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Photochemical hole burning for 1,3,5,7-octatetraene in *n*-hexane

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It is now well established that the unsubstituted linear polyene 1,3,5,7-octatetraene efficiently undergoes *cis*–*trans* photoisomerization even when substituted in an *n*-alkane matrix cooled to liquid-helium temperatures. The fact that this photochemical reaction takes place under these conditions opens the possibility of using the techniques of photochemical hole burning to uncover details of the microscopic mechanism of this isomerization. In this paper we report the demonstration of photochemical hole burning for all-*trans*-octatetraene in *n*-hexane, show that the hole width for the zero-phonon component of the 0–0 band in the limit of zero temperature and zero hole depth is within experimental error equal to the value predicted from the measured fluorescence lifetime, analyze the dependence of hole width on temperature, and show that the relative quantum yield for hole burning increases by approximately a factor of 35 as vibrational energy in the excited state is increased beyond a threshold of approximately 950 cm^{-1} . This threshold agrees well with the previously determined barrier to *trans*, *cis* isomerization.

I. INTRODUCTION

Our understanding of the fundamental features of singlet state electronic structure for the linear polyene 1,3,5,7-octatetraene is quite complete. In particular, the lowest energy excited state is not that derived from the ground state by the promotion of a single electron from the highest energy occupied molecular orbital (HOMO) to the lowest energy unoccupied molecular orbital (LUMO) but, rather, is the 2^1A_g state whose dominant configuration differs from the ground-state configuration by a double excitation from the HOMO to the LUMO.^{1,2} A similar state ordering is found for all linear polyenes for which the order of excited singlet states has been unambiguously established ($\text{C}_{2N}\text{H}_{2N+2}$, $2 < N < 10$).^{2–5} What is special about octatetraene is the quantity and quality of the available experimental data and, especially, the fact that photoisomerization has been clearly demonstrated to occur under exactly the same conditions as those that give fully vibrationally resolved optical spectra.

Fluorescence and one- and two-photon fluorescence excitation spectra at liquid-helium temperatures have been measured for all three double-bond isomers of octatetraene in a number of *n*-alkane hosts.^{2,6–8} In any given host the low-temperature spectrum of each isomer is distinct and easily distinguished from the spectra of the other two. It is primarily the fact that under the conditions of our experiments the different isomers are spectroscopically unique that has allowed us to integrate spectroscopic, dynamic, and photochemical measurements into a rather detailed microscopic picture for the photoisomerization of octatetraene in low-temperature *n*-alkane hosts.⁹ Since the detailed arguments are given in Ref. 9, here we just summarize the two elements of this picture that are most important for this paper.

(1) Isomerization takes place primarily on the 2^1A_g excited state surface either (a) as a direct process in competition with vibrational relaxation for excitation high in the

2^1A_g manifold or (b) as a thermally activated process in competition with radiative decay if the lattice temperature is higher than 55 K.

(2) Setting the zero of energy for the 2^1A_g potential-energy surface at the zero-point level of the all-*trans* isomer, the zero-point levels of the *cis*, *trans* and *cis*, *cis* isomers are at approximately 480 and 690 cm^{-1} , respectively. The barrier (in the Arrhenius sense) to the interconversion of any two isomers is 870 cm^{-1} above the zero-point level of the all-*trans* isomer.

Although very narrow with respect to typical vibrational intervals, the 1–4 cm^{-1} HWHM width of the zero-phonon component of the 0–0 band of any of the isomers of octatetraene in a 4.2 K *n*-alkane host is 4 orders of magnitude broader than the lifetime limit (100 ns corresponding to approximately 10^{-4} cm^{-1}).¹⁰ The presence of this residual inhomogeneous broadening in a system that is both spectroscopically well characterized and photochemically active invites the application of photochemical hole burning techniques^{11,12} to the further determination of the mechanism of *cis* to *trans* photoisomerization.

