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Site-selective photochemistry and vibrational analysis of matrix-isolated 1,3,5,7-octatetraene radical cations in different conformations

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Upon ionization by x irradiation, *all-trans* 1,3,5,7-octatetraene (OT) gives an electronic absorption (EA) spectrum which indicates the formation of at least five different (peri)planar conformations ("rotamers") of OT⁺ next to the parent cation. Some of these undergo specific photochemical interconversions which are discussed on the basis of a complete scheme of OT⁺ rotamers and their connections via single bond-rotation processes. None of these photoreactions lead to any other than the initially observed six species which seem to form a distinguished set within the 20 possible OT⁺ rotamers. By very narrow bandwidth irradiation, interconversions can be induced to take place in a site-selective fashion. The resulting well-resolved difference spectra allow an analysis of the site dependence of the different ion's first two EA bands. Surprisingly, the extent of this site dependence varies greatly between different OT⁺ rotamers and between different electronic transitions of a given rotamer. Finally, a detailed vibrational analysis of the first two absorption bands of *all-trans* OT⁺ is given.

I. INTRODUCTION

The spectroscopy and photochemistry of linear conjugated polyenes¹ isolated in cryogenic matrices or in jet expansions has been a topic of considerable interest in recent years.² 1,3,5,7-Octatetraene (OT) thereby received the most attention, being the simplest member of this class of compounds for which the long-standing controversy about the identity of the first excited state² has been unequivocally settled.³ Thus, the subtle differences in relative energy and vibrational structure of *S*₁ and *S*₂ (*2*¹*A*_g and *1*¹*B*_u, respectively) in different isomers and/or conformers of matrix-isolated OT (*trans-trans*,⁴ *cis-trans*,⁵ *cis-cis*,⁶ *s-cis*⁷) as well as their photochemical interconversions were explored in great detail. At the next level, the influence of different host materials on the above properties was investigated^{4(c),5(b),8} and now even different sites in a given matrix have come under scrutiny.^{6(b),9}

On the other hand, a wave of interest in matrix-isolated polyene radical cations¹⁰ has been recently begun to surge with the appearance in short order of publications dealing with hexatriene,^{11,12} octatetraene,^{13,14} and decapentaene¹⁵ cations and their photochemical formation from (poly)cyclic isomers.

The electronic structure of polyene cations expresses itself through a strong high energy and a weak low energy absorption whose intensity ratio increases as the chain gets longer. Interestingly, these features cannot be explained on the basis of single determinant theory as employed in the various models used (very successfully) in discussing polyene photoelectron (PE) spectra. As in the case of neutral polyenes, configuration interaction plays a crucial role in determining the relative position of excited states and the oscillator strengths for electronic transitions from the ground state.^{10,16}

The electronic absorption (EA) spectra obtained after ionization of polyenes embedded in noble gas matrices are, however, usually rather complex and indicate the presence of more than one species. In the case of hexatriene⁺ it has been shown that certain components of these spectra can be selectively removed by narrow-bandwidth photolysis^{11,12} and that the spectra of the species thus bleached all show a similar habitus typical for polyene cations. Hence it was concluded that they are due to different conformations of the polyene cation, attained from the *all-trans* variety through bond rotation processes in the course of ionization. A similar conclusion was reached for the case of OT⁺ generated from cyclic isomers.^{13,14}

In discussing bond rotation processes in polyene cations one has to bear in mind that upon removing a π electron from a polyene, the distinction between essential single and double bonds and hence the differentiation between isomers and conformers is lost. We therefore proposed the term rotamers to describe different (peri)planar geometries of polyene cation chains.¹² Judging from the thoroughly analyzed case of hexatriene⁺,¹¹ the band maxima for different polyene cation rotamers are sufficiently displaced to allow their EA-spectral distinction and sometimes even the observation of specific interconversions among them.^{12,14} However, the number of *observed* rotamers does not seem to rise in parallel with the number of *possible* rotamers¹⁷ as the chain length increases [butadiene⁺: 2 possible, 1(2) observed^{10,18}; hexatriene⁺: 6 possible, 5 observed¹²; octatetraene⁺: 20 possible, 7 observed¹⁴]. One could argue that the number of bond rotation processes occurring in the course of polyene ionization is limited and that the number of observed rotamers will therefore converge, but the fact that the very same set of rotamers is also observed after ionization and subsequent photolysis of (poly)cyclic isomers conflicts with this interpretation.

