Direct absorption spectroscopy of jet-cooled polyenes. II. The $1\,^1B_u^+ \leftarrow 1\,^1A_g^-$ transitions of butadienes and hexatrienes

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(Received 14 February 1984; accepted 4 May 1984)

In the present paper, we report the direct absorption spectra of the $1\,^1B_u^+ \leftarrow 1\,^1A_g^-$ transitions of gas phase butadiene, deuterated and methylated butadienes, and the cis and trans isomers of hexatriene cooled to low rotational and vibrational temperatures in supersonic molecular jets. These jet absorption spectra allow the more accurate determinations of Franck–Condon factors, upper state vibrational intervals and vibronic band homogeneous widths. We discuss the experimental constraints that the measurements reported here and in the previous paper of this series impose on theoretical models of the equilibrium structures and relaxation dynamics of the $1\,^1B_u^+$ excited states of the small linear polyenes.

I. INTRODUCTION

A detailed understanding of the excited state structures and dynamics of the simplest conjugated molecule 1,3-butadiene and its longer homologs 1,3,5-hexatriene and 1,3,5,7-octatetraene is crucial to the delineation of the cis–trans photoisomerization process is unsaturated hydrocarbons and to the development of theoretical models of delocalized π-bonded systems. Despite the fundamental importance of linear polyene photophysics, however, and the considerable amount of experimental and theoretical effort that has been focused on this topic since the pioneering studies by Hauser and co-workers in the mid-1930’s, 1-12 there remain to this date conspicuous gaps in our knowledge of many of the fundamental excited state properties of the small polyenes. These include, e.g., the equilibrium geometries, the energy ordering, and the relaxation dynamics of their excited valence states.

The potential surfaces that control the photochemistry of the lowest $1\,^1B_u^+$ and $2\,^1A_g^-$ excited states of the small linear polyenes are not yet well understood. Of particular importance in mapping out the mechanism of the distinctive polyene photophysics of cis–trans isomerization are the displacements along double-bond torsional coordinates of the equilibrium geometries of the excited states with respect to those of the planar $1\,^1A_g^-$ ground states. A wide range of excited state torsional geometries appear plausible for butadiene and hexatriene, as the $1\,^1B_u^+$ state of ethylene is twisted by 90°, 6 while both the $1\,^1B_u^+$ and $2\,^1A_g^-$ states of octatetraene appear to be planar. 7-10 Predictions of the numerous theoretical calculations reported for the $1\,^1B_u^+$ and $2\,^1A_g^-$ states of the short polyenes span the same range. 11-14 The spectroscopic information that has been extracted from the strongly allowed $1\,^1B_u^+ \rightarrow 1\,^1A_g^-$ absorption systems of butadiene and hexatriene is inadequate to accurately establish their upper state equilibrium geometries, but an approximately planar $1\,^1B_u^+$ state has been sug-

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suggested for both systems on the basis of Franck–Condon analyses of their low-temperature matrix spectra compared with those of the longer polyenes. 15 However, the lack of detectable fluorescence from butadiene and hexatriene, 7 the diffuseness of their absorption spectra in low-temperature crystals, 6 and, for butadiene, the electron energy dependence of its electron impact excitation spectrum 16 have been interpreted in terms of a substantially twisted $1\,^1B_u^+$ state. Experimental information concerning the spectroscopically less accessible $2\,^1A_g^-$ states is even sparser for these systems, although theoretical results suggest a greater degree of distortion than is predicted for the corresponding $1\,^1B_u^+$ state. 12,17

In addition, the ordering of the lowest excited states of the short polyenes is a subject of considerable controversy. 3,18,19 In octatetraene and several longer polyenes, a $2\,^1A_g^-$ state, to which a one-photon transition from the $1\,^1A_g^-$ ground state is parity forbidden, has been demonstrated to lie below the $1\,^1B_u^+$ state in the condensed phase. 7,8,20 However, the $2\,^1A_g^-$ states of butadiene, hexatriene and gas phase octatetraene have not unambiguously been identified experimentally, 21 and theoretical investigations have yielded conflicting results for the ordering of the $2\,^1A_g^-$ and $1\,^1B_u^+$ states of these systems and the energy gap between them: 12,22-25 Vibronic coupling effects between these excited states have been invoked by many investigators to rationalize several apparently anomalous aspects of the spectroscopic properties of these systems. 9,12,26 For example, gas phase octatetraene is reported to emit from its $1\,^1B_u^+$ state, yielding a fluorescence spectrum which displays no Stokes shift and is a mirror image of the $1\,^1B_u^+ \rightarrow 1\,^1A_g^-$ absorption spectrum; however, the observed radiative lifetime exceeds that expected from the integrated absorption spectrum by about an order of magnitude. 8 On the other hand, no emission has been observed from butadiene or hexatriene despite considerable effort. 27-28 In addition, the $1\,^1B_u^+ \rightarrow 1\,^1A_g^-$ absorption spectra of these systems display extremely diffuse vibronic bands with widths exceeding ~300 cm$^{-1}$ for hexatriene and ~1100 cm$^{-1}$ for butadiene. 15,28,29 If these bandwidths are largely homogeneous, they, together with the immeasurably low fluorescence quantum yields of these systems, suggest the existence of

4218 J. Chem. Phys. 81 (10), 15 November 1984 0021-9606/84/224218-12$02.10 © 1984 American Institute of Physics

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exceedingly efficient radiationless transition processes in butadiene and hexatriene whose detailed mechanisms have yet to be delineated.\textsuperscript{12,30}

The spectroscopic data required to solve the multidimensional problems of linear polyene photophysics are difficult to obtain due to the substantial contributions of vibrational sequence band congestion to the room temperature absorption spectra of these large, nonrigid molecules. Attempts to reduce these effects by cooling butadiene and hexatriene in low temperature crystals have been hindered by the substantial matrix-induced broadening observed for these systems, which result in spectra even more diffuse than those obtained in the gas phase at room temperature.\textsuperscript{4,15} In the present paper, we report the direct absorption spectra of the $^1B_u^+ \rightarrow 1^1A_g^-$ transitions of gas phase butadiene, deuterated and methylated butadienes, and the cis and trans isomers of hexatriene cooled to low rotational and vibrational temperatures in supersonic molecular jets. The jet absorption spectra are substantially sharpened over those observed in either the room temperature static gas or in low-temperature crystals, allowing the more accurate determinations of Franck-Condon factors, upper state vibrational intervals, and vibronic band homogeneous widths. These measurements, combined with those reported for jet-cooled octetraene in the previous paper,\textsuperscript{10} provide important experimental constraints on theoretical models of the equilibrium structures and relaxation dynamics of the $^1B_u^+$ excited states of the small linear polyenes.

II. EXPERIMENTAL

The direct UV absorption molecular jet technique has been described previously,\textsuperscript{10,31} so we include in this section only those details that pertain specifically to the present study. The experiments reported here employed a 1 mm diam room temperature nozzle operated at $\sim 50$ Hz with 4 ms pulse widths. Argon was used as the carrier gas and stagnation pressures and dilution ratios were varied as described below. The samples were probed 7–10 mm from the nozzle with an instrumental resolution of 2 Å; the same bandwidths were observed up to an instrumental resolution of 0.5 Å. Absorbances measured were below 0.01. Wavelengths were calibrated against mercury arc lines and were corrected to vacuum.