The experiments reported here sketch the phenomenology of photochemical hole burning in the system all-*trans*-1,3,5,7-octatetraene in *n*-hexane. There are two reasons for choosing *n*-hexane as the host. First, it was for this host that we first demonstrated the direct photochemical conversion of the *trans*–*trans* isomer to the *cis*, *trans* isomer at liquid-helium temperatures.¹³ Thus, the nature of the photochemistry is well defined. Second, in this host even the *trans*, *trans* isomer is not rigorously centrosymmetric.¹⁴ Of course, the ability to see the zero-phonon component of the 1^1A_g to 2^1A_g 0–0 band in one-photon excitation greatly simplifies the experimental protocol. There is good evidence that the only result of the small matrix induced perturbations is a relaxation of symmetry selection rules and that these perturbations do not significantly alter the potentials that determine the vibrational development of the optical spectra and the photochemistry.

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^{b)} DFG postdoctoral fellow.

The experiments reported here used one-photon fluorescence excitation techniques to measure the profiles of photochemical holes burned into the zero-phonon component of the 1^1A_g to 2^1A_g 0-0 band and to determine the dependence of these hole profiles on hole depth and temperature. Additionally, we have measured the photochemical hole profiles for irradiating higher lying vibronic bands and have determined the dependence of the efficiency of hole burning on the vibronic level.

II. THE EXPERIMENTS

The all-*trans*-octatetraene was synthesized using the previously published procedure of Spangler and Little.¹⁵ The material was stored as a dilute (approximately 10^{-2} molar) solution in *n*-pentane in a -10°C freezer. All sample preparation operations were carried out under dim room lights. Just prior to each experiment an aliquot was removed from the stock solution, concentrated by evaporation, and purified by passage through a short alumina column (Woelm activity I—97% *n*-hexane 3% diethyl ether solvent). Purity was then checked by room temperature absorption, 77 K fluorescence and 77 K fluorescence excitation spectroscopy. Isomers were then separated by HPLC using an alumina column (Brownlee Labs, Alox-T) and a mixture of 97% by volume UV grade hexane and 3% by volume unpreserved diethyl ether (both from Burdick and Jackson). The final check on isomeric purity was the measurement of the 4.2 K fluorescence excitation spectrum. The final sample consisted of approximately 0.2 ml of a 0.3 to 0.6 millimolar solution of isomerically pure all-*trans*-octatetraene in UV grade *n*-hexane contained in a quartz cell approximately 2 mm thick \times 10 mm \times 10 mm. Samples were used immediately after preparation.

The sample solution was cooled quickly from room temperature to 4.2 K by lowering the sample cell into the cryostat within 2 minutes. The exciting laser beam made an angle of 90° with the axis of the detection system. The sample was positioned such that this angle was bisected by the axis perpendicular to the flat face of the sample cell.

All line profiles were measured by monitoring fluorescence intensity as a function of excitation wavelength. Excitation at the $1^1A_g - 2^1A_g$ origin (348 nm) and higher lying vibronic bands of octatetraene utilized a single frequency ring dye laser system (Coherent Model 699/29) with LD688 (exciton) in a mixture of ethylene glycol and glycerol as the dye solution. An intracavity frequency doubler (Coherent Model 7500) provided tunable single frequency output in the near ultraviolet at powers of a few mW.

Fluorescence was collected at $f/3.5$, filtered through a Jarrell Ash 0.25 m monochromator tuned to 390 nm (band-pass 20 nm), and detected by a cooled photomultiplier (Amperex 6256B). A second photomultiplier monitored the laser intensity. Photocurrents from both the signal and reference photomultipliers were measured by two electrometers (Kiethley 610C). The digitized analog outputs of these electrometers together with the laser wavelength as measured by the built-in wave meter made up the data points in the spectra which were stored on discs. Further analysis utilized a microcomputer (Hewlett-Packard 310).