The present paper describes a detailed study of different OT⁺ rotamers with the aim of assessing in particular whether each of the six band systems observed after ioniza-

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tion does indeed correspond to only one rotamer. We had previously observed that the EA-band structure of OT^+ is considerably complicated by site effects,¹⁴ which led us to develop a new technique of narrow-bandwidth (FWHM = 0.3 to 1 nm) variable-wavelength photolysis (see Sec. II) for the study of site-specific photoreactions. Since the actual EA spectra often suffer only very small changes in the course of such reactions, we will take recourse to *difference spectra* for the presentation of these results since we found that specific interconversions can often be most lucidly visualized in this fashion. In addition, these measures proved to be rewarding in that the resulting spectra are often sufficiently well resolved to permit extensive vibrational analyses.

II. EXPERIMENTAL

The sample preparation vacuum line and matrix isolation apparatus was identical to that described

earlier.^{10,12(a),14} Using this, 1:2 mixtures of OT and CH_2Cl_2 diluted with a 1000–2000 molar excess of Ar (relative to OT) were prepared and deposited at a rate of ~ 1 mmol/h onto a sapphire window held at ~ 20 K. Ionization was effected by 2 h x irradiation through a beryllium window. Due to the strong neutral absorption the ion yield could not be determined but is assumed to lie in the 15%–20% range in analogy with earlier cases.¹² Optical spectra were recorded on a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer, transferred and worked up digitally on a PDP 11/34 minicomputer. Full spectra were usually recorded with a spectral slitwidth of 0.4 nm and five data points per nm. For vibrational analysis, partial spectra taken at twice the above resolution were used.

In order to record reliably the often very small changes in absorbance before and after narrow-bandwidth photolyses, a precise and constant alignment of the sample in the optical beam of the spectrophotometer is crucial. This is optimally guaranteed if the sample position remains un-