The mixed hexatriene isomers, purchased from Aldrich, were separated by freezing and fractional melting.\textsuperscript{32} The purity of the trans-hexatriene product was verified gas chromatographically. The sample enriched in the cis isomer was found to contain a small amount of trans-hexatriene, for which the resulting jet absorption spectrum was corrected by subtraction of the pure trans-hexatriene jet spectrum weighted according to the relative abundances and extinction coefficients of the two isomers. The trans-hexatriene spectrum shown here was obtained at 5% dilution at a stagnation pressure of 50 Torr. Spectra obtained at 3% dilution and 100 Torr displayed the same bandwidths. The cis-hexatriene spectrum shown was obtained under the latter expansion conditions. Trans-1,3-butadiene (purchased from Matheson) and trans-1,3-butadiene-$d_6$ (purchased from Merck) were each diluted $\sim 5\%$ in argon and expanded at 100–120 Torr. The methylated butadienes studied were obtained from Aldrich and the jet spectra reported were measured at 30% dilution and 30–50 Torr stagnation pressures. At higher stagnation pressures abundant clustering occurred, as manifested by an unexpected rise in absorption intensity toward higher energies. This effect was particularly striking for the terminally substituted dienes; for example, an expansion of 10% trans-2, trans-4-hexadiene in argon or butane at 100 Torr behind the 1-mm diam nozzle resulted in a jet absorption spectrum whose intensity at the high energy tail of the $^1B_u^+ \rightarrow 1^1A_g^-$ transition at 50 250 cm$^{-1}$ exceeded that at the 46 320 cm$^{-1}$ main band. The overall contours of the jet spectra displayed here appear consistent with those obtained for the static gas phase methylated dienes at room temperature; however, the possibility of some residual cluster-generated absorption intensity cannot be entirely discounted.

III. RESULTS

A. Trans-1,3,5-hexatriene

Figure 1 displays the jet absorption spectrum of the $^1B_u^+ \rightarrow 1^1A_g^-$ transition of trans-1,3,5-hexatriene. Vibronic bands in the jet spectrum are substantially narrowed from their widths in the gas phase at room temperature.\textsuperscript{28} For example, the origin band at 39 786(3) cm$^{-1}$ is reduced in width by $\sim 50\%$ on jet cooling, from 290 to 155 cm$^{-1}$. As in the case of octetraene,\textsuperscript{10} we attribute this band sharpening largely to the reduction on cooling of unresolved vibrational sequence structure, a particularly severe source of spectral congestion in flexible polyatomics whose ground state Boltzmann populations are distributed over many low-lying vibrational levels at room temperature.

The general appearance of the jet spectrum suggests that the upper state equilibrium geometry is not greatly distorted with respect to that of the ground state, as indicated by the relative strength of the origin band and the lack of extended vibrational progressions. Therefore, the most prominent features observed in this allowed transition of the vibrationally relaxed sample are likely to be associated with upper state vibrational levels of $a_g$ symmetry. The vibronic bands listed in Table I have been assigned to transitions from the zero point level of the $^1A_g^-$ state to levels of the $^1B_u^+$ state.

![FIG. 1. Jet absorption spectrum of trans-1,3,5-hexatriene.](image-url)
TABLE I. Jet absorption bands of trans-1,3,5-hexatriene.

<table>
<thead>
<tr>
<th>Observed band position (vac cm⁻¹)</th>
<th>Relative height</th>
<th>Observed bandwidth (FWHM, cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>39 786(3)</td>
<td>100</td>
<td>155</td>
<td>0.0</td>
</tr>
<tr>
<td>40 099(19)</td>
<td>18</td>
<td></td>
<td>313</td>
</tr>
<tr>
<td>40 504(19)</td>
<td>10</td>
<td></td>
<td>718</td>
</tr>
<tr>
<td>41 010(6)</td>
<td>41</td>
<td>180</td>
<td>1224</td>
</tr>
<tr>
<td>41 417(4)</td>
<td>81</td>
<td>200</td>
<td>1631</td>
</tr>
<tr>
<td>42 236(30)</td>
<td>18</td>
<td>2x1224;</td>
<td>718 + 1631</td>
</tr>
<tr>
<td>42 645(6)</td>
<td>37</td>
<td>240</td>
<td>1224 + 1631</td>
</tr>
<tr>
<td>43 038(6)</td>
<td>40</td>
<td>260</td>
<td>2x1631</td>
</tr>
<tr>
<td>43 868(30)</td>
<td>16</td>
<td>2x1224 + 1631</td>
<td></td>
</tr>
<tr>
<td>44 261(9)</td>
<td>18</td>
<td>1224 + 2x1631</td>
<td></td>
</tr>
<tr>
<td>44 646(12)</td>
<td>15</td>
<td>3x1631</td>
<td></td>
</tr>
</tbody>
</table>

state involving vibrational modes with fundamental frequencies of 313(17), 718(17), 1224(4), and 1631(3) cm⁻¹. The activity of an additional upper state mode at 471(40) cm⁻¹ is suggested by the shoulder observed on the 40 099 cm⁻¹ band.

Although the problem of vibronic band overlap is greatly reduced in the sharpened jet spectrum of trans-hexatriene, there remains a relatively intense diffuse background underlying the resolved structure. Scans taken under various expansion conditions, including an effusive expansion of the room temperature sample whose spectrum agreed with the literature spectrum, suggest that this diffuse background is not due to impurities in the trans-hexatriene sample or to clusters generated in the expansion. This conclusion is supported by preliminary results of a Franck–Condon analysis of the jet spectrum based on least-squares fits of upper state frequencies and displacements to the best-resolved vibronic features. These results indicate that the overlapping tails of partially resolved peaks, combined with a large number of relatively weak unresolved overtones and combination bands, can account for the diffuse background observed. The intensities and bandwidths listed in Table I, which were measured directly from the observed spectrum, may thus represent contributions from multiple vibronic excitations.

The assignments of the observed upper state intervals to specific normal modes of vibration are straightforward in the case of trans-hexatriene due to the complementary resonance Raman study recently reported by Myers et al. The strong progression in 1631(3) cm⁻¹ intervals is assigned to the in-phase carbon–carbon double bond stretching motion associated with the ground state 1627 cm⁻¹ mode which gives rise to the most intense line in the Raman spectrum. The out-of-phase C=C stretching motion at ~1580 cm⁻¹ in the ground state gives rise to a relatively weak Raman line whose intensity may reflect the contribution of this mode to the upper state 1631 cm⁻¹ mode. Such a normal coordinate rotation appears likely in view of the results of a recent normal mode analysis of octatetraene, indicating that the double bond stretching mode most active in the 1 B_u ← 1 A_g transition of this system maps onto both totally symmetric C=C stretching modes in the ground state. Alternatively, the second Raman line may indicate the activity of a second, much (~15 x) weaker fundamental vibronic band in the hexatriene 1 B_u ← 1 A_g spectrum. Such a feature, not identified in the jet spectrum, would probably be submerged beneath the ~200 cm⁻¹ wide 1631 cm⁻¹ band.

The second most intense progression observed in the jet spectrum involves a 1224(4) upper state interval, which can be identified with the 1190 cm⁻¹ ground state carbon–carbon single bond stretching mode which is the most prominent in this frequency region of the Raman spectrum. This ground state assignment follows the alternate scheme proposed by Lippincott, wherein the 1245 cm⁻¹ Raman line is assigned to the CH in-plane bend rather than to the C=C stretch. Two weaker lines observed in this region of the resonance Raman spectrum for which no corresponding features are resolved in the jet spectrum occur at 1287 and 1398 cm⁻¹, and are described as in-plane bending motions of the vinyl C-H and the CH₂ groups, respectively. Again, it is possible that the Raman activities of these modes reflect Duschinsky effects, as the normal modes in this frequency region involve contributions from a mixture of stretching and bending internal coordinates.

