Radiationless decay of 1,3,5,7octatetraene

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Radiationless decay of 1,3,5,7-octatetraene

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The decay kinetics of the $2\,^1A_g$ state of the linear polyene 1,3,5,7-octatetraene in hydrocarbon solutions have been measured by nanosecond and picosecond techniques from 10 to 320 K. The observed decrease in emission lifetime with increasing temperature is well described in terms of a temperature activated intramolecular radiationless decay process proceeding over a ~4 kcal Arrhenius barrier. This barrier is not significantly affected by intermolecular interactions such as sample viscosity or phase and may be related to rotation about essential single bonds in the excited state.

I. INTRODUCTION

Linear polyenes are of considerable theoretical and experimental[1] interest. They have played a key role in the development of our ideas of the electronic structure of conjugated organic molecules and have reinforced the potential importance of electron correlation in these systems. The characterization of the low-lying singlet excited states of the mid-sized polyenes (4–6 double bonds in conjugation) is sufficiently in hand that it is now reasonable to address questions relating to the coupling between electronic excitation and nuclear motion that leads to the distinctive photochemistry (cis – trans isomerization) of these systems.

The tetraene 1,3,5,7-octatetraene is in many respects the ideal subject for such an inquiry. We have previously reported well-resolved one- and two-photon excitation spectra for this molecule substituted in a polycrystalline n-octane matrix maintained at liquid helium temperatures.[2] These studies clearly established that the lowest energy excited singlet state ($S1$) is $2\,^1A_g$, that the next higher singlet ($S2$) is $1\,^1B_u$, and have provided a good vibrational characterization of both of these states. Of particular importance for the photochemistry of these systems is the observation that, under these conditions, the 0–0 $S1 \rightarrow S0$ transition is strictly one-photon forbidden and two-photon allowed implying that the $S1$ potential surface has a significant minimum that is not displaced with respect to the ground state along *any* odd symmetry coordinate.

Fluorescence spectra of comparable quality can also be obtained[3,2(b)] and all of these spectra can be interpreted consistently in terms of model potential surfaces as will be discussed in a later paper.

We have also reported the cis to trans photoisomerization of this molecule under the same conditions needed to obtain high quality optical spectra, i.e., in n-alkane matrices at temperatures near absolute zero.[3] This suggests that the mechanism of photoisomerization for such polyenes differs from that of mono-olefins such as ethylene or stilbene.[4]

Since this kind of photochemistry is of great intrinsic interest and is involved in the functioning of such biological complexes as the visual pigments, further study seems warranted. In this paper we report measurements of the temperature dependence of the fluorescence kinetics of the all-*trans* isomer of 1,3,5,7-octatetraene in three solvents. These data clearly show a temperature activated decay channel in the excited $2\,^1A_g$ state proceeding over a ~4 kcal Arrhenius barrier. This process reflects an intrinsic property of the octatetraene molecule which is independent of external factors such as solvent viscosity.

II. EXPERIMENTAL

A. Sample preparation and characterization

All-*trans* 1,3,5,7-octatetraene was prepared and purified as described previously.[5,6] All of the nanosecond experiments utilized HPLC pure isomers.

N-octane and n-hexane (Chemical Samples Co.) and cyclohexane (Mallinckrodt Spectral Grade) were purified by passing them through silver nitrate activated alumina and, when examined in blank runs, exhibited no detectable emission under the conditions of our experiments. Verification of the identity of the emitting species in n-octane and cyclohexane was effected by exchanging the solvent for n-hexane via repeated dilution and evaporation cycles then comparing the high resolution fluorescence spectra to those of the HPLC purified authentic materials previously reported.[3] Representative fluorescence spectra for the $S0 \leftarrow S1$ origin region at 4.2 K of all-*trans* octatetraene in n-octane and in n-hexane are shown in Fig. 1. Reversing this solvent exchange procedure established that the sample composition was not changed by these manipulations. Sample concentrations were approximately 10^{-3} M.