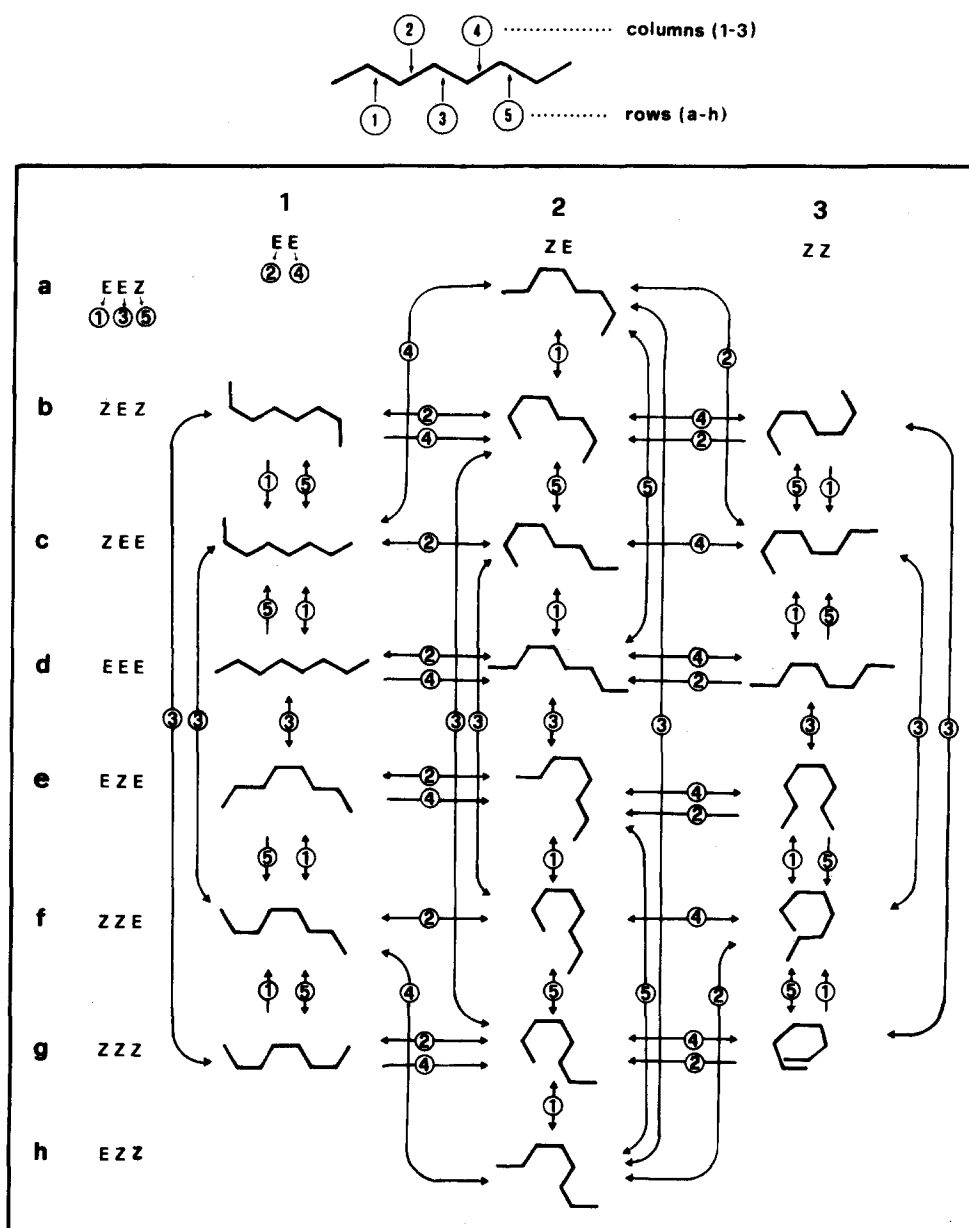


FIG. 1. Scheme of OT^+ rotamers and their interconversion pathways. Rotamers with the same configuration around bonds 2 and 4 (double bonds in neutral OT) are in the same column, those with the same configuration around bonds 1, 3, and 5 (essential single bonds in neutral OT) in the same row. Circled numbers indicate bonds around which rotation is to occur to yield adjacent rotamers. For geometries with twofold symmetry (rows b, d, e, and g of columns 1 and 3) additional *unidirectional* arrows lead to adjacent rotamers to indicate equivalence of rotation around bonds 1/5 or 2/4 in these cases. Individual species are identified by the column number (1–3) followed by the row letter (a–h), i.e., 1d for all-*trans* OT^+ . Note that *EEZ/ZEE* and *ZZE/EZZ* are equivalent in columns 1 and 3 but not in column 2.