The lowest frequency upper state interval of 313(17) cm⁻¹ observed in the jet spectrum is likely to be identified with the strong Raman line at 359 cm⁻¹, associated with the lower frequency of two in-plane skeletal bending vibrations in the ground state. The vibronic feature observed 718(17) cm⁻¹ from the origin band in the jet spectrum corresponds to a shoulder in the room temperature spectrum previously assigned to the first overtone of this same mode. However, in the better resolved jet spectrum, neither the intensity nor the frequency of this feature appears consistent with this assignment under the assumption of harmonic potentials. Rather, we assign the 718(17) cm⁻¹ upper state interval as a fundamental corresponding to the 932 cm⁻¹ Raman line observed by Myers et al. Based on the results of normal mode calculations of hexatriene and octatetraene, we attribute this ground state frequency to the CH₂ in-plane bending mode to which Raman lines near 1130 cm⁻¹ in both systems have previously been assigned.

Finally, the 471(40) cm⁻¹ upper state interval suggested by the shoulder near 40 260 cm⁻¹ is likely to be associated with the only other low frequency a₈ in-plane skeletal bending mode in the ground state, whose frequency is 444 cm⁻¹. No corresponding feature is reported in the resonance Raman study. This assignment is supported by the observed activities in the analogous transition of octatetraene of all three of that molecule's low frequency a₈ in-plane skeletal bending vibrations. However, it is also possible that the 470 cm⁻¹ interval corresponds to an upper state combination level of overall a₈ symmetry, or that the shoulder observed actually is composed of multiple excitations.

The vibrational assignments discussed above are summarized in Table II. These assignments, with the exceptions noted earlier, are in agreement with the previous analysis of the 1 B_u ← 1 A_g room temperature spectrum by Gavin et al.

Excited state normal mode displacements can be estimated from the relative integrated intensities of vibronic bands observed in the jet absorption spectrum if it is assumed...
TABLE II. Vibrational frequencies of trans- and cis-1,3,5-hexatriene.*

<table>
<thead>
<tr>
<th>Mode</th>
<th>Description</th>
<th>Symmetry</th>
<th>Trans-hexatriene&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Cis-hexatriene&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν&lt;sub&gt;12&lt;/sub&gt;</td>
<td>Skeletal angle bend</td>
<td>a&lt;sub&gt;e&lt;/sub&gt; (a&lt;sub&gt;i&lt;/sub&gt;)</td>
<td>359</td>
<td>313(17)</td>
</tr>
<tr>
<td>ν&lt;sub&gt;12&lt;/sub&gt;</td>
<td>Skeletal angle bend</td>
<td>e&lt;sub&gt;e&lt;/sub&gt;</td>
<td>444</td>
<td>327(40)</td>
</tr>
<tr>
<td>ν&lt;sub&gt;11&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt; rock</td>
<td>e&lt;sub&gt;e&lt;/sub&gt;</td>
<td>932</td>
<td>718(17)</td>
</tr>
<tr>
<td>ν&lt;sub&gt;9&lt;/sub&gt;</td>
<td>C-C stretch</td>
<td>e&lt;sub&gt;e&lt;/sub&gt;</td>
<td>1190</td>
<td>1224(4)</td>
</tr>
<tr>
<td>ν&lt;sub&gt;5&lt;/sub&gt;</td>
<td>C=C stretch</td>
<td>e&lt;sub&gt;e&lt;/sub&gt;</td>
<td>1627</td>
<td>1631(3)</td>
</tr>
</tbody>
</table>

<sup>*All frequencies are in cm<sup>-1</sup>.</sup>

<sup><sup>a</sup>1<sup>A</sup><sub>e</sub> frequencies for the trans isomer are from Ref. 33 except the 444 cm<sup>-1</sup> mode, which is from Ref. 34.</sup>

<sup><sup>b</sup>1<sup>A</sup><sub>e</sub> frequencies for the cis isomer are from Ref. 34, using the alternative assignment proposed there for the C-C stretching mode, which is designated here as ν<sub>5</sub>.</sup>

that the normal mode eigenvectors of the ground and excited states are nearly identical (i.e., that Duschinsky mixing is negligible) and that the potential surfaces are harmonic at low vibrational energies. Then, the intensity of the 1→0 vibronic transition for the<i>i</i>th normal mode (I(0<i>→</i>1)) relative to that of the origin band (I(0→0)) is related to the dimensionless displacement along the<i>i</i>th mode on excitation (Δ<i>i</i>) as follows:

<sup>Δ</sup><i>i</i> = 2 \left( \frac{I(0→1)}{I(0→0)} \right)^{1/2}

(1)

Similar relations for transitions to higher vibrational levels are less useful in the present analysis since the relative intensities of the 1→0 vibronic bands observed in the trans-hexatriene jet absorption spectrum can be measured most precisely. The integrated absorption intensities of the three bands at 1631, 1224, and 313 cm<sup>-1</sup> determined from the data in Table I (taking the width of the 313 cm<sup>-1</sup> shoulder to be about the same as that of the origin band) indicate dimensionless excited state displacements of 1.45, 0.98, and 0.6 for the three most active normal modes. The displacements of the 1224 and 313 cm<sup>-1</sup> modes relative to that of the 1631 cm<sup>-1</sup> mode determined from the jet absorption spectrum thus agree to within 10% with those obtained by Myers et al. solely from the preresonance Raman spectrum. However, our results indicate a somewhat higher absolute scaling of the Δ's than was obtained in the latter study from a fit to the gas phase room temperature absorption spectrum, which suggested a displacement of only 1.17 for the ∼1630 cm<sup>-1</sup> mode. The displacement along the 932 cm<sup>-1</sup> mode is more difficult to determine from the jet absorption spectrum due to the relatively intense background underlying the 718 cm<sup>-1</sup> vibronic band. However, from the height of the resolved portion of this band (∼4% of the origin band) and an assumed ∼155 cm<sup>-1</sup> bandwidth, a lower limit of 0.28 can be estimated for the excited state displacement along this mode. This indicates a displacement relative to that of the ∼1630 cm<sup>-1</sup> mode of at least 0.19, consistent with the estimate of 0.22 based on the preresonance Raman intensities.

B. Cis-1,3,5-hexatriene

The jet absorption spectrum of cis-hexatriene is displayed in Fig. 2, and the positions of the most prominent vibronic bands observed are listed in Table III. The vibrational assignments presented there and in Table II are analogous to those proposed in the last section for the trans-isomer and agree with the assignments suggested in the room temperature gas phase study of Gavin et al. As in the trans-hexatriene spectrum, the strongest vibrational progression displays intervals of ∼1600 cm<sup>-1</sup> and has been assigned to the carbon-carbon double bond stretching mode. The partially resolved feature near 1200 cm<sup>-1</sup> has tentatively been assigned to the single bond stretching mode, although the additional activities in this region of C-H bending modes are likely in view of the preresonance Raman results for trans-hexatriene discussed above.