All holes were burned with the unfocused laser beam at an intensity of $10\text{--}30\text{ mW cm}^{-2}$. The burn times used were seconds for the zero-phonon component of the 0-0 band at 1.4 K, minutes for the zero-phonon component of the 0-0 band at 4.2 K and hours for the vibronic bands. To determine the line profile, the laser intensity was lowered by a factor of 10 and the profile was scanned in a total time of approximately 20% of the burn time. The only situation where we were unable to realize a scan time that was significantly shorter than the burn time was when we burned holes in the zero-phonon component of the 0-0 band at 1.4 K in which case burn times were limited to a few seconds. Even in this case, by making a number of consecutive scans we established that the line profile was not being detectably modified by the scanning process.

Two different methods were used to quantify the hole profile. For holes burned into the zero-phonon component of the 0-0 band, the hole and its immediate neighborhood [a frequency range 6 times the apparent hole full width at half maximum (FWHM) centered at the burn frequency] were fit by a negative amplitude Lorentzian plus a sloping baseline by least-squares adjustment of the slope and intercept of the baseline at the center of the Lorentzian, and the center, width, and amplitude of the Lorentzian. If a Gaussian profile were used instead of the Lorentzian, the standard deviation of fit was significantly increased and the deviations between calculated and measured points became distinctly nonrandom.

For burning in the higher lying vibrational levels, it was no longer reasonable to work in the approximation that the width of the homogeneous profile was small with respect to the width of the excitation energy distribution. Accordingly, excitation profiles were fitted by the convolution that gives the photochemically modified absorption spectrum $A(\omega)$ for different burn times τ in the limit that the laser bandwidth is negligible with respect to the widths of the transition energy distribution $D(\omega)$ (assumed to be Gaussian) and the homogeneous line profile $H(\omega)$ (assumed to be Lorentzian):

$$A(\omega) = A_0 \int_{-\infty}^{\infty} D(\omega') e^{-H(\omega' - \omega_B)\alpha\tau} H(\omega' - \omega) d\omega'. \quad (1)$$

The scaling constants A_0 and α are absorption intensity times fluorescence quantum yield and absorption intensity times photochemical quantum yield, respectively. The frequency at which the hole was burned is ω_B . For a given vibronic transition, the profiles at all burn times were simultaneously fitted by Eq. (1) with the constraint that the parameters for the transition energy distribution and the homogeneous width be the same for all burn times.

III. THE RESULTS

A. Zero-phonon band

Figure 1 shows that photochemical holes can be burned into the zero phonon band of the all-*trans*-1,3,5,7-octatetraene 1^1A_g to 2^1A_g origin and indicates the increase in spectroscopic resolution that this phenomenon affords. The left panel shows the fluorescence excitation origin as measured with N_2 laser pumped dye laser (Instrumental resolu-

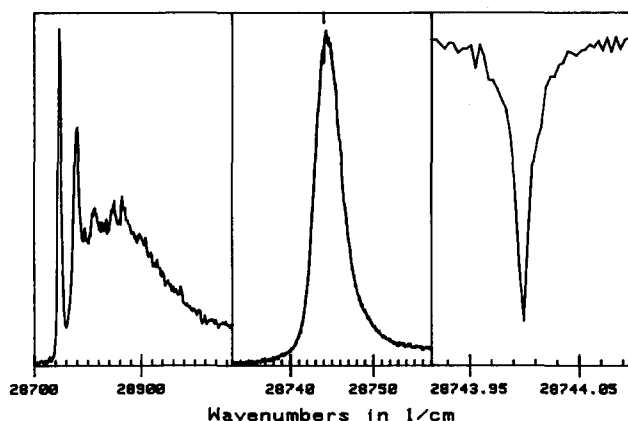


FIG. 1. Photochemical hole burning for all-*trans* octatetraene in *n*-hexane at 4.2 K. The left-hand panel shows a low resolution (approximately 6 cm^{-1}) scan over the $1^1A_g \rightarrow 2^1A_g$ 0-0 band. In higher resolution scans the 32 cm^{-1} progression in the phonon wing is almost completely resolved. The center panel shows the zero-phonon component of the 0-0 band at higher resolution. (approximately 0.01 cm^{-1}). The right-hand panel shows a high resolution (approximately 4 MHz) scan through a photochemical hole burned at $28\,744.00\text{ cm}^{-1}$.