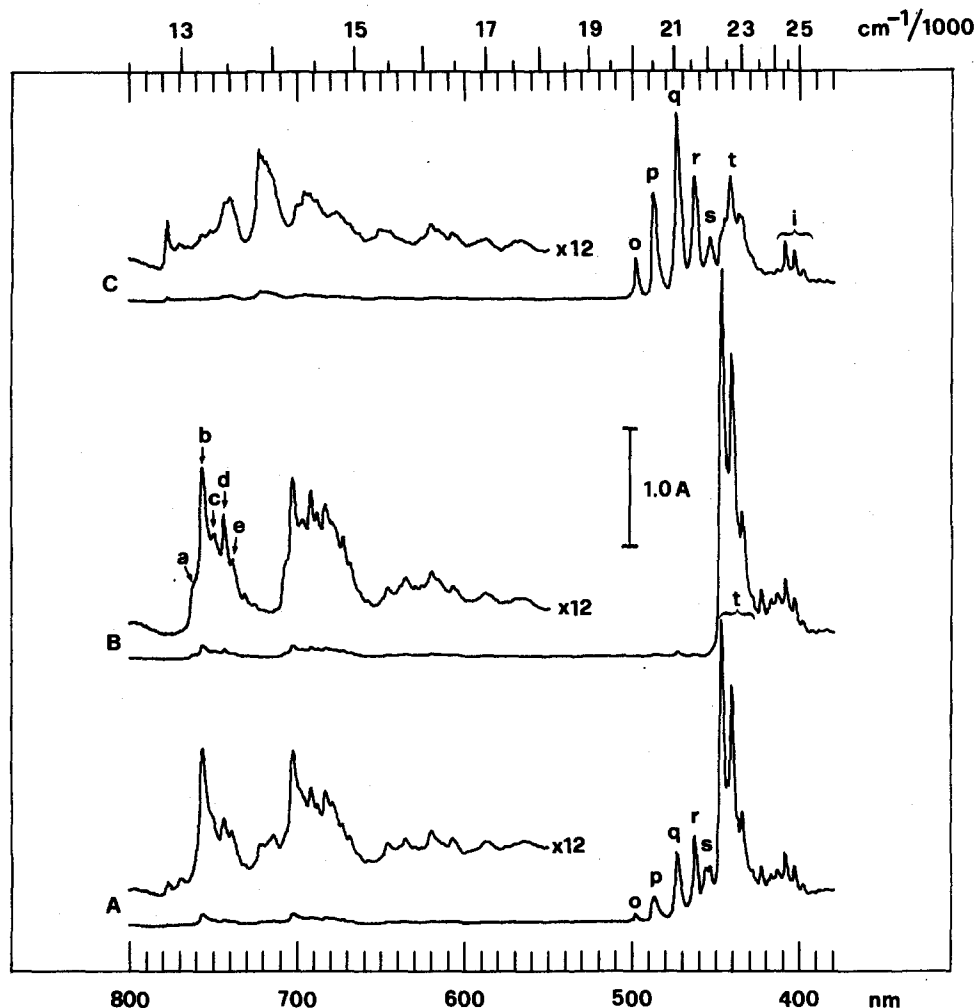


FIG. 2. Spectra of all-*trans* octatetraene (OT) embedded in an Ar matrix doped with $\sim 0.1\%$ CH_2Cl_2 (A) after 2 h x irradiation, (B) after bleaching of all absorptions between 500 and 455 nm, and (C) after 5 nm FWHM irradiation at 447 nm. The scale is identical for all three spectra (vertical bar). *o*–*t* represent different OT^+ rotamers, *a*–*e* different sites of *t* (see the text).

changed over the course of an entire experiment. Therefore, all photolyses were carried out using the double monochromator of the Lambda 9 spectrophotometer as a precise optical filtering element. Since the power of the built-in tungsten lamp proved insufficient, the light from a 1 kW argon plasma arc¹⁹ was focused through a new opening into the optical system of the spectrophotometer such that optimal light throughput was achieved. This setup usually permitted exhaustive bleaching of individual sites of the highly photolabile OT^+ rotamers within 30–90 min at 0.5 nm FWHM, somewhat longer at even smaller slit widths. At all times, the sample compartment remained carefully shielded from ambient light which had been found to induce rapid photorearrangements even at low levels.

Octatetraene was synthesized according to Gavin *et al.*,²⁰ avoiding, however, exposure to air after the pyrolysis. Instead of the proposed recrystallization or column chromatography, the crude material was purified by fractional condensation under high vacuum using a series of traps held at different temperatures. The resulting samples were of greater than 99% purity according to NMR and GC and did not undergo any noticeable change upon prolonged storage under vacuum in a freezer. CH_2Cl_2 used as an electron scavenger was analytical grade and Ar was of 99.995% purity.

III. OUTLINE OF PROBLEM

Figure 1 shows a scheme of all possible (peri)planar

OT^+ rotamers and the pathways for their interconversions via single bond-rotation processes. The scheme was arranged such that rotations around the original internal $\text{C}=\text{C}$ bonds of neutral OT (bonds 2 and 4) occur between adjacent columns while rotations around the original $\text{C}-\text{C}$ bonds (1, 3, and 5) occur between adjacent rows.

Since there are *five* internal bonds in OT^+ , each rotamer is in principal connected to five others, a number which reduces to three for geometries with twofold symmetry (C_{2h} or C_{2v}) where bonds 1/5 and 2/4 are equivalent (indicated by additional unidirectional arrows in Fig. 1). Compared to the previously analyzed case of hexatriene⁺ (six possible rotamers, *three* internal bonds¹²) the present scheme is therefore of such complexity that an identification of all rotamers cannot be envisaged. Nevertheless, it shall serve as a basis for the discussion of the various photoinduced interconversions among OT^+ rotamers described below.

IV. RESULTS AND DISCUSSION

A. Primary spectra

As a reminder, the spectrum of matrix-isolated all-*trans* OT after 2 h x irradiation is displayed in Fig. 2(A). As is to be expected for a polyene cation, it consists of a weak red and an intense blue system of absorptions. Concerning the latter we first note a dominant set of bands labeled *t* which are