The low frequency feature near 400 cm<sup>-1</sup> in the cis-hexatriene jet spectrum has been assigned to the "terminal" skeletal in-plane bending motion whose ground state frequency is 393 cm<sup>-1</sup>. This is the analog of the 444 cm<sup>-1</sup> bending mode of the trans isomer, which we have suggested may give rise to the weak shoulder on the more intense vibronic band assigned to the 359 cm<sup>-1</sup> in-plane bending mode. The analog of the latter feature is not resolved in the spectrum of the cis isomer. However, the ground state frequency of this mode in cis-hexatriene is only 167 cm<sup>-1</sup> and the upper state interval is likely to be even lower in view of the frequency reduction observed on excitation in trans-hexatriene. Such a low-frequency interval might well be obscured in the cis-hexatriene jet spectrum; for example, the FWHM of the origin band, the sharpest feature, is ∼250 cm<sup>-1</sup>. The semiempirical calculations of Petelenz and Petelenz have predicted that, due to the increased repulsive interactions between hydrogen atoms on carbons 2 and 5 of hexatriene when in the cis configuration, the activity of this low frequency in-plane bending mode is likely to be much greater in the spectrum of the cis than of the trans isomer. This type of activity might largely be responsible for the more congested appearance of the cis-hexatriene jet spectrum. It may be noted that the smooth contour of the origin band in the jet absorption spectrum and the lack of a significant wavelength shift on cooling are consistent with its composition mainly by a single vibronic excitation. However, additional experimental results, such as those that might be obtained by preresonance Raman studies, are clearly needed for a more detailed vibrational analysis of the cis-hexatriene absorption spectrum.
C. Butadiene-$h_6$ and $-d_6$

Figure 3 displays the jet absorption spectra of the $1^1B_u^+ \rightarrow 1^1A_g^+$ transitions of butadiene-$h_6$ and butadiene-$d_6$. In agreement with our earlier report, the three extremely diffuse bands that comprise the room temperature spectra persist in the spectra of the jet-cooled butadienes; scans at 5 cm$^{-1}$ resolution revealed no additional discrete structure. However, the observed bands narrow in the jet spectra, indicating that at least part of their room temperature widths result from thermal broadening effects. For example, the half width of the lowest energy band of butadiene decreases by $\sim$15% on cooling, from 580 cm$^{-1}$ at 25 °C to 490 cm$^{-1}$ in the jet spectrum. The bandwidth of the jet-cooled perdeuterated isomer is 360 cm$^{-1}$, a decrease of 150 cm$^{-1}$ (30%) from the room-temperature width and 70 cm$^{-1}$ less than the width observed at 78 °C.\(^{29}\)

Clear evidence for the vibrational cooling of the butadiene samples monitored in these experiments is provided by the sharp Rydberg structure superimposed on the high-energy tails of the $1^1B_u^+ \rightarrow 1^1A_g^+$ transitions. This region of the butadiene-$h_6$ system is expanded in Fig. 4, where the supersonic jet spectrum is compared with that obtained under the same detection conditions for an effusive expansion of the uncooled sample. The intense feature observed at 50 574 ± 10 cm$^{-1}$ in both traces has previously been assigned to a transition from the zero point level of the $1^1A_g^+$ state to $v = 1$ of the upper state 144 cm$^{-1}$ CH$_2$ twisting mode, one of several $a_u$ vibrations that vibronically induce the one-photon transition to this $1^1B_u$ Rydberg state.\(^{29,40}\) The weaker band observed $\sim$300 cm$^{-1}$ lower in energy in the spectrum of the uncooled sample (upper trace) has been assigned in part to a $\sim$0 transition to the C–C torsional level.\(^{29}\) However, a significant hot band contribution to the absorption in this region is indicated by its reduced intensity in the spectrum of the sample cooled in the supersonic jet (lower trace). The most likely symmetry-allowed assignment for this hot band is to a transition from the first overtone of the C–C torsional mode at 323 cm$^{-1}$ in the ground state\(^{41}\) to the 444 cm$^{-1}$ upper state level. The decrease in the intensity of this feature to below the noise level in the lower spectrum of Fig. 4 indicates that the vibrational temperature of the jet-cooled sample is below 170 K. Direct absorption jet studies of related molecules suggest that the actual vibrational temperatures of the jet-cooled butadienes are likely to be considerably below this upper limit; e.g., a temperature of $\sim$20 K has been estimated for the low-frequency vibrational modes of styrene cooled under similar expansion conditions.\(^{42}\)

Rotational temperatures are estimated from argon jet systematics\(^{43}\) to be $\lesssim$10 K for the expansion conditions employed in the butadiene experiments.

These considerations suggest that thermal broadening effects arising from vibrational sequence structure or rotational band congestion do not contribute substantially to the diffuseness of the jet-cooled butadiene spectrum. It is noteworthy that the reduction in observed bandwidths from 490 cm$^{-1}$ (HWHM) for butadiene to 360 cm$^{-1}$ for butadiene-$d_6$ is in accord with the expected effect of deuteration in extending the lifetimes of excited states whose major relaxation pathways involve internal conversion.\(^{44}\) Possible mechanisms for the considerable line broadening observed in the

![Graph showing jet absorption spectrum of cis-1,3,5-hexatriene](image)

**TABLE III.** Jet absorption bands of cis-1,3,5-hexatriene.

<table>
<thead>
<tr>
<th>Observed band position (vac cm$^{-1}$)</th>
<th>Relative height</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>39 666(8)</td>
<td>100</td>
<td>0–0</td>
</tr>
<tr>
<td>40 055(23)</td>
<td>40</td>
<td>389</td>
</tr>
<tr>
<td>40 914(38)</td>
<td>53</td>
<td>1248</td>
</tr>
<tr>
<td>41 284(23)</td>
<td>97</td>
<td>1618</td>
</tr>
<tr>
<td>41 697(38)</td>
<td>49</td>
<td>389 + 1618</td>
</tr>
<tr>
<td>42 539(28)</td>
<td>56</td>
<td>1248 + 1618</td>
</tr>
<tr>
<td>42 892(28)</td>
<td>67</td>
<td>2 × 1618</td>
</tr>
</tbody>
</table>

![Graph showing jet absorption spectra of $1^1B_u^+ \rightarrow 1^1A_g^+$ transitions of butadiene](image)

**FIG. 3.** Jet absorption spectra of the $1^1B_u^+ \rightarrow 1^1A_g^+$ transitions of butadiene (upper trace) and perdeuterated butadiene (lower trace). The maxima of the lowest energy bands occur at 46 260(20) cm$^{-1}$ for butadiene and 46 470(20) cm$^{-1}$ for butadiene-$d_6$. Left and right axes give relative absorbances for the $C_4D_8$ and $C_4H_8$ spectra, respectively.

butadiene spectra are discussed further in Sec. IV B.

The positions and relative intensities of the features observed in the jet spectra of butadiene and butadiene-$d_6$ are listed in Table IV. The positions of the lowest energy bands (labeled “band I” in the table) indicate a deuterium shift of $210 \pm 40$ cm$^{-1}$, with the absorption band of the deuterated isomer shifted to higher energy. The direction of this shift implies a decrease in the overall sum of vibrational frequencies on electronic excitation. The observed deuterium shift, combined with the known frequencies of the ground state vibrational modes of butadiene and butadiene-$d_6$, provide a useful constraint for theoretical calculations of vibrational frequencies in the $1^1B_u^+$ states.

Unfortunately, the broad bandwidths associated with the $1^1B_u^+ \rightarrow 1^1A_g^-$ transition of butadiene-$h_6$ render its spectrum fairly uninformative even when the molecule is jet cooled. The vibronic developments of the analogous transitions of hexatriene and octatetraene,$^{10}$ as well as preresonance Raman data for butadiene,$^{45}$ suggest that progressions in carbon–carbon single and double bond stretching intervals will make major contributions to the butadiene spectrum. However, the extremely diffuse spectrum of butadiene can be fairly well modeled simply as a somewhat anharmonic single progression if vibronic bandwidths are allowed to increase with energy, as do those in the jet spectra of hexatriene and octatetraene.$^{15}$ Furthermore, the observed intervals (see Table IV) are approximately midway between the single and the double bond stretching frequencies typically observed near 1200 and 1600 cm$^{-1}$ in polyene $1^1B_u^+ \rightarrow 1^1A_g^-$ spectra. If both modes do contribute to the butadiene spectrum, it is not clear which is the more prominent, and experimental investigations have reached different conclusions on this point.$^{15,45}$

The spectrum of butadiene-$d_6$, in contrast, sharpens sufficiently on cooling to provide some additional insight into the $1^1B_u^+ \rightarrow 1^1A_g^-$ transition. In this case, the jet spectrum clearly cannot be modeled by three Lorentzians; the shape of the red edge of the second band as well as the flattened profile of the third band strongly suggest the activity of more than one vibrational progression. In addition, the observed spacings of 1550 and 1540 cm$^{-1}$ are quite close to the 1580 cm$^{-1}$ ground state frequency of the carbon–carbon double bond stretching mode of butadiene-$d_6$.$^{46}$ This strongly suggests that this mode forms the dominant vibrational progression in the $1^1B_u^+ \rightarrow 1^1A_g^-$ spectra of the butadienes, as it does in those of the longer polyenes.$^{4,10,15}$

Finally, we note that the increase in the interval between the first and second bands from 1460 $\pm$ 40 cm$^{-1}$ in the butadiene jet spectrum to 1550 $\pm$ 40 cm$^{-1}$ in the spectrum of butadiene-$d_6$ is rather surprising if (as has traditionally been assumed)$^{47,48}$ this interval represents a single upper state vibrational frequency—every normal mode in the ground state shifts to lower frequency in the perdeuterated isomer.$^{46}$ On the other hand, if the bands observed in the

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Band I (vac cm$^{-1}$)</th>
<th>Intervals (cm$^{-1}$)</th>
<th>Relative heights</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Position</td>
<td>Width</td>
<td>$A_{max}$</td>
</tr>
<tr>
<td>Butadiene</td>
<td>46 260</td>
<td>490</td>
<td>209.6</td>
</tr>
<tr>
<td>Butadiene-$d_6$</td>
<td>46 470</td>
<td>360</td>
<td>-1.4</td>
</tr>
<tr>
<td>Isoprene (2-methylbutadiene)</td>
<td>44 970</td>
<td>490</td>
<td>+5.8</td>
</tr>
<tr>
<td>Trans-piperylene (trans-1-methylbutadiene)</td>
<td>45 410</td>
<td>570</td>
<td>+3.9</td>
</tr>
<tr>
<td>2,3-dimethylbutadiene</td>
<td>43 970</td>
<td>670</td>
<td>+10.8</td>
</tr>
<tr>
<td>Trans-2,trans-4-hexadiene</td>
<td>43 710</td>
<td>530</td>
<td>+6.3</td>
</tr>
</tbody>
</table>

* The three main bands observed in the diene spectra are numbered from low to high energy; i.e., band I corresponds to the "origin" band. Error estimates are $\pm 20$ cm$^{-1}$ for the position of band I, $\pm 40$ cm$^{-1}$ for the I-II interval, and $\pm 60$ cm$^{-1}$ for the II-III interval. In addition to these diffuse bands, sharp Rydberg peaks are observed in the jet spectra of butadiene and butadiene-$d_6$, at 50 574 $\pm$ 10 cm$^{-1}$ and 50 480 $\pm$ 10 cm$^{-1}$, respectively.

* $A_{max}$ are given as shifts in nm of band II of each diene with respect to that of butadiene, and are accurate to $\pm 0.4$ nm.
butadiene spectra are actually each composed of several overlapping vibronic features, their observed contours will depend on both the positions of those features (i.e., on the upper state vibrational intervals) and on their bandwidths. Thus, the observed intervals between the maxima of bands I and II will also depend on both of these factors. Since bandwidths in the jet spectra of butadiene and butadiene-d₆ differ substantially, with the width of band I of the butadiene spectrum exceeding that of the butadiene-d₆ spectrum by 40%, it appears likely that the increased interval between bands I and II in the latter spectrum is due mainly to its sharper bandwidths rather than to an increase in its upper state vibronic frequencies. Convincing evidence for this conjecture is provided by a comparison of the room temperature and the jet spectra of butadiene-d₁₀, which also exhibit an increase (of ∼50 cm⁻¹) in the interval observed in the sharper spectrum. That is, as bandwidths decrease and the overlapping of nearby bands becomes less severe, contributions of less intense vibronic transitions to the interval between bands I and II are reduced, and this interval increases toward that associated with the main, higher frequency carbon–carbon stretching mode.

D. Methylated butadienes

The corresponding transitions of methyl-substituted butadienes have recently been the subject of several theoretical and experimental studies. The room temperature spectra of many of these systems are even less informative than that of butadiene, due in part to the additional sequence band congestion introduced by the low-frequency torsional and bending vibrational modes of the methyl groups. The resulting spectral broadening is so severe in many of these systems, such as the monosubstituted butadiene trans-piperylene and the disubstituted dienes 2,3-dimethylbutadiene and trans-2,trans-4-hexadiene, as to completely obscure the valley between the first and second absorption bands. However, as shown in Fig. 5, jet cooling under the very moderate expansion conditions described in Sec. II sharpens the spectra, revealing in all of these systems the characteristic threecumped profile observed in the spectra of the unsaturated butadienes. Even in isoprene, whose room temperature bands are the least broad, the observed HWHM of the lowest energy band at 44 970 cm⁻¹ decreases markedly on cooling, from ∼700 cm⁻¹ at room temperature to ∼490 cm⁻¹ in the jet spectrum. In isoprene, as in butadiene-d₁₀, whose room temperature bandwidths undergo a comparable reduction on cooling, this sharpening is accompanied by a slight (∼100 cm⁻¹) blue shift of the maximum of the second absorption band. As shown in Table IV, the resulting spectrum of jet-cooled isoprene displays intervals and widths nearly identical to those observed in the spectrum of butadiene.

The methylbutadiene jet spectra are sharpened sufficiently to provide an experimental test of recent theoretical calculations which have predicted a distribution of absorption intensity between closely spaced excited states in butadienes methylated at interior positions. According to these results, the inductive effects of such methyl groups extensively mix the excited A⁻ and B⁻ states, producing a substantial increase in the oscillator strength of the 2 A⁻ → 1 A⁻ transition, whereas substitution at terminal positions leaves these states unmixed. While this model can account quantitatively for the red shifts observed in the absorption maxima of isoprene and 2,3-dimethylbutadiene relative to that of butadiene, it predicts a broadening of the spectrum of isoprene (2-methylbutadiene) relative to that of piperylene (1-methylbutadiene) that is not supported by our experimental results.

IV. DISCUSSION

A. Vibrational structure of the 1 B⁺ → 1 A⁻ absorption systems

A comparison of the 1 B⁺ → 1 A⁻ absorption systems of butadiene and trans-hexatriene to that of trans-transoctatetraene is of considerable interest in view of the dramatically different photophysical behavior of these closely related systems. Gas phase octatetraene has been reported to fluoresce from its 1 B⁺ state with a quantum yield of 0.10 ± 0.08 in the condensed phase at 77 K, relaxed emission from the lower-lying 2 A⁻ state is observed with a quantum yield of 0.58 ± 0.15. In contrast, no emission has been observed from butadiene or hexatriene following excitation into their 1 B⁺ states, and an upper limit of 5 x 10⁻⁵ has been estimated for the fluorescence quantum yield of hexatriene in 77 K solutions. One explanation that has
been proposed for the very different relaxation behaviors of butadiene and hexatriene from that of octatetraene is that the $1^1B_u^+$ states of the shorter polyenes may be substantially more distorted with respect to their ground states along C–C stretching or torsional coordinates, resulting in an increased rate of radiationless relaxation. The low temperature spectral bandwidths of these systems in the condensed phase have also been interpreted in terms of more distorted excited states for butadiene and hexatriene than for octatetraene. For example, although the $1^1B_u^+ \rightarrow 1^1A_g^-$ absorption bandwidths of octatetraene in solution are reduced from $\sim 890$ cm$^{-1}$ in 77 K hydrocarbon glasses$^{15}$ to $\sim 150$ cm$^{-1}$ in 4 K single site n-octane crystals,$^{7}$ the amorphous 77 K hexatriene spectrum does not become well resolved in single site n-hexane crystals at 4 K.$^{4}$ It has been suggested that this may reflect a larger geometry change associated with $1^1B_u^+ \rightarrow 1^1A_g^-$ excitation in the hexatriene system, resulting in increased matrix-induced broadening due to extensive phonon sideband excitation.$^3$

In view of these expectations, the most striking characteristic of the $1^1B_u^+ \rightarrow 1^1A_g^-$ jet absorption spectra of hexatriene and octatetraene, shown in Fig. 6, is the marked similarity in their vibrational developments. According to the vibrational analyses discussed above and in Ref. 10, the vibronic structure observed in both systems is dominated by totally symmetric C–C single and double bond stretching modes and skeletal deformations, indicating that the ground state planarity of both molecules is preserved in their excited $1^1B_u^+$ states. The ground and excited state frequencies of the three most active vibrational modes, listed in Table V, display similar shifts in both systems. In addition, the dimensionless normal mode displacements listed in the table, which were obtained from the integrated intensities of the vibronic bands observed in the jet absorption spectra, are very similar in the hexatriene and octatetraene systems for the three most active modes. The trend suggested in the table of greater displacements in the hexatriene system is consistent with the predictions of theoretical calculations,$^{17,35}$ but may simply represent larger contributions from nearby unresolved vibronic excitations to the more diffuse bands of the hexatriene spectrum.

As noted in Sec. III A, the relative displacements estimated in the preresonance Raman analysis of Myers et al.$^{33}$ for the three most prominent modes of the $1^1B_u^+ \rightarrow 1^1A_g^-$ spectrum of hexatriene agree to within 10% with the displacements obtained from the jet absorption spectrum reported here. In light of this good agreement, it is of considerable interest to compare to these the displacements obtained by the same preresonance Raman technique for butadiene$^{35}$ and isoprene,$^{33}$ whose jet absorption spectra are on their own relatively uninformative. In these analyses, the Raman band intensity information was used to establish relative normal mode displacements, and these were scaled for an optimum fit to the gas phase absorption spectra.$^{33,45}$ Good agreement with the observed gas phase spectra was obtained from the calculated displacements if widths of 500–600 cm$^{-1}$ were assumed for the inhomogeneously broadened room temperature vibronic bands$^{33,45}$; the extent of band narrowing observed in the jet spectra reported here support the validity of this assumption. As shown in Table V, the results of the Raman analyses suggest that the three vibrational modes most active in the $1^1B_u^+ \rightarrow 1^1A_g^-$ transitions of octatetraene and hexatriene also make the largest contributions to the corresponding diene transitions. The preresonance Raman analyses also indicate that the most prominent vibrational progressions in the absorption systems of both dienes occur along C–C stretching coordinates, as is the case for hexatriene and octatetraene. This assignment is supported by the jet absorption spectrum of perdeuterated butadiene, in which the separations between the observed diffuse features appear to increase toward the expected double bond interval of $\sim 1600$ cm$^{-1}$ as the bandwidths narrow on cooling (see Sec. III C). As shown in Table V, the quantitative normal mode displacements obtained from the Raman analyses for butadiene and isoprene are similar to those obtained here for hexatriene and octatetraene for the three most active modes.

In summary, the vibronic structure observed in the $1^1B_u^+ \rightarrow 1^1A_g^-$ absorption spectra of jet-cooled trans-hexatriene and octatetraene provides no evidence for a significantly more distorted excited state for the shorter polyene, in contrast to the expectations outlined at the start of this section. Furthermore, bandwidths and intervals observed in the

![Figure 6](https://example.com/fig6.png)
TABLE V. Frequencies and displacements for the most active vibrational modes in the $1^1B_u$ $\rightarrow$ $1^1A_g$ transitions of octatetraene, hexatriene, and butadienes.\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>C=C stretch ($\omega_x$)</th>
<th>C-C stretch ($\omega_y$)</th>
<th>C-C-C bend ($\omega_z$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$1^1A_g$</td>
<td>$1^1B_u$ $\Delta$</td>
<td>$1^1A_g$ $\Delta$</td>
</tr>
<tr>
<td>1,2-octatetraene</td>
<td>1612</td>
<td>1645(6)</td>
<td>1185</td>
</tr>
<tr>
<td>1-hexatriene</td>
<td>1627</td>
<td>1631(3)</td>
<td>1190</td>
</tr>
<tr>
<td>butadiene</td>
<td>1638</td>
<td>...</td>
<td>1203</td>
</tr>
<tr>
<td>isoprene</td>
<td>1640</td>
<td>...</td>
<td>1293</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Frequencies are given in cm\textsuperscript{-1}. Dimensionless normal mode displacements ($\Delta$) were obtained for octatetraene (Ref. 10) and hexatriene (this work) from the relative integrated intensities of the (0,0) and (0,1) vibrionic bands observed in the jet absorption spectra, using Eq. (1). The butadiene and isoprene displacements listed were obtained in Refs. 45 and 33, respectively, from resonance Raman data; for butadiene, results of Ref. 45 for the non-Duschinsky model are listed. The active modes in the isoprene spectrum were assigned to in-plane ($a'$) vibrations following the ground state assignments reported in Ref. 51.

\textsuperscript{b}The displacement along the $1190$ cm\textsuperscript{-1} mode in the hexatriene system is likely to be overestimated due to the contributions of unresolved vibrionic bands in this frequency region (see Sec. III A).

jet absorption spectra of butadiene and butadiene-\textit{d}_{4} (as well as the consonant results of the hexatriene analyses presented here and in Ref. 33) support the resonance Raman analyses of butadiene\textsuperscript{45} and isoprene\textsuperscript{33} which suggest similar degrees of distortion along in-plane modes in these systems and in the longer polyenes. Thus, the strikingly different relaxation behaviors of the $1^1B_u$ states of butadiene and hexatriene from that of octatetraene, and the congested appearance of the butadiene absorption spectrum as contrasted with the relatively sparse spectrum of octatetraene, do not appear explicable in terms of the in-plane vibrational activity that dominates the jet absorption and resonance Raman spectra of these systems. However, some insight concerning the dissimilar excited state properties of these systems is provided by a comparison of the bandwidths observed in the $1^1B_u$ $\rightarrow$ $1^1A_g$ absorption spectra of the jet-cooled molecules.

B. Vibronic bandwidths

The jet absorption spectra displayed in Fig. 6 exhibit a dramatic increase in vibronic bandwidths with decreasing chain length. As noted in Table VI, the origin band of jet-cooled octatetraene has a measured full width at half-maximum intensity of $18$ cm\textsuperscript{-1}.\textsuperscript{10} The origin band of \textit{trans}-hexatriene is about eight times broader, with a width of $155$ cm\textsuperscript{-1}, and the ~$1000$ cm\textsuperscript{-1} wide lowest energy band observed in the butadiene jet spectrum is in turn six times broader than that of hexatriene. It is noteworthy that this trend is not evident in the gas phase room temperature spectra. As is indicated in the table, the room temperature origin bands are broadened by at least $130$--$190$ cm\textsuperscript{-1} by thermal effects in all three systems. As a result, the bandwidths of the hexatriene and octatetraene spectra appear to be similar, and the butadiene bandwidths appear anomalously diffuse. The results reported here indicate, however, that when thermal broadening effects are reduced, the $1^1B_u$ $\rightarrow$ $1^1A_g$ spectra of the isolated molecules display a smooth increase in vibronic bandwidths with decreasing chain length. The remainder of this section explores possible explanations for this intriguing phenomenon.

The mechanism for band broadening in the isolated molecules studied here appears to be different from that operative in the condensed phase spectra. As reported by Snow \textit{et al.}\textsuperscript{15}, the bandwidths of the $1^1B_u$ $\rightarrow$ $1^1A_g$ transitions of the linear polyene series from butadiene to dodecahexaene in $300$ and $77$ K hydrocarbon solutions are also found to vary as a smooth function of chain length. These bandwidths (which for both the room temperature and the low temperature glasses exceed those observed in the gas phase at room temperature) are attributed to conformational disorder involving static torsions about the ends of the polyene chain.\textsuperscript{15} This type of broadening mechanism generally results in bandwidths that vary approximately inversely with the square of the number of double bonds in the molecule.\textsuperscript{15} It is clear from Table VI, however, that this function does not describe the bandwidth variation observed in the spectra of the cold, isolated molecules.

A second type of inhomogeneous broadening mechanism that can probably be discounted as making a major contribution to the observed trend in bandwidths is thermal broadening arising from rotational band or vibrational sequence band congestion. As noted above, the rotational temperature of the jet-cooled molecules is probably close to the terminal translational temperature of the supersonic argon jet, which we estimate to be below $10$ K under the expansion conditions employed in these studies. At these temperatures, rotational band congestion is not likely to account for a significant fraction of the observed bandwidths. The rotational

| Trans,trans-octatetraene\textsuperscript{b} | 210 | 18 | (192) |
| Trans-hexatriene | 290\textsuperscript{c} | 155 | (135) |
| Butadiene ($h_0$) | 1150 | 980 | (170) |

\textsuperscript{a}FWHM in cm\textsuperscript{-1}. The butadiene width listed is twice that of the low energy half of the first band.

\textsuperscript{b}Reference 10.

\textsuperscript{c}Reference 28.

contours of the octatetraene $1B_u^- \rightarrow 1A_g^-$ bands have been estimated to be only a few wave numbers even at room temperature, and the estimated rotational contour of the jet-cooled butadiene bands is about two orders of magnitude narrower than the observed bandwidths. The vibrational cooling of the samples is more difficult to estimate. However, the substantial narrowing of 130–190 cm$^{-1}$ observed in all three systems on cooling, and the consistencies of the bandwidths observed in the jet spectra when stagnation pressures were changed by factors of ~3, suggest that the contribution of vibrational sequence band congestion to the observed linewidths has been largely eliminated. In any case, residual sequence band broadening in the jet spectra is likely to be most significant in the octatetraene system, due both to its narrower bandwidths and its denser ground state vibrational manifold (requiring lower vibrational "temperatures") to achieve a substantial zero-point population and thus cannot account for the trend observed in the polyene series.

A broadening mechanism that may also be considered is that arising from unresolved vibronic excitations from the $1A_g^-$ state zero point level to low frequency vibrational levels in the excited $1B_u^-$ state. In order to make substantial contributions, these upper levels would have to have intervals small compared to the observed bandwidths and relatively large Franck–Condon factors. The activities of such vibrations in the butadiene and hexatriene spectra are not suggested by the preresonance Raman results for these systems. The lowest frequency feature observed in the preresonance Raman spectrum of hexatriene is the 359 cm$^{-1}$ in-plane bending mode which gives rise to a vibronic feature in the jet absorption spectrum that is well spaced from the origin band. Similarly, the preresonance Raman spectra of butadiene and isoprene do not display any features below 500 cm$^{-1}$, and the skeletal deformation mode near this frequency has a Raman intensity indicative of a relative small (0/1) Franck–Condon factor below 30% of that of the origin band. However, these preresonance Raman results do not rule out significant activities of nontotally symmetric vibrations. As has been noted by several investigators, the lowest excited single states of dienes as well as longer polyenes are likely to have highly anharmonic upper state torsional and bending modes. Unresolved transitions to closely spaced levels associated with such anharmonic potentials may produce considerable spectral congestion even in the absence of thermal broadening effects. Clearly, the contributions of this sort of broadening mechanism to the bandwidths observed in the jet spectra cannot be estimated without additional information, such as might be obtained from overtone and combination band intensities observed in rigorous resonance Raman spectra.

Another type of broadening mechanism that has been proposed for the diene $1B_u^- \rightarrow 1A_g^-$ spectra involves the overlapping of a nearby $2A_g^- \rightarrow 1A_g^-$ transition which might attain significant oscillator strength via vibronic coupling. However, this possibility is not supported by the relative constancy of vibronic bandwidths observed among the dienes studied here despite the wide range in their $1B_u^- \rightarrow 1A_g^-$ transition energies (see Table IV). For example, the half-widths observed in the very similar jet absorption spectra of butadiene and isoprene are the same to within experimental error although their transition frequencies differ by ~1300 cm$^{-1}$. In order to maintain an observed bandwidth within this narrow range, it would appear that the $2A_g^-$ and $1B_u^+$ states would have to track each other improbably closely over a relatively large range in transition frequencies. Results of PPP calculations including doubly excited configurations suggest, in contrast, a separation between the $1B_u^+$ and $2A_g^-$ states in the isoprene system that exceeds that in the butadiene system by more than 1000 cm$^{-1}$.

A similar broadening mechanism has been suggested for gas phase octatetraene, in which the $2A_g^-$ state is estimated to lie ~6400 cm$^{-1}$ below the $1B_u^+$ state. According to this proposal, weak vibronic coupling of the $1B_u^+$ levels with a dense manifold of levels from the lower-lying $2A_g^-$ state may account for the jet-cooled bandwidths. This coupling scheme would predict an increase in vibronic bandwidths with increasing transition frequency, since the density of coupled $2A_g^- / 1B_u^+$ levels increases rapidly with excess energy in both vibrational manifolds. This trend is, in fact, observed in the jet absorption spectrum of octatetraene, which exhibits a three- to fourfold increase in vibronic bandwidths within ~3000 cm$^{-1}$ of the origin band. The hexatriene jet absorption spectrum displays a similar although less dramatic broadening effect (see Table I). Clearly, these observations can also be accounted for by alternative mechanisms, such as increased anharmonic coupling within the pure $1B_u^+$ manifold with excess vibrational energy, or reduced excited state lifetimes due to the opening of photochemical channels at higher energies.

The nonfluorescence of the shortest polyenes suggest that the observed bandwidths may be due mainly to extremely short excited state lifetimes. For example, an upper limit of 5 x 10$^{-5}$ has been placed on the quantum yield of fluorescence from hexatriene following $1B_u^+ \rightarrow 1A_g^-$ excitation in low temperature matrices. An estimated oscillator strength of 0.7 for the $1B_u^+ \rightarrow 1A_g^-$ band of hexatriene suggests an intrinsic radiative lifetime of about 1.4 ms. In order to display a fluorescence quantum yield of less than 5 x 10$^{-5}$, molecule must escape the initially prepared excited state level in ~10$^{-13}$ s. This extremely short excited state lifetime corresponds to a natural linewidth of several hundred wave numbers. The 155 cm$^{-1}$ bandwidth observed in the hexatriene spectrum, then, is of a reasonable order of magnitude for the natural linewidth in this absorption system, in view of its large oscillator strength and its lack of fluorescence. A similar argument can be advanced for the nonfluorescent butadiene system.

Thus, the bandwidths observed in the jet spectra may indicate simply that the lifetimes of the linear polyene $1B_u^+$ states decrease rapidly with decreased chain length. This is not likely to be due mainly to photochemical deactivation rates, in view of the relatively low (<10%) photochemical yields that have been reported for methyl-substituted butadienes as well as longer polyenes. Intersystem crossing yields for excitation into the $1B_u^+$ states of the short polyenes are reported to be negligible. The observed bandwidths do appear compatible with a primary broadening.
mechanism involving internal conversion from the 1\(^1\)B\(_{u}^+\) state to a lower-lying excited singlet; S\(_i\) \rightarrow S\(_f\); internal conversion processes have rates of 10\(^{11}\)–10\(^{13}\) s\(^{-1}\) in most organic molecules studied.\(^{44}\) Clearly, the importance of such a mechanism cannot be present be confidently evaluated, in view of the unknown ordering among the lowest excited singlet states of gas phase butadiene, hexatriene, and octetraene. However, we note that internal conversion from the 1\(^1\)B\(_{u}^+\) excited state directly to the ground state via in-plane acceptor modes appears unlikely to account for the linewidths observed in this polynylene series. With origins for the 1\(^1\)B\(_{u}^+\) \rightarrow 1\(^1\)A\(_g^-\) transitions of these systems increasing from 35 553(3) cm\(^{-1}\) for octetraene, to 39 786(3) cm\(^{-1}\) for hexatriene, and to 46 260(20) cm\(^{-1}\) for butadiene, the rate of internal conversion to the ground state is calculated to be several orders of magnitude slower for the butadiene than for the octetraene 1\(^1\)B\(_{u}^+\) states when only in-plane relaxation is considered.\(^{30}\) The expected trend among internal conversion rates may, however, be significantly altered by the presence in some or all of these systems of very flat upper state potentials. For example, the semipirical theoretical calculations reported by Inuzuka and Becker for piperylene find extremely low barriers for twisting about terminal C–C double bonds in the lowest excited singlet and triplet states; the torsional barrier in the first allowed singlet (their S\(_i\)) is predicted to be below 1 kcal/mol.\(^{53}\) As these investigators point out, the energy separation between the 1\(^1\)B\(_{u}^+\) state and the planar ground state will decrease as the molecule twists to larger torsional angles, resulting in an increased probability of internal conversion.\(^{53}\) In order to account for the observed variation in linewidths, this mechanism would have to make greater contributions to the efficiency of 1\(^1\)B\(_{u}^+\) \rightarrow 1\(^1\)A\(_g^-\) internal conversion in the shorter polynynes. Such a trend is, in fact, supported by results of the semipirical calculations of Dinur et al., which find that barriers for torsion about the terminal C–C double bonds in the 1\(^1\)B\(_{u}^+\) states of octetraene, hexatriene and butadiene decrease rapidly with decreased chain length.\(^{12}\)

V. CONCLUDING REMARKS

The first allowed \(\pi^* \rightarrow \pi\) transitions of butadiene, butadiene-d\(_4\), several methyl-substituted butadienes and the trans- and cis-hexatriene isomers have been investigated by direct UV absorption supersonic jet spectroscopy. Due largely to the alleviation of vibrational sequence band congestion on cooling, vibronic bands observed in the jet absorption spectra are significantly sharpened over their room temperature counterparts, e.g., the origin bandwidths are decreased by over 100 cm\(^{-1}\) in all of the systems investigated. A comparison of the vibronic structure observed in the jet spectrum of trans-hexatriene with that reported in the previous paper\(^{10}\) for trans,trans-octetraene finds similar vibrational developments for the 1\(^1\)B\(_{u}^+\) \rightarrow 1\(^1\)A\(_g^-\) excitations of the two systems. In addition, bandwidths and intervals observed in the jet absorption spectra of the butadienes support the results of prereesonance Raman studies\(^{33,45}\) which have indicated normal mode displacements similar to those obtained here for the longer polynynes. Thus, the jet absorption results provide no evidence for a substantially more distorted 1\(^1\)B\(_{u}^+\) state in butadiene and hexatriene than in octetetraene, despite the dramatically different photophysical behaviors of these systems. In addition, the absorption spectra of this polynylene series reveal a smooth increase in bandwidths with decreased chain length. Possible explanations for this trend include increased coupling of the 1\(^1\)B\(_{u}^+\) states with lower-lying excited states in the shorter polynynes, or increased involvement of very flat upper state potential surfaces in their photophysics.

ACKNOWLEDGMENTS

The authors would like to thank Mr. John Schmidhauser and Dr. Yu-Tai Tao for separating the hexatriene isomers, and Mr. Roland Dunbrack for obtaining room temperature spectra. Financial support from the National Science Foundation is gratefully acknowledged.

\(^{16}\)R. McDardmid and J. P. Doering, J. Chem. Phys. 73, 4192 (1980).
46T. Shimamouchi, Table of Molecular Vibrational Frequencies, Consolidated Volume I (U.S. GPO, Washington, D.C., 1972), pp. 139, 143.
56This level density was calculated for harmonic potentials using experimental ground state frequencies where available (from Ref. 4) supplemented by calculated frequencies (from Ref. 17).
57An oscillator strength of 0.74 and an $\epsilon_{\text{max}}$ of 30 200 L/m cm has been reported for 1,6-dimethylhexatriene in hexane at room temperature [P. Nayler and M. C.Whiting, J. Chem. Soc. 3037 (1955)]. The much larger $\epsilon_{\text{max}}$ of 53 000 L/m cm reported in Ref. 32 for trans-hexatriene in isoctane would suggest that the oscillator strength of the unsubstituted molecule may be even larger. However, the $\epsilon_{\text{max}}$ of 21 000 L/m cm for gas phase hexatriene at room temperature reported in Ref. 28 suggests an oscillator strength of only 0.2 This does not appear to be an accurate estimate in view of the solution data; in addition, it implies a substantially lower oscillator strength for hexatriene than for butadiene, which does not seem likely (Ref. 4).
58The intrinsic lifetime $\tau$ was estimated from the oscillator strength, $f$, using $\tau = 1.514 f / \epsilon_{\text{max}}$, where $\tau$ is in seconds and $\epsilon_{\text{max}}$ is in cm. [J. I. Steinfeld, Molecules and Radiation (MIT, Cambridge, Mass., 1978), p. 28].