B. Picosecond kinetics

The picosecond system is based on a Nd/YAG laser emitting 20 ps FWHM pulses at 1064 nm. A single pulse is amplified and quadrupled using KDP crystals to give pulses at the excitation wavelength of 266 nm. This overlaps to the fourth vibronic feature of the $1\,^1B_u$ (approximately 4800 cm^{-1} above the vibrationless level of

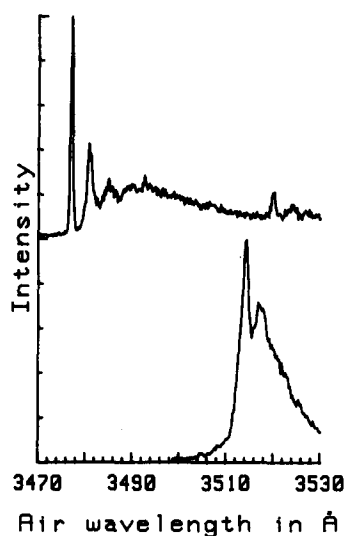[a] Present address: University of Tel Aviv, Ramat Aviv, Tel Aviv, Israel.

FIG. 1.   Fluorescence of octatetraene in *n*-octane and *n*-hexane at 4.2 K.   The lower curve shows the false origin of the all-*trans* isomer in *n*-octane.   The upper curve shows the origin for the all-*trans* isomer in *n*-hexane.

*S*2) of all-*trans* octatetraene.

Detection utilized a Hadland Photonics Imacon 675 Photochrom II streak camera coupled to a Princeton Applied Research vidicon/OMA, and Data General Nova minicomputer.   This apparatus has been described in detail by Barbara, Brus, and Rentzepis.[7]   Octatetraene emission was focused onto the streak camera slits through one or more Schott WG5 UV cutoff filters.   Except for these filters which blocked scattered laser light, the emission (from 350 to 500 nm) was detected broadband.   No change in the emission kinetics could be seen when the detection system included vignetting filters exhibiting 10 nm bandpasses in the region 320 to 500 nm.

To test for saturation, the power of each laser pulse was measured and compared to the peak intensities of the curves of fluorescence versus time.   The intensities were linear with laser power within experimental error.   When the power was increased to the point where the response was nonlinear, picosecond transients were observed but these features are clearly unrelated to the linear photodynamics of the octatetraene molecule.

The isomeric content of the samples used was checked before and after the kinetic measurements by measuring the liquid helium temperature emission spectra.   These compositions were constant to within the experimentally detectable limits of approximately 3%.

C.   Nanosecond kinetics

The excitation source for the nanosecond data was a nitrogen laser (Molectron UV24) pumped dye laser (Molectron DL400 with rhodamine *B*).   The 6 ns FWHM pulses were frequency doubled to 305 nm in KDP to provide excitation at the 0–0 of the $1\,^1B_u$.   No dependence of the fluorescence decay kinetics on excitation wavelength was observed.   The sample was installed in a closed cycle Helium refrigerator (Cryogenics Technologies Inc.) modified to permit an atmosphere of either hydrogen or helium over the sample thus insuring good thermal contact.   The emission was collected by *f*/12
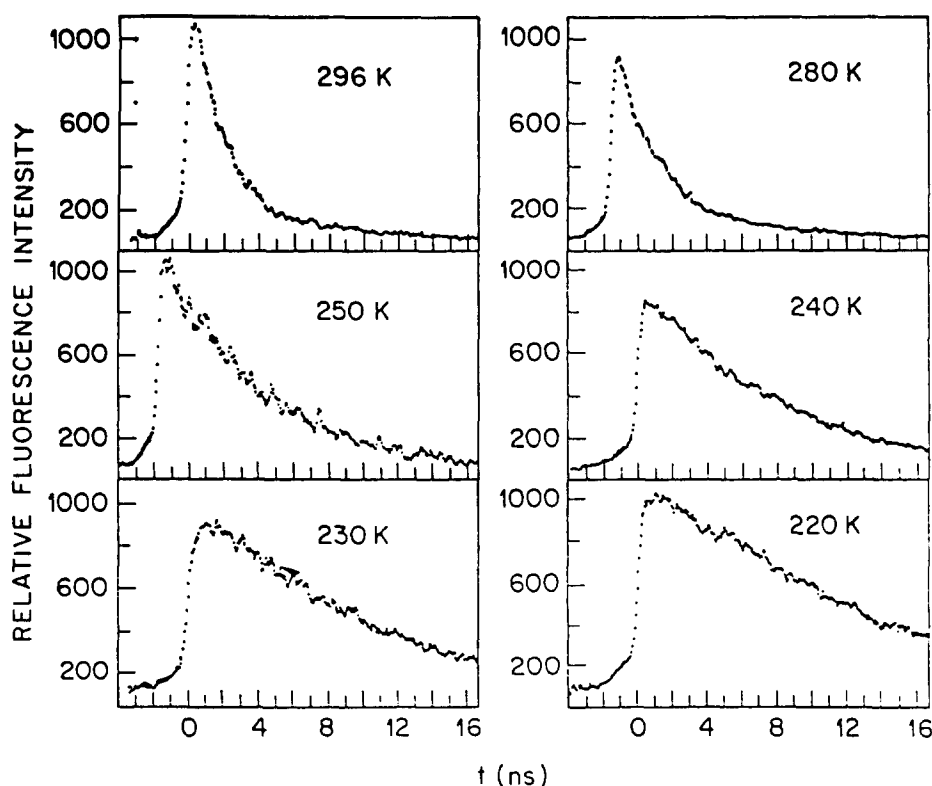

FIG. 2.   Emission intensity as a function of time for all-*trans* octatetraene in *n*-octane at various temperatures as determined on the picosecond apparatus.

TABLE I. Observed emission lifetimes of all *trans*-octatetraene in *n*-octane. Measurements were made with the nanosecond apparatus except where indicated. All temperatures are + or − 1 K.

T (K)	τ (ns)	T (K)	τ (ns)	T (K)	τ (ns)	τ(ns) by picosecond measurements
10	225.8(2.1)	109	147.9(1.3)	220		24.0(2.4)
18	223.5(2.2)	119	141.6(1.2)	223	30.2(0.4)	
28	223.8(2.3)	129	137.3(1.1)	230	24.6(0.4)	19.0(1.9)
38	216.7(2.4)	139	132.5(1.0)	240	18.1(0.3)	15.0(1.5)
43	209.3(2.4)	149	128.6(0.9)	250	13.5(0.3)	12.0(1.2)
48	203.3(2.2)	159	125.3(0.8)	260		10.2(1.0)
53	200.0(2.0)	169	121.4(0.8)	270		8.8(0.9)
58	190.5(2.1)	179	116.5(0.8)	280		6.2(0.6)
68	182.3(2.0)	189	110.6(0.7)	290		5.0(0.5)
78	173.5(1.9)	199	110.7(0.7)	296		4.4(0.5)
89	163.4(1.6)	209	97.2(0.6)			
99	155.1(1.4)	217	35.9(0.5)			

optics into a Jobin–Yvon HR1500 monochromator set for a bandpass of no more than 2.6 Å. The wavelength selected emission was detected by an Amperex XP-1002 photomultiplier and processed by a Tektronix 7912AD programmable digitizer. Data collection and analysis utilized a Hewlett–Packard 9835A computer. Each decay curve was deconvolved over the instrument response as determined by measuring the time profile of the scattered laser light. As in the picosecond measurements, high resolution fluorescence was used to check for sample photolysis.

III. RESULTS

A. Picosecond kinetics

Representative records of fluorescence intensity as a function of time on the picosecond scale for all-*trans* 1, 3, 5, 7-octatetraene in *n*-octane are shown in Fig. 2. At all temperatures studied (220 to 296 K) the fluorescence risetime could not be resolved, i.e., the fluorescence appeared in a time less than the 10 ps resolution of the instrument. A recent report on the picosecond resolved, wavelength dispersed fluorescence kinetics of diphenyloctatetraene by Felder, Choi, and Topp[8] indicates that, even in a system where $1\,^1B_u$ fluorescence can be observed, the $2\,^1A_g$ fluorescence risetime is pulse limited.

At room temperature the decay is well described by a single exponential of lifetime 4.4 ns, in agreement with the value reported by Gavin, Weisman, McVey, and Rice.[9] As can be clearly seen in Fig. 2, the emission lifetime increases with decreasing temperature. Below 217 K, the melting point of *n*-octane, the lifetime is too long to be reliably determined with the picosecond apparatus. From 220 to 296 K the temperature dependence of the fluorescence lifetime is reasonably fit by an Arrhenius expression as discussed below. The lifetimes as determined on the picosecond apparatus are summarized in Table I.

B. Nanosecond kinetics

Given the lack of any resolvable picosecond phenomena, we extended the measurements to lower tempera-

tures and other solvents using the simpler nanosecond techniques. The kinetics of the wavelengh resolved emission of all-*trans* octatetraene in *n*-hexane, cyclohexane, and *n*-octane were measured with the nanosecond apparatus described above. Emission for the *n*-alkane solutions was monitored at the fluorescence origins: 3478 Å for all-*trans* octatetraene in *n*-hexane and 3514 Å for all-*trans* octatetraene in *n*-octane. The sample containing all-*trans* octatetraene in cyclohexane was monitored at 3650 Å (the first prominent vibronic feature).

A typical record of emission intensity versus time together with that computed from a least-squares fit of the function

$$I = I_0 \exp(-t/\tau) \int_0^t L(t') \exp(t'/\tau)\, dt' \tag{1}$$

to the data is shown in Fig. 3. $L(t)$ is the laser pulse profile measured in a separate experiment. For some of the longer decays the tail of the decay was fit by

TABLE II. Observed emission lifetimes for all *trans*-octatetraene in *n*-hexane. All temperatures are + or − 1 K.

T (K)	τ (in ns)	T (K)	τ (in ns)
10	123.3 (2.2)	149	94.5 (2.0)
17	121.5 (2.2)	159	91.8 (1.8)
18	121.7 (2.2)	169	90.2 (1.7)
28	117.3 (2.3)	179	90.5 (1.5)
38	110.8 (2.4)	189	71.0 (1.2)
48	110.2 (2.4)	199	58.3 (1.0)
58	106.3 (2.5)	209	42.4 (0.8)
68	104.6 (2.5)	219	31.1 (0.6)
73	104.6 (2.5)	230	22.6 (0.5)
78	107.8 (2.5)	240	17.3 (0.4)
89	106.2 (2.5)	250	12.1 (0.2)
99	105.7 (2.5)	260	9.1 (0.2)
109	102.4 (2.4)	270	6.6 (0.1)
119	97.8 (2.0)	280	5.3 (0.1)
129	96.7 (2.0)	290	4.3 (0.1)
139	96.7 (2.0)		

TABLE III. Observed emission lifetimes of all *trans*-octatetraene in cyclohexane. All temperatures are + or −1 K.

T (K)	τ (in ns)	T (K)	τ (in ns)
10	126.2 (1.7)	169	92.3 (0.3)
18	127.0 (1.5)	179	86.3 (0.3)
28	126.1 (1.8)	189	75.0 (0.3)
38	124.6 (1.8)	199	64.9 (0.3)
48	121.9 (1.3)	209	53.8 (0.3)
58	123.7 (1.2)	219	39.5 (0.3)
68	124.4 (1.0)	230	31.3 (0.2)
78	122.1 (1.0)	240	24.4 (0.2)
89	116.8 (0.9)	250	18.0 (0.2)
99	113.1 (0.8)	260	12.5 (0.2)
109	109.3 (0.7)	270	9.6 (0.2)
119	107.7 (0.7)	280	6.1 (0.1)
129	104.5 (0.6)	290	3.8 (0.1)
139	101.7 (0.4)	300	3.1 (0.1)
149	97.6 (0.3)	310	2.8 (0.1)
159	95.3 (0.3)	320	2.5 (0.1)

$$I = I_0 \exp(-t/\tau) . \qquad (2)$$

All of the lifetime versus temperature data are summarized in Figs. 4–7 and tabulated in Tables I–III.

IV. DISCUSSION

The lifetime versus temperature behavior of each of these samples exhibit qualitatively similar features. In the low temperature region ($T \sim 40$ K) each sample reaches a limiting temperature independent lifetime: 122 ns for all-*trans* octatetraene in n-hexane, 126 ns for all-*trans* octatetraene in cyclohexane, and 225 ns for all-*trans* octatetraene in n-octane. The lifetime of the all-*trans* isomer decreases monotonically with increasing temperature for all systems studied. The decrease in lifetime with increasing temperature is especially pronounced in the region 200 to 250 K. In all three solvents the lifetime decreases from 35+/−5

ns at ~ 220 K to 4.0+/−0.5 ns at ~ 300 K. In this temperature regime n-hexane is a liquid, cyclohexane is a solid, and n-octane goes from a liquid to a solid (melting point = 217 K). Thus, whatever the nature of the temperature dependent radiationless process is, it clearly represents intramolecular phenomena intrinsic to the octratetraene $2\,^1A_g$ excited state.