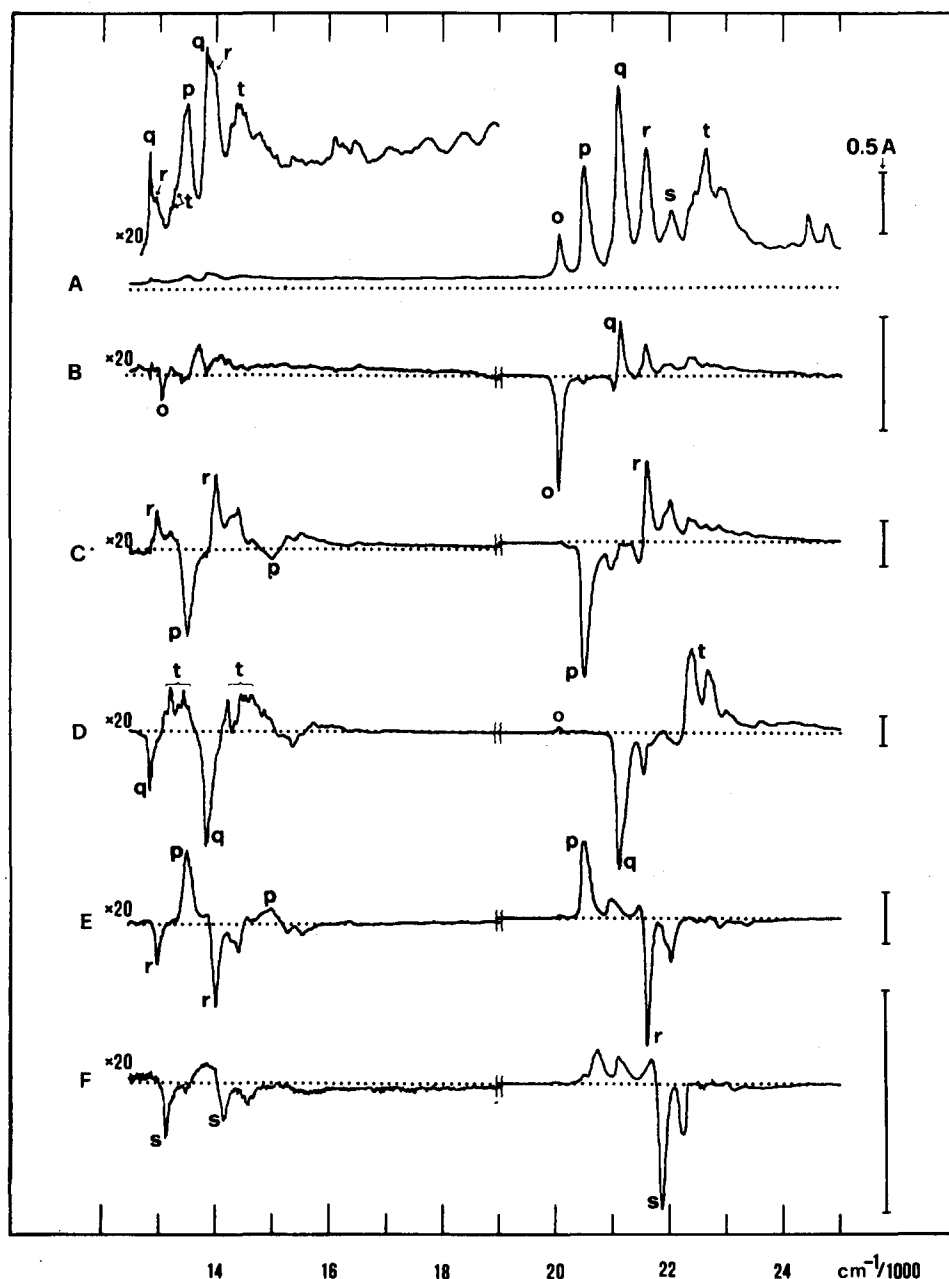


FIG. 3. Selective bleaching of bands *o*–*s* (description of procedure and analysis, see the text), starting with the spectrum shown in trace (A). The difference spectra (B)–(F) were recorded in two parts (13–18.5 and 18.5–24.5 $\text{cm}^{-1}/1000$) and are displayed such that the low-energy part is always 20 times expanded relative to the high-energy part. Absolute scales for the latter are displayed on the right (vertical bars). Horizontal dotted lines represent the 0A line.

assigned to the parent cation, i.e., *all-trans* OT^+ . Furthermore, it shows a group of bands labeled *o* through *s*²¹ due to other, partially *cis*-configured OT^+ rotamers formed in the process of ionization. Exposure to light between 500 and 450 nm ²² leads to the disappearance of these latter bands together with some of the corresponding weak red absorptions and a concomitant increase in the *t* absorptions. We believe that the resulting spectrum 2(B) represents that of essentially pure *all-trans* OT^+ (except for the peaks below 410 nm , see below).

From previous studies¹⁴ whose results are fully confirmed by the selