1}$
1	3172.4	57.1
2	3147.8	58.2
3	3127.7	58.8

^a The peak designations are shown in Figs. 3-6.

$$\begin{aligned}
 -\frac{d[A]}{dt} &= \frac{d[P]}{dt} \\
 &= \frac{k_1 k_3(E)}{k_2[M] + k_3(E)} [A] [h\nu] \\
 &= k_{\text{app}} [A] [h\nu].
 \end{aligned}
 \quad (7)$$

Solving the above rate equation, we find

$$-\ln \frac{[A]}{[A]_0} = k_{\text{app}} [h\nu] \tau, \quad (8)$$

where $[A]_0$ is the concentration of A in the photolysis cell at $t = 0$, and $[A]$ that at $t = \tau$. Because each product molecule comes from one reactant molecule, we can rewrite Eq. (8) as

$$-\ln(1 - [P]/[A]_0) = k_{\text{app}} [h\nu] \tau. \quad (9)$$

Since $[P]/[A]_0 \ll 1$, which is true under our experimental conditions, we expand the left-hand side of Eq. (9) and keep the first nonvanishing term

$$[P]/[A]_0 = k_{\text{app}} [h\nu] \tau. \quad (10)$$

The maximum error introduced is only 1%.

The product apparent rate constant k_{app} can thus be calculated by measuring the product yield after photolyzing an initial concentration $[A]_0$ of reactant for a period of time τ under intracavity laser intensity I_i . Here I_i cannot be measured directly. However, by knowing the transmittance of the dye laser end mirror at the photolysis wavelength, we can calculate I_i and hence $[h\nu]$ by measuring the laser output intensity I_0 outside the cavity. We use the relation between $[h\nu]$ and I_0 ,

$$[h\nu] = 2 \times (5.04 \times 10^{14} \lambda I_0 / T) c A_{\text{eff}}, \quad (11)$$

where λ is the photon wavelength (\AA), I_0 is the laser output intensity (W), T is the transmittance of the dye laser end mirror at λ , c is the speed of light (cm s^{-1}), and A_{eff} is the effective cross sectional area (cm^2) of the cell defined as the cell volume divided by the cell length. The factor of 2 in Eq. (11) arises from the fact that there are photons traveling both toward and away from the end mirror; they all pass through the photolysis cell but only those traveling toward the end mirror get transmitted.³

From Eq. (7), we have

$$k_{\text{app}}^{-1} = \frac{k_2}{k_1 k_3(E)} [M] + \frac{1}{k_1} \quad (12)$$

or

$$k_1/k_{\text{app}} = \frac{k_2}{k_3(E)} [M] + 1. \quad (13)$$

Here k_1 is the photoexcitation rate constant and is equal to the absorption cross section σ times the speed of light c , and k_2 is the collision rate constant between A^\dagger and M. A plot of k_1/k_{app} vs pressure has a slope $k_2/k_3(E)$. Therefore, $k_3(E)$ can be extracted from such a reduced Stern-Volmer plot by calculating the collision rate constant k_2 . We assume hard sphere collisions for which $k_2 = \sigma(8RT/\pi\mu)^{1/2}(N/V)$, where μ is the reduced mass. The above analysis has proved useful for many systems studied before.

A linear power dependence of product yield by exciting 1 Torr of *cis*-1, 3, 5-hexatriene at 707.0 nm is a check of the single-photon nature of the energization process. The result

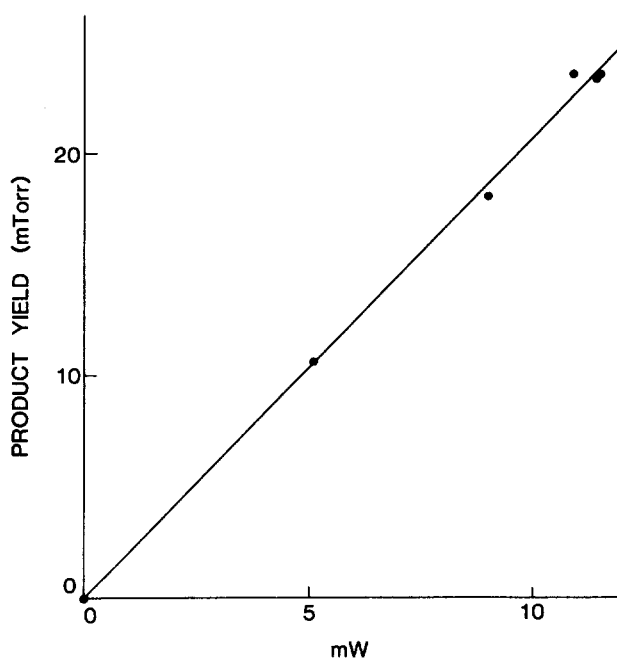


FIG. 8. Power dependence of the electrocyclic product yield at 707.0 nm (the 5–0 C–H stretch feature labeled I in Fig. 4).

of this experiment is shown in Fig. 8. The straight line going through the origin is a consequence of the fact that no background reaction was observed with the laser off.

Two-photon transitions of *cis*- and *trans*-1, 3, 5-hexatriene have been observed to occur in the frequency range of $2\omega = 30\,000$ – $50\,000\text{ cm}^{-1}$ in the liquid phase through CARS and CSRS line shape analysis.²⁸ The single-photon frequencies in the two-photon transitions are higher than the frequency range of the present study. The long excitation wavelengths used as well as the linear power dependence observed in our study exclude any possibility of nonlinear processes.

To understand more fully the role of the triplet state, an experiment was performed by exciting the 7–0 (the sixth overtone) around 520–560 nm, which is estimated to be near the peak of the triplet (T_1).²⁰ *Trans*-1, 3, 5-hexatriene was the predominant product of the photolysis. This is unexpected from the Arrhenius parameters of Orchard and Thrush,¹⁵ and is in contrast to the IR multiphoton study of Weitz *et al.*²⁹ In both of these cases the ground electronic state reactions are believed to occur and 1, 3-cyclohexadiene is the major product.

When the laser was tuned off the sixth overtone to the blue, an 85% decrease in k_{app} for cyclohexadiene was observed but k_{app} for *trans*-1, 3, 5-hexatriene was unaffected.³⁰ This shows that the background absorption in the neighborhood of 7–0 overtone which presumably arises from the triplet state, influences the two isomerization reactions in completely different manners.

Figures 9 and 10 present the reduced Stern-Volmer plots obtained by exciting the third and fourth overtones, respectively. Each data point is an average of at least three measurements. A typical error bar is $\pm 2\%$ and no worse than $\pm 5\%$. The best fit lines from the least square procedure are presented in each plot.

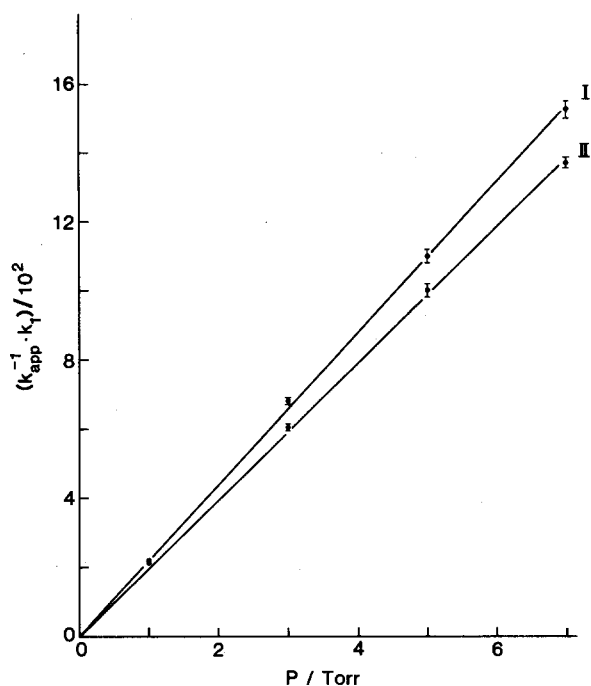


FIG. 9. Reduced Stern-Volmer plot obtained by pumping different features of the 4-0 C-H stretch. The Roman numerals match with those in Fig. 3.

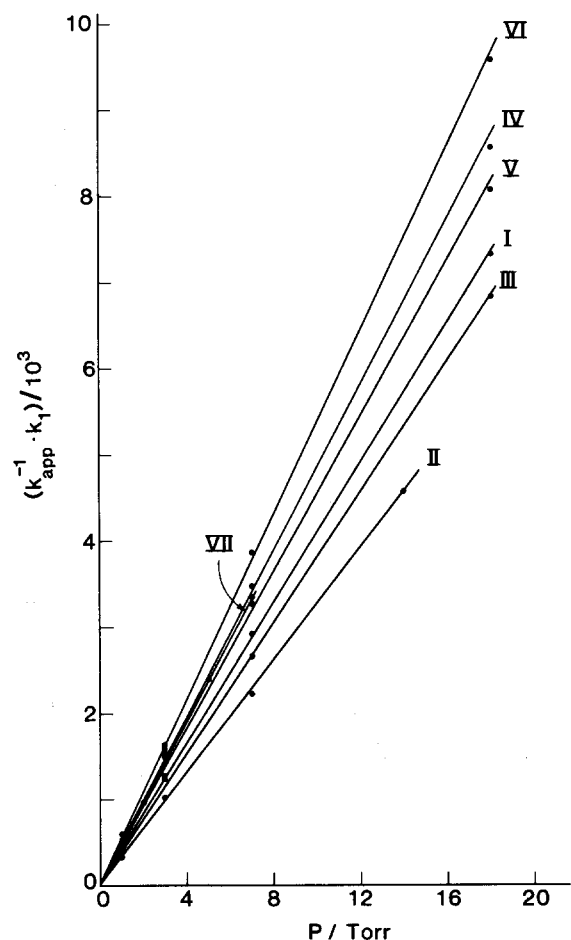


FIG. 10. Reduced Stern-Volmer plot obtained by pumping different features of the 5-0 C-H stretch. The Roman numerals match with those in Fig. 4. Error bars are omitted for clarity. The typical error of each data point is $\pm 2\%$ and is no worse than $\pm 5\%$.

TABLE III. Unimolecular reaction rate constants for the isomerization of *cis*-1, 3, 5-hexatriene to 1, 3-cyclohexadiene.

Wavelength/nm	$k_3(\text{exp})/\text{s}^{-1}$	$k_3(\text{RRKM})/\text{s}^{-1}$
875.3	$(7.08 \pm 0.32) \times 10^3$	5.45×10^2
866.0	$(6.63 \pm 0.13) \times 10^3$	5.83×10^2
740.0	$(4.84 \pm 0.13) \times 10^4$	2.08×10^4
723.6	$(3.55 \pm 0.10) \times 10^4$	3.03×10^4
720.7	$(3.18 \pm 0.15) \times 10^4$	3.01×10^4
718.5	$(3.76 \pm 0.14) \times 10^4$	3.27×10^4
714.2	$(3.54 \pm 0.15) \times 10^4$	3.55×10^4
710.7	$(4.41 \pm 0.12) \times 10^4$	3.76×10^4
708.3	$(5.21 \pm 0.16) \times 10^4$	4.05×10^4
707.0	$(4.16 \pm 0.23) \times 10^4$	4.08×10^4

In the 5-0 region, seven different excitation wavelengths were studied; two wavelengths were used in the 4-0 region. Table III lists the values of $k_3(E)$ extracted from the slopes of the best fit lines by assuming a hard sphere collision diameter of 6.5 \AA ($k_2 = 1.7 \times 10^7 \text{ s}^{-1} \text{ Torr}^{-1}$). The error bars of the $k_3(E)$ values are the standard deviations derived from the least squares calculations. The excitation wavelengths are also marked in Figs. 3 and 4.

Another set of observations by exciting in the continuum to the red of the overtone band at 740 nm were made as well. Four pressure points at 1, 3, 5, and 7 Torr were studied and the reduced Stern-Volmer plot is shown in Fig. 11. The lower bound for the rate constant obtained by assuming an upper bound of absorption cross section, $1/30 \times 2.4 \times 10^{-24} \text{ cm}^2$, was calculated and is also listed in Table III.

Obvious nonmonotonic behavior of $k_3(E)$ values with wavelength variation are observed, although some of the error bars just overlap. A general trend in the fourth overtone

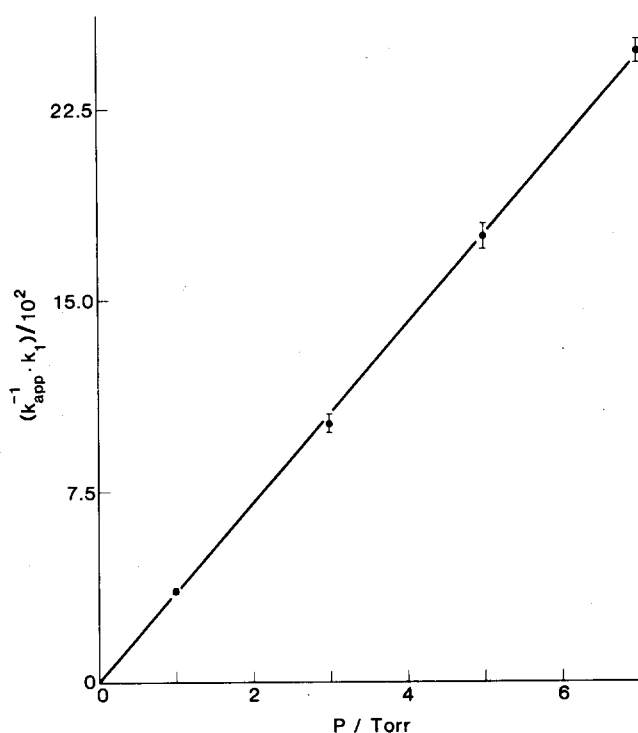


FIG. 11. Reduced Stern-Volmer plot obtained by pumping in the continuum region (740.0 nm) near the 5-0 C-H stretch labeled as VIII in Fig. 4.

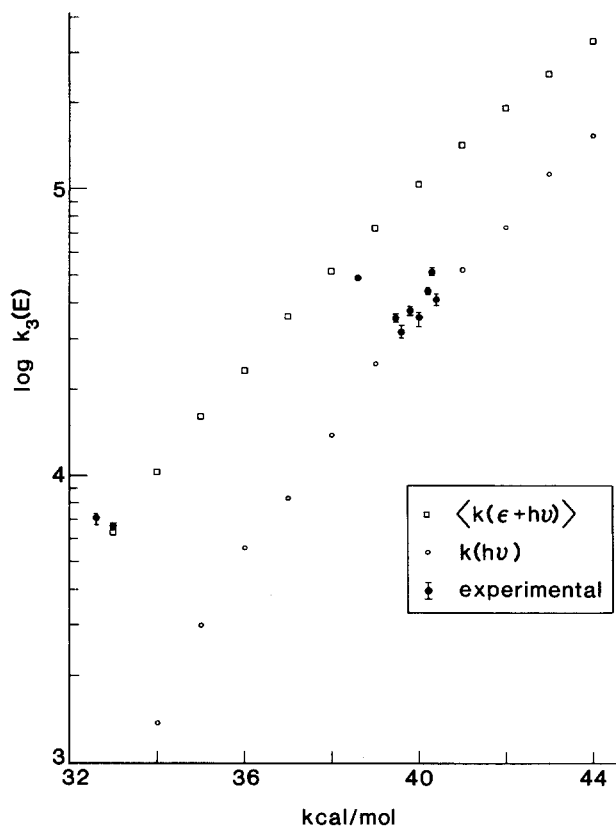


FIG. 12. Unimolecular reaction rate constant for the electrocyclic reaction as a function of energy. The meanings of the symbols are shown in the legend. The closed circle without an error bar at 38.6 kcal/mol is the lower bound of the experimentally measured rate constant obtained using 740.0 nm excitation.

region is that those rates obtained by exciting to the red of a peak are always faster than those *at* the peak.

C. Statistical calculations of the electrocyclization rate

Reaction (1a) was modeled using the Hase-Bunker RRKM program.³¹ We chose the vibrational and rotational parameters suggested by Lewis and Steiner¹⁹ in their study with the exception that the lowest frequency vibration of the reactant was adjusted to 180 cm^{-1} (rather than 320 cm^{-1}). This choice is more consistent with the Raman scattering data²⁵ and causes the calculated rate constants to match well with the experimental ones at 707.0, 714.2, and 720.7 nm. This program was run with the following options: direct counting for the sum of states; the Whitten-Rabinovitch approximation³² for the density of states; the adiabatic rotations and harmonic vibrations throughout. Table III lists the calculated $k_3(E)$ values. Due to the direct counting algorithm for the sum of states, slight nonmonotonic fluctuations occur in the $k_3(E)$ curve. However, the fluctuations around the 4–0 overtone region are less than 5%, and those around the 5–0 region are less than 1%, which are all much smaller than the nonmonotonic changes of the experimentally observed $k_3(E)$ values. To explore the sensitivity of the calculated $k_3(E)$ values to the choice of the transition state, the vibrational and rotational parameters were altered to those suggested by Rose, Seyse, and Crane.³³ It was found that the $k_3(E)$ values were essentially unchanged when the calculation matched

closely the thermal Arrhenius parameters.¹⁹ Changing the threshold energy by 2 to 3 kcal/mol shifts the origin of the $k_3(E)$ curve but leaves the shape of the curve unaffected in the energy region of interest.

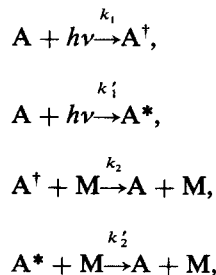
A Boltzmann average⁵ (see Sec. IV) of $k_3(\epsilon + h\nu)$ was also performed, where ϵ is the thermal energy content of the reactant molecule and $h\nu$ is the photon energy supplied by the laser. Rate constants calculated in this manner are close to the observed 4–0 data, but are a factor of 3 larger than for the 5–0 transitions. A plot of $k_3(E)$ vs E is shown in Fig. 12, which compares the experimental data with the RRKM calculation as well as with the Boltzmann averaged $\langle k_3(\epsilon + h\nu) \rangle$ values. It is seen that neither calculation is able to reproduce in full the observed electrocyclization rates.

IV. DISCUSSION

To make a meaningful comparison between the experimental data and the calculated results, a knowledge about the spectral purity and the energy content of the molecules prepared by vibrational overtone pumping is of crucial importance. The energy content, however, depends on the nature of the widths of the overtone transitions, a controversial subject under active research.^{26,34} For small molecules there is a considerable body of evidence for heterogeneous contributions to their overtone transitions. For example, HCN, C_2H_2 , NH_3 , CH_4 studied by Klemperer and co-workers,^{35–38} SiH_4 , SiD_3H studied by Bernheim *et al.*,^{39,40} and CD_3H studied by Zewail and by Quack and co-workers,⁴¹ clearly show the existence of rotational contributions. However for medium to large polyatomic systems, clearcut evidence for heterogeneous broadening effects seems to be absent. In $(\text{CF}_3)_3\text{CH}$,²⁷ homogeneous broadened widths are measurable even in the fundamental absorptions. The general wisdom in the past has favored pure homogeneous broadening in the high overtone region for large molecules. In what follows we first consider the possibility that there is spectral contamination from other electronic states, then the possibility that the widths of overtone transitions are entirely homogeneous, and finally that they have an important heterogeneous component.