tion approximately 7 cm^{-1}). The center panel shows the zero-phonon component of the fluorescence excitation origin band as measured with the Coherent 699/29 laser system. The inhomogeneous width in this case is 1.9 cm^{-1} half width at half maximum (HWHM). The very small dip near the band maximum is not noise but is a hole that was burned at 4.2 K. This hole is much more clearly seen in the expanded scan in the rightmost panel. Figure 2 shows the fit of a Lorentzian to a photochemical hole burned in the zero-phonon component of the 0-0 band.

The widths of the photochemical holes in the origin zero-phonon band decrease dramatically as the temperature is lowered and the hole depth is reduced. Figure 3 shows the measured width of the photochemical hole as a function of hole area at 1.4 K. Extrapolation to zero hole area gives a

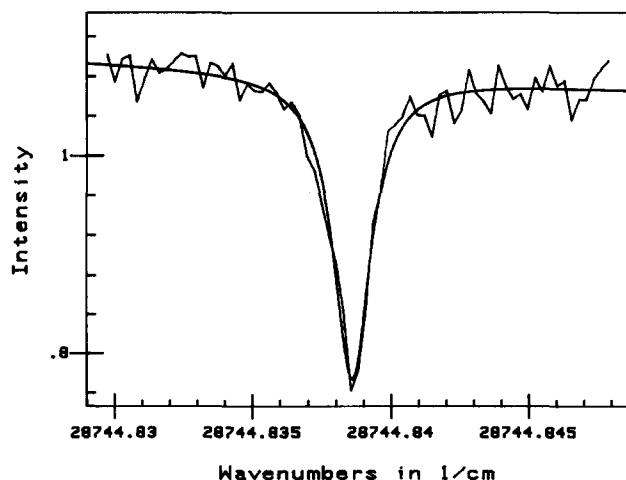


FIG. 2. Photochemical hole in the zero-phonon component of the $1^1A_g \rightarrow 2^1A_g$ 0-0 band for all-*trans* octatetraene in *n*-hexane. The hole was burned at 4.2 K. The smooth curve is the best-fit Lorentzian profile (HWHM 87 MHz).

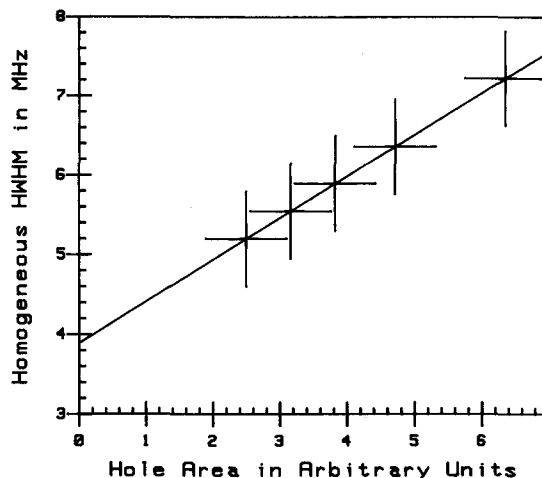


FIG. 3. Homogeneous widths estimated as one-half times the width of photochemical holes burned in the zero-phonon component of the $1^1A_g \rightarrow 2^1A_g$ 0-0 band of all-*trans* octatetraene in *n*-hexane at 1.4 K as a function of the hole area. Widths and areas were determined by least-squares fitting a Lorentzian to the hole profile.

limiting Lorentzian HWHM of $4.2 \pm 0.5\text{ MHz}$. This width is a convolution of the homogeneous line profile with the laser profile. After correcting for the laser bandwidth (estimated to correspond to a 2 MHz HWHM Gaussian), the hole width in the limit of zero hole area at 1.4 K is $1.7 \pm 0.5\text{ MHz}$. The measured lifetime at 4.2 K is $100 \pm 5\text{ ns}$.¹⁰ Thus, to within current experimental error, the hole width in the limit of zero hole depth corresponds to the lifetime limit of 1.6 MHz.