A more detailed analysis further characterizes these processes.

A. All-*trans* octatetraene in *n*-hexane and cyclohexane

From 10 to 290 K the behavior of the fluorescence lifetime of all-*trans* octatetraene in these solvents is similar (Figs. 4 and 5). In cyclohexane, the lifetime decreases from 126 ns at 10 K to 90 ns at 179 K and then decreases rapidly to 2.5 ns at 320 K describing a sigmoidal curve with an inflection at ~ 200 K. In n-hexane the behavior of the lifetime is similar, decreasing from 122 ns at 10 K to 90 ns at 179 K then dropping rapidly to 4.3 ns at 290 K, again following a sigmoidal curve with an inflection at ~ 200 K. The lifetimes of all-*trans* octatetraene in n-hexane agree well with those reported by Gavin, Weisman, McVey, and Rice.[9] They reported lifetimes of 4.4 ns at 295 K and 111 ns at 77 K. We measure 4.3 ns at 290 K and 107.8 ns at 78 K.

In both solvents the temperature dependence of the fluorescence lifetime in the region 150 to 300 K are well fit by

$$\tau = 1/[\, A \exp(- E/RT) + 1/\tau_0 \,] , \qquad (3)$$

i. e., the sum of an Arrhenius and a temperature independent spontaneous emission process.

To obtain quantitative agreement with the data over the entire temperature range a second temperature dependent process has to be invoked in order to account for the small inflection at ~ 50 K. All of the data are well fit by

All trans octatetraene in n-octane
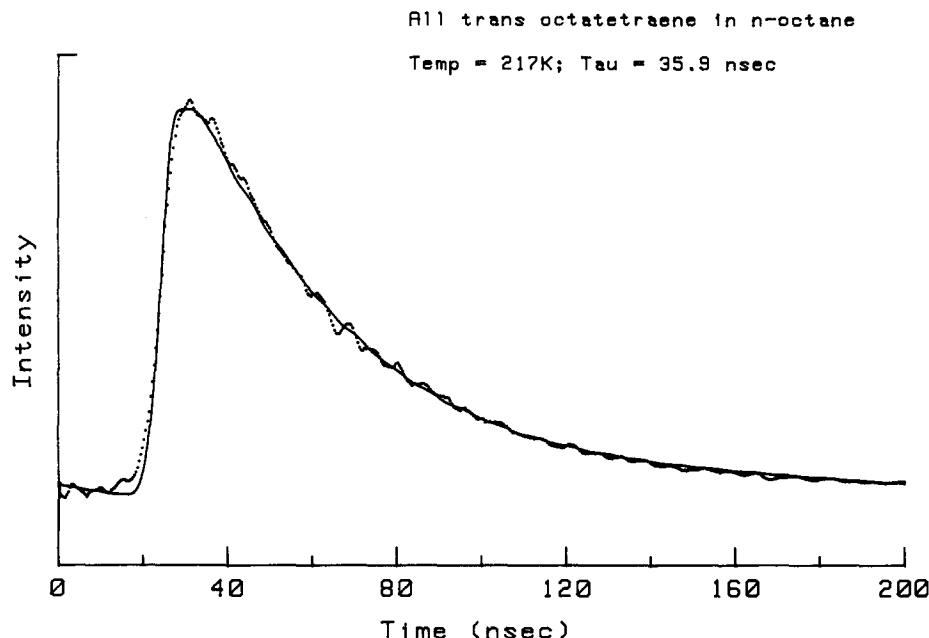
Temp = 217K; Tau = 35.9 nsec

FIG. 3. Emission intensity as a function of time for all-*trans* octatetraene in n-octane at 217 K as determined on the nanosecond apparatus. The points are the experimental data, and the solid wave is the function $I = I_0 e^{-t/\tau} \int_0^t L(t') e^{t'/\tau} dt'$, where $L(t')$ is the time profile of the laser as determined in a separate experiment. The parameters I_0 and τ were adjusted by nonlinear least-squares techniques to obtain a best fit to the data.

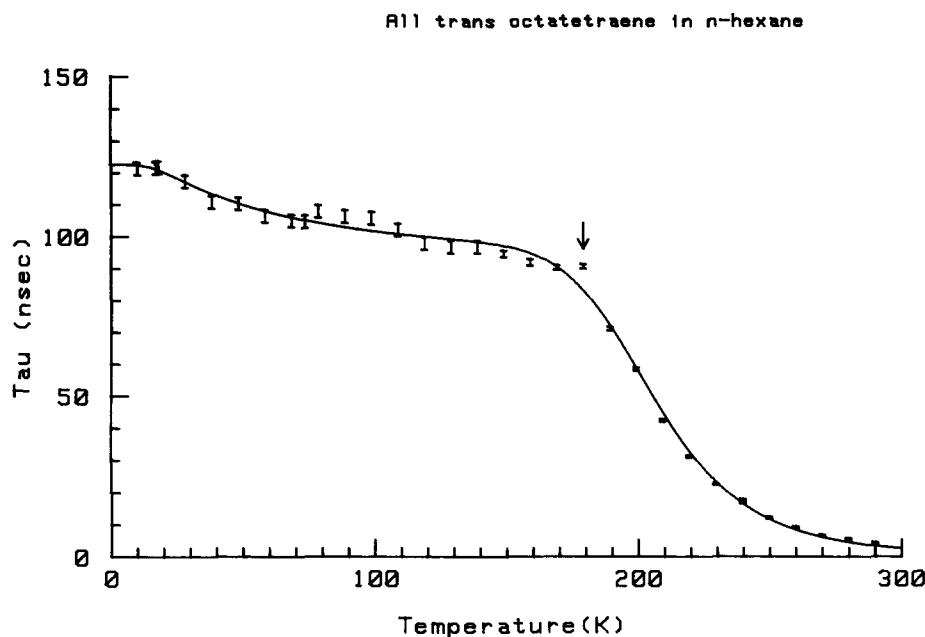All trans octatetraene in n-hexane

FIG. 4. Fluorescence lifetime of all-*trans* octatetraene in *n*-hexane as a function of temperature. The points are the lifetimes as determined by least-squares fitting exponentials to the observed decay curves as described in the text. The solid line is the best fit of these lifetimes by the function $\tau = [A_1 \exp(-E_1/RT) + A_2 \exp(-E_2/RT) + (1/\tau_0)]^{-1}$. The values of the frequency factors A_1 and A_2, activation energies E_1 and E_2, and τ_0 are summarized in Table IV. The arrow indicates the sample melting point.

$$\tau = 1/[A_1 \exp(-E_1/RT) + A_2 \exp(-E_2/RT) + 1/\tau_0] \ . \qquad (4)$$

This latter process can be connected to the disappearance of octatetraene photoproducts. The Arrhenius parameters and their standard deviations are summarized in Table IV.

We emphasize that solvent viscosity has no significant bearing on the observed lifetime. *n*-hexane melts at 178 K. Above and below the melting point the lifetime is approximately 90 ns and shows no discontinuity. Cyclohexane melts at 280 K but the lifetime only changes from 6.1 at 279 K to 3.8 ns at 290 K. This forces us to seek an explanation in terms of processes intrinsic to octatetraene and rules out models for the radiationless deactivation in which the solvent plays an important role.

B. All-*trans* octatetraene in *n*-octane

Because of the center of symmetry present in the site in *n*-octane, all-*trans* octatetraene exhibits longer lifetimes in this solvent than in *n*-hexane or cyclohexane throughout the low temperature region. At temperatures less than 40 K the lifetime is constant at 225 ns which agrees with the estimated radiative lifetime of 220 ns derived by Gavin, Weisman, McVey, and Rice[9] from lifetime and quantum yield measurements in *n*-hexane. The twofold increase in low temperature lifetime in *n*-octane over that observed in *n*-hexane or cyclohexane is reasonably attributed to increased dipole strength induced in the symmetry forbidden transition by the loss of the inversion center for octatetraene in *n*-hexane and cyclohexane. As the temperature is increased
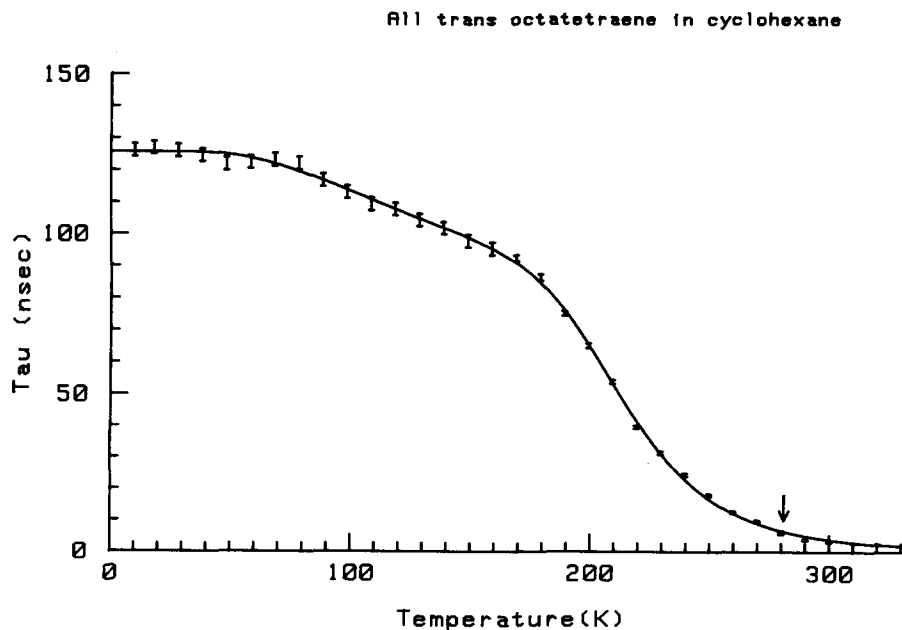
All trans octatetraene in cyclohexane

FIG. 5. Fluorescence lifetime of all-*trans* octatetraene in cyclohexane as a function of temperature. The points are the lifetimes as determined by least-square fitting exponentials to the observed decay curves as described in the text. The solid line is the best fit of these lifetimes by the function $\tau = [A_1 \exp(-E_1/RT) + A_2 \exp(-E_2/RT) + (1/\tau_0)]^{-1}$. The values of the frequency factors A_1 and A_2, activation energies E_1 and E_2, and τ_0 are summarized in Table IV. The arrow indicates the sample melting point.
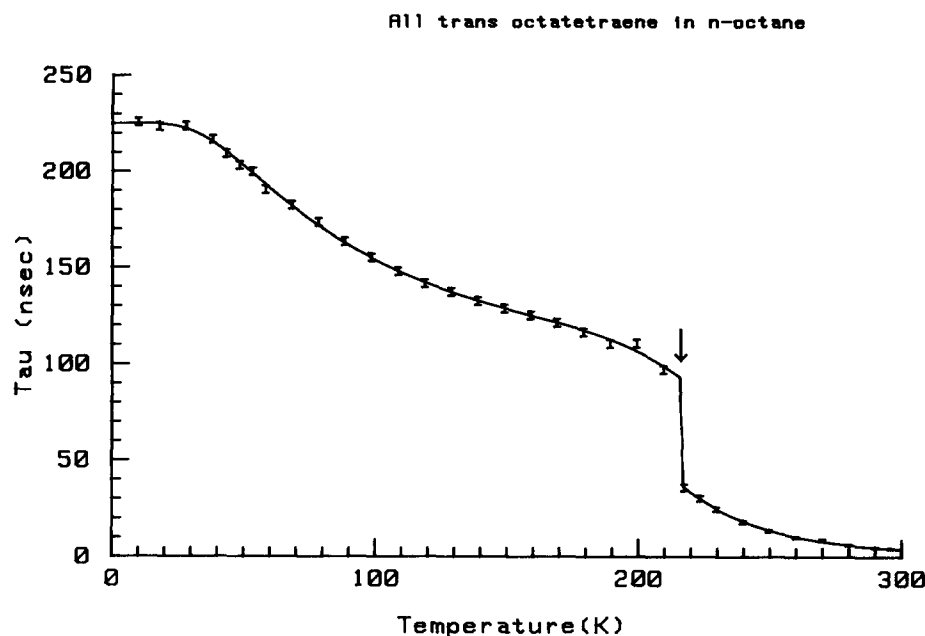
All trans octatetraene in n-octane

FIG. 6. Fluorescence lifetime of all-*trans* octatetraene in n-octane as a function of temperature. The points are the lifetimes as determined by least-squares fitting exponentials to the observed decay curves as described in the text. The solid line is the best fit of these lifetimes by the function $\tau = [A_1 \exp(-E_1/RT) + A_2 \exp(-E_2/RT) + (1/\tau_0)]^{-1}$. One of two additional parameters is added to the fit: either E_s, which is added to activation energy E_1 in the solid phase, or A_{lq}, which is added to frequency factor A_1 in the liquid phase. The values of the frequency factors A_1, A_{lq}, and A_2, activation energies E_1, E_2, and E_s and τ_0 are summarized in Table IV. The arrow indicates the sample melting point.

from 40 to 210 K the emission lifetime decreases from 225 to 97 ns. As in the previously discussed cases, the inflection at ~50 K is quantitatively accounted for on the basis of the sum of an Arrhenius and a temperature independent decay process.