A. Spectral purity

As pointed out in the spectroscopy section as well as in all the previous studies, there is an absorption continuum throughout the entire overtone region. Also it has been mentioned that there is a triplet state (T_1) of 1, 3, 5-hexatriene around 660–350 nm. If the continuum observed in the present study arises from the absorption of the triplet state, the following mechanism describes this situation:





The rate equation derived from this mechanism is

$$\frac{d[P]}{dt} = \frac{k_1 k_3 [A] [h\nu]}{k_2 [M] + k_3} + \frac{k_1' k_3' [A] [h\nu]}{k_2' [M] + k_3'} \quad (15)$$

and

$$k_{\text{app}} = \frac{k_1 k_3}{k_2 [M] + k_3} + \frac{k_1' k_3'}{k_2' [M] + k_3'} \quad (16)$$

To a first approximation, k_2 equals k_2' .

At 740.0 nm excitation, the contribution from the continuum predominates, and shows a larger rate constant than excitation of the 5-0 transition. Thus, the excitation into A^* should enhance the reaction. From Fig. 12, such a situation is possible only when the observed rate constants are compared to $k(h\nu)$, instead of $\langle k(\epsilon + h\nu) \rangle$. However, in order to fit the experimental data quantitatively at 740 and 866 nm, k_1' must be 1/30 of $k_1(\lambda = 707 \text{ nm}) = 7.2 \times 10^{-14} \text{ cm}^3/\text{s}$ and greater than or equal to 1/6 of $k_1(\lambda = 866 \text{ nm}) = 6.0 \times 10^{-13} \text{ cm}^3/\text{s}$, respectively, if the reaction rate constant of A^* does not vary or it increases with energy. The decrease in absorption cross section of the continuum with respect to the increase in energy is opposite to what would be expected from having a triplet state at higher energy. Therefore, we reject the hypothesis that the triplet state contributes to electrocyclic product formation by excitation of the 4-0 and 5-0 transitions. This conclusion is in keeping with the concept of exchange integral control of reaction multiplicity in which pericyclic reactions tend to involve singlet states while double bond twisting tends to involve triplet states.⁴²

The origin of the first allowed singlet transition occurs at 252 nm and is also at higher energy than the overtone transitions under study.⁴³ Hence, spectral contamination from electronic transitions is ruled out in the present study. The observed reaction does occur on the ground electronic state potential surface.

B. Pure homogeneous broadening

Under the assumption of a pure homogeneous width, as was made in most previous studies,¹⁻¹⁴ the reactants absorb photons of a given wavelength with equal probability independent of the initial energy content of the molecules. The net effect of the transition is to shift the energy distribution of the whole ensemble by $h\nu$ with a probability determined by the absorption cross section.

The measured rate constant should be the ensemble averaged value of $k_3(\epsilon + h\nu)$,

$$\langle k_3(\epsilon + h\nu) \rangle = \int_0^\infty k_3(\epsilon + h\nu) \rho(\epsilon) e^{-\epsilon/kT} d\epsilon / \int_0^\infty \rho(\epsilon) e^{-\epsilon/kT} d\epsilon, \quad (17)$$

where ϵ is the thermal energy of the reactant molecule, and $\rho(\epsilon)$ is the density of states of the reactant at energy ϵ . To a very crude approximation, $k_3(\langle \epsilon \rangle + h\nu)$ may replace $\langle k_3(\epsilon + h\nu) \rangle$.

Based on pure homogeneous broadening, the reaction

rate constants derived from pumping in the third overtone region should be regarded as "normal" and those from exciting in the fourth overtone region as "too low" (see Fig. 12).

Possible explanations are considered below

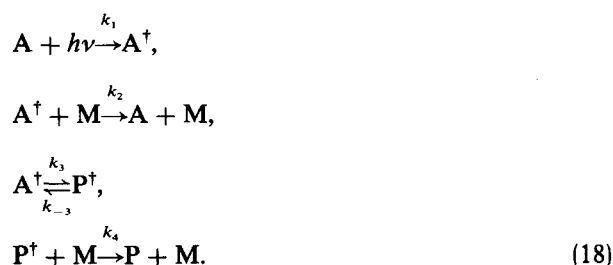
1. Collisional effects

If more than a single collision is needed to deactivate the energized molecule (weak collisions), and each collision removes $\langle \Delta E \rangle$, more collisions are required to quench the reaction when the fourth overtone is excited than the third overtone. The measured rates at higher total energy should be faster than those calculated from $\langle k(\epsilon + h\nu) \rangle$, which is just opposite to observation. Therefore, an explanation based on weak collisions is ruled out.

An increase in collisional deactivation efficiency with increasing energy can explain the gross trend. Experimentally, $k_3(E)$ values are derived from the slope of the reduced Stern-Volmer plot and are equal to $k_2/(\text{slope})$. For a given slope, larger k_2 implies faster $k_3(E)$. In order to increase the observed $k_3(E)$ to fit the calculated $\langle k_3(\epsilon + h\nu) \rangle$ for the 5-0 transitions, however, an increase of k_2 by a factor of 3 must be made, which leads to an unacceptably large value for the hard sphere diameter (11 Å). The nonmonotonic increase in $k_2(E)$ values across an overtone feature is even more difficult to rationalize by collisional effects.

2. Reverse reaction

The following mechanism includes this effect:



The steady-state approximation leads to

$$\frac{d[P]}{dt} = \frac{k_1 k_3 k_4 [A] [h\nu]}{k_2 k_4 [M] + (k_2 k_{-3} + k_4 k_3)}$$

and

$$\begin{aligned}
 \frac{k_1}{k_{\text{app}}} &= \frac{k_2}{k_3} [M] + 1 + \frac{k_2 k_{-3}}{k_4 k_3} \\
 &\simeq \frac{k_2}{k_3} [M] + 1 + \frac{k_{-3}}{k_3}.
 \end{aligned}
 \quad (19)$$

An RRKM calculation was performed to calculate k_{-3} with vibrational frequencies of 1, 3-cyclohexadiene assigned by DiLauro *et al.*⁴⁴ The calculated k_{-3}/k_3 ratios in the energy range of interest are less than 25, which will at most affect the determination of $k_3(E)$ by 5% and hence will not explain the observed discrepancy between the calculated and the experimental results.

The failure to find a suitable explanation for the experimental observation within the context of pure homogeneous broadening forces us to abandon this assumption for the electrocyclic reaction system under study. Very recently, several elegant experiments have cast further doubt on the

assumption of pure homogeneous broadening in the overtone transitions of moderate to large polyatomics, particularly two studies by Crim and co-workers.^{45,46} In one such study, Rizzo, Ticich, and Crim⁴⁵ have measured the relative internal state population of the OH fragment when HOOH is excited by pumping the 5–0 O–H stretching overtone. They find the OH population distribution changes markedly as the photolysis laser is scanned across the overtone feature. In a second experiment, McGinley and Crim⁴⁶ have monitored chemiluminescent emission when a seeded beam of tetramethyldioxetane is crossed by a photolysis laser which excites the 4–0 C–H stretching overtone. The excitation spectra changes its appearance when different pressures of carrier gases are used in the nozzle expansion. These two observations strongly argue that the overtone transitions are not purely homogeneous in these two cases.

C. Inhomogeneous broadening

When there is an inhomogeneous contribution to the width of an overtone transition, the energy content of the excited molecule *cannot* be calculated directly without complete assignment of the final states. However, we can reasonably assume that the ground vibrational state molecules do absorb near the peak of the overtone transitions, and the observed rate constants should be compared to $k_3(h\nu)$ values at those wavelengths. The deviations of the observation from the calculations may then be attributed to two possible effects: (1) the presence of “hot bands” in which thermally populated vibrational levels in the initial states absorb radiation; and (2) rotational effects due to the variation of the unimolecular reaction rate constant on the rotational structure (J, K) of the excited state.

1. Hot band transitions

For hot band transitions, the total active energy of the absorbing molecule equals $\epsilon + h\nu$ where ϵ is the energy of the initial state. Since hot band transitions usually absorb to the red of the cold band transitions, nonmonotonic changes of $k_3(h\nu)$ with respect to photon energy is expected to occur. The total active energy of these molecules reacting faster than the predictions can be determined by interpolating the measured k_3 values using the calculated $k_3(E)$ vs E curves. The initial thermal energy content of those molecules absorbing at 708.3, 710.7, 718.5, and 723.6 nm are around 140–200 cm^{-1} derived from interpolation, which is the range of the lowest frequency vibration of *cis*-1, 3, 5-hexatriene. The ϵ of molecules excited at 740.0 nm (far from the overtone peak) is estimated, however, to be much larger (770 cm^{-1}). Judging from the low oscillator strength, at most 1/30 of that at 707.0 nm, which is of the same order as $\exp(-770 \text{ cm}^{-1}/kT)$, it is not unreasonable to assume that such a hot band may be responsible for the observed deviation of this rate constant. Thus the contribution from hot bands may explain the variation in rate constants with wavelength for the 5–0 overtone region.

2. Rotational Effects

Although the discrepancies between the measured $k_3(E)$'s and the calculated ones at 866.0 and 875.3 nm are too

large to be accounted for by hot band transitions alone, rotational effects may well be very important at these longer wavelengths.

Rotational effects are very subtle and may affect the reaction rates by orders of magnitude close to threshold. A recent study by Troe⁴⁷ on the reactions of formaldehyde (CH_2O) to yield $\text{CHO} + \text{H}$ and $\text{H}_2 + \text{CO}$ demonstrated the importance of such an effect. For the 4–0 transitions where the excess energies above the activation energy are only around 1000 cm^{-1} and the reaction rates are relatively slow, even a small rotational effect may enhance enormously the reaction rate. Recalling that the reaction coordinate of the electrocyclic reaction is a disrotatory motion of the two terminal vinyl groups around the C–C single bonds (see inset in Fig. 1), a strong interaction between this motion and the external rotation of the molecule is very likely. The rotational effect might well be the most important factor causing the one-order-of-magnitude increase in the measured rate constants to those calculated using the RRKM model.

3. Concluding remarks

From the previous discussion, it appears that all experimental observations can be explained, at least qualitatively, with a combination of hot band and rotational effects. The rotational effects are important in the third overtone region where the reaction occurs near the threshold, and hot band transitions appear to explain the measurements in the fourth overtone region in detail. It is not necessary to invoke non-statistical behavior, although our present studies certainly cannot prove of course that such departures are absent. However, the linearity of the reduced Stern–Volmer plots and the long reaction time scale compared to reasonable times for energy randomization give us no justification at present for appealing to such models. We conclude that a deeper understanding of the nature of vibrational overtone transitions is urgently needed for proper interpretation of vibrational overtone photochemistry. We have provided evidence against the pure homogeneous broadening assumption from a point of view based on a study of the unimolecular reaction rates. Complementary studies, such as temperature-dependent spectroscopic measurements in the gas phase, might provide additional information about the nature of the heterogeneous components found in the overtone region. For some particularly simple model systems we might also look forward to a detailed spectroscopic analysis of the transitions comprising what is called a vibrational overtone feature.

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