Temperature dependence. The profile of a vibronic band after photochemical hole burning for a time τ is given by Eq. (1). As is well known, in the limit of short burn times and homogeneous widths that are much narrower than the distribution of site energies $D(\omega)$, the hole profile is just the convolution of the homogeneous line profile with itself—the hole width is 2 times the width of the homogeneous line. In practice, this limiting hole profile is very difficult to realize. Nonetheless, it is easy to show that even for finite burn times the width of the resulting hole is proportional to the width of the homogeneous line.

To obtain preliminary information on the temperature dependence of the homogeneous linewidth, we have determined the temperature dependence of the widths of shallow holes burned into the zero-phonon component of the 0-0 band at 1.4 K. The constraints of signal to noise vs modification of the hole on reading limited these studies to just a few points over a very narrow temperature regime.

The dependence of the width of a photochemical hole burned at 1.4 K on temperature is shown in Fig. 4. Although this study of the temperature dependence of phase relaxation is only in a preliminary stage, the data of two different runs with different initial hole depths and widths are nicely fit by the optical exchange model^{16,17} with an effective phonon activation energy of $17 \pm 3\text{ cm}^{-1}$. The fact that the phonon side-band consists primarily of a regular 32 cm^{-1} progression (see, for example, the left-hand panel of Fig. 1) reinforces this interpretation since, with quadratic coupling, the strongly coupled phonon modes appear in the spectrum only

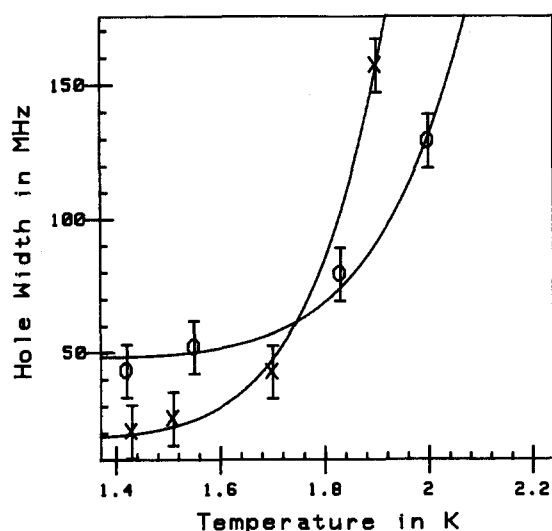


FIG. 4. The temperature dependence of the widths of two different photochemical holes burned in the zero-phonon component of the $1^1A_g \rightarrow 2^1A_g$ 0-0 band of all-*trans* octatetraene in *n*-hexane at 1.4 K. The curves are the best fit of the function $\omega = \omega_0 + \omega_1 \exp(-\Delta E/kT)$ (with ΔE constrained to be the same for both data sets) to the data. $\Delta E = 17 \pm 3 \text{ cm}^{-1}$.

with even quantum numbers. This has motivated a more detailed study of this relaxation which is in progress.

B. Vibrationally excited levels

Fundamentals of frequencies 347 cm^{-1} (skeletal bend), 1092 cm^{-1} (C-H wag), 1224 cm^{-1} (C-C stretch) and 1760 cm^{-1} (C=C stretch)¹⁸ are prominent in the fluorescence excitation spectrum. Since no emission originating from these excited vibrational levels can be observed, their lifetimes must be less than 100 ps, that is, less than 10^{-3} of the observed fluorescence decay time. Accordingly, holes burned into these vibronic bands are expected to be at least 1000 times broader than holes burned into the zero-phonon component of the origin. Relaxation broadened holes for excited vibronic levels have been observed in a number of studies.^{11,19-22} In fact, in our case, irradiating one of these vibronic bands at the band center does not generate a distinguishable hole but, rather, just reduces the peak intensity as is shown in Fig. 5. An example of the calculated profiles for the best fit of Eq. (1) to these kinds of data are also shown in Fig. 5.