The behavior in the vicinity of 217 K is complicated by the coincidental melting of the n-octane host. Because of this, the model employed for the n-hexane and cyclohexane data does not give exact quantitative agreement, although the qualitative features of the data are well modeled. If a small step in the octatetraene lifetime at the n-octane melting point is introduced, quantative agreement is recovered. This agreement at the sample melting point may be obtained by allowing for a discontinuity in either an activation energy or a frequency factor in Eq. (4). From Fig. 1 and Ref. 3 it is clear that the emission of the all-*trans* isomer in n-octane at 4.2 K shows less intensity in the zero phonon line relative to the phonon sideband than is seen for either the all-*trans* or mono-*cis* isomer in n-hexane. This increased lattice interaction could in part account for an evidence of slightly stronger dependence of the octatetraene life-time on melting in n-octane.

A summary of the analysis of the all-*trans* octatetraene in n-octane data is included in Table IV.

V. SUMMARY

These data establish that the $1\,^1A_g - 2\,^1A_g$ radiationless transition rate in *trans*-octatetraene is largely governed by intramolecular potentials. The dominant process proceeds over a barrier ~4 kcal high in the excited state and is almost independent of solvent. This behavior is in strong contrast to systems where fluorescence and photoisomerization rates are strongly affected by intermolecular interactions as reported for mono-olefins such as the stilbenes[10] and tetraphenyl ethylene.[11] The exact nature of the relaxation process in the polyenes cannot be established until further spectroscopic and kinetic studies on isotopically labeled materials are completed. However, given the corre-

TABLE IV. Summary of Arrhenius parameters obtained when the octatetraene lifetime vs temperature data is fit by nonlinear least-squares techniques to the equation $\tau = [A_1 \exp(-E_1/RT) + A_2 \exp(-E_2/RT) + (1/\tau_0)]^{-1}$. The data for all *trans*-octatetraene in n-octane is fit using one of two additional parameters: E_S which is added to activation energy E_1 in the solid phase ($T < 217$ K), or A_{lq} which is added to frequency factor A_1 in the liquid phase ($T > 217$ K). Parameter standard deviations are indicated in parentheses.

System	A_1 (s^{-1})	A_{lq}	$E_1 \left(\dfrac{\text{kcal}}{\text{mol}}\right)$	A_2 (s^{-1})	$E_2 \left(\dfrac{\text{kcal}}{\text{mol}}\right)$	$E_s \left(\dfrac{\text{kcal}}{\text{mol}}\right)$	τ_0 (ns)
All *trans*-octatetraene in n-octane	$2.09\ (0.93) \times 10^{11}$	$\cdots$	$3.99\ (0.20)$	$8.74\ (0.20) \times 10^6$	$0.285\ (0.006)$	$0.96\ (0.05)$	$225\ (1)$
	$2.2\ (1.1) \times 10^{10}$	$2.04\ (0.92) \times 10^{11}$	$4.02\ (0.21)$	$8.59\ (0.21) \times 10^6$	$0.282\ (0.006)$	$\cdots$	$225\ (1)$
All *trans*-octatetraene in n-hexane	$1.10\ (0.42) \times 10^{12}$	$\cdots$	$4.72\ (0.17)$	$3.01\ (0.25) \times 10^6$	$0.114\ (0.019)$	$\cdots$	$123\ (1)$
All *trans*-octatetraene in cyclohexane	$8.5\ (2.2) \times 10^{11}$	$\cdots$	$4.82\ (0.13)$	$1.30\ (0.17) \times 10^7$	$0.535\ (0.037)$	$\cdots$	$126\ (1)$

spondence of the measured barrier to that usually cited for single-bond rotations,[12] it is not unreasonable to speculate that this is the type of motion associated with the radiationless deactivation of the excited ^1A_g state.

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