The results of similar measurements and analysis on the other vibronic lines is summarized in Table I. The width of the transition energy distribution function is similar for all of the bands. The homogeneous width of any particular band corresponds to a lifetime of a few ps and does not change between 1.4 and 4.2 K.

C. Relative yield as a function of vibrational level

The ratio of the integrated intensity of a photochemical hole A_{hole} for a given irradiation time τ to the integrated intensity of the band before burning A_{band} gives a measure of the relative photochemical yield. We define a relative yield φ by

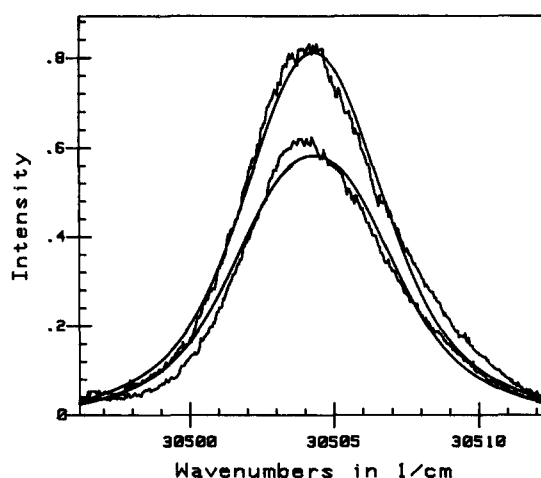


FIG. 5. Photochemical hole burning in the zero-phonon component of a vibrationally excited band (C=C stretch, 1760 cm^{-1} above the 0-0) of the $1^1A_g \rightarrow 2^1A_g$ transition for all-*trans* octatetraene in *n*-hexane at 4.2 K. The upper curve shows the band profile before burning at the band center, the lower curve shows the profile after burning. The noisy lines are the experimental data, the smooth curves are the best fits of the photochemical model described in the text to the data.

$$\varphi = \frac{A_{\text{hole}}}{A_{\text{band}}} \cdot \frac{10^5 \text{ s}}{\tau} \quad (2)$$

At low conversion Eq. (2) accurately gives the relative yield φ , a quantity that is independent of irradiation time and absorption intensity. The burn times used were seconds for the zero-phonon component of the 0-0 band at 1.4 K, minutes for the zero-phonon component of the 0-0 band at 4.2 K, and hours for the vibronic bands. The φ 's for the different vibronic bands are summarized in Table I and plotted in Fig. 6. These data are well fit by the function

$$\varphi_r = \varphi_0 / (1 + e^{\alpha(\Delta E - E)}), \quad (3)$$

where φ_0 and α are scaling constants, ΔE is the effective barrier height and E is the vibrational energy. Equation (3) is the limiting energy gap law that results from a number of different kinetic models.²³ From this analysis, the energy barrier for *trans* to *cis* isomerization on the excited 2^1A_g

TABLE I. Summary of photochemical hole burning in the $1^1A_g \rightarrow 2^1A_g$ transition of all-*trans* octatetraene in *n*-hexane at 4.2 K. Energy is vibronic energy relative to the 0-0 band. Γ_{inhom} is the HWHM of the Gaussian excitation energy distribution, T_1 is the lifetime deduced from the HWHM of the Lorentzian homogeneous line profile [that is, $T_1 = 1/(2\pi\Gamma_{\text{inhom}})$] and φ_r is the relative efficiency of hole burning. Γ_{inhom} and Γ_{hom} were determined as described in the text.

Line	Energy (cm^{-1})	Γ_{inhom} (cm^{-1})	T_1 (ps)	Φ_r
Origin 1.4 K	0	1.9 ± 0.1	10^5 ^a	0.19 ± 0.04
4.2 K	0	1.9 ± 0.1	10^5 ^a	0.15 ± 0.04
Phonon	32	1.9 ± 0.2	1.9 ± 0.5	0.2 ± 0.1
Vibrations	347	1.9 ± 0.2	7.0 ± 2.5	0.15 ± 0.15
	1092	1.8 ± 0.2	5.2 ± 1.0	3.7 ± 0.5
Single bond	1224	1.7 ± 0.2	5.7 ± 1.0	4.5 ± 0.5
Double bond	1760	2.0 ± 0.2	4.0 ± 1.0	5.5 ± 0.5

^a 100 ns decay measured in Ref. 10.

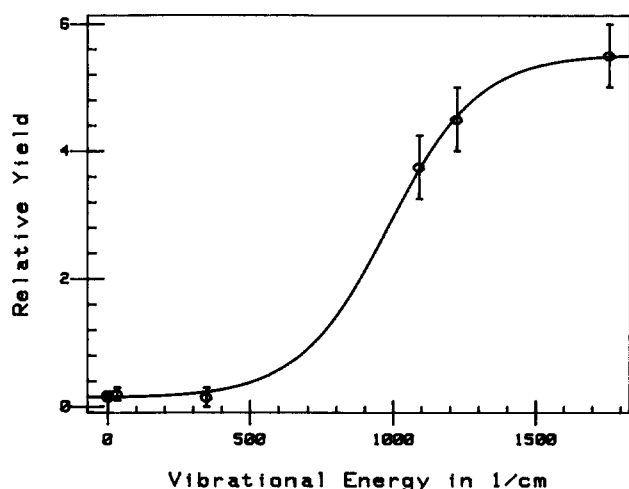


FIG. 6. The efficiency of photochemical hole burning in the $1^1A_g \rightarrow 2^1A_g$ transition of all-*trans* octatetraene in *n*-hexane at 4.2 K as a function of vibrational energy. The smooth curve is the best fit to the data by the energy gap expression $\phi_r = \phi_0 / (1 + e^{\alpha(\Delta E - E)})$. The best-fit value for the energy gap ΔE is $950 \pm 30 \text{ cm}^{-1}$.

surface ΔE is estimated to be $950 \pm 30 \text{ cm}^{-1}$. This is gratifyingly close to our previous estimate of 870 cm^{-1} which was derived from thermodynamic, kinetic, and spectroscopic data.⁹

IV. SUMMARY AND CONCLUSIONS

We have shown that the low-temperature photoisomerization of the unsubstituted linear polyene octatetraene may be investigated by the techniques of photochemical hole burning. In the case of all-*trans*-octatetraene in *n*-hexane, the holes have a Lorentzian profile with a HWHM width in the limit of zero temperature and zero hole depth that is 4 MHz. When the laser bandwidth is taken into account this is within experimental error equal to the lifetime limited value predicted from the measured fluorescence lifetime of 100 ns. This width is 4 orders of magnitude narrower than the HWHM of the inhomogeneous band profile of 1.9 cm^{-1} . The increase in hole width with increasing temperature is well fit by an exchange model with an effective phonon frequency of $17 \pm 3 \text{ cm}^{-1}$. The phonon side band of the 0-0 band is dominated by a 32 cm^{-1} progression. Thus, it is reasonable to postulate that this progression is made up of even numbers of quanta of a strongly quadratically coupled 16 cm^{-1} mode that is primarily responsible for the dephasing. In the higher lying vibrational bands of the 1^1A_g to

2^1A_g transition, the holes are considerably broader as is consistent with T_1 relaxation times of a few ps. The efficiency of hole burning as a function of vibrational energy increases by approximately a factor of 35 as vibrational energy in the excited state is increased beyond a threshold of approximately 950 cm^{-1} . The dependence of relative yield on vibrational energy is well fit by a simple energy gap expression with a threshold value that agrees with previous estimates of the barrier to isomerization on the 2^1A_g potential-energy surface.

It is clear that further investigations using these techniques will contribute significantly to our understanding of *cis-trans* photoisomerization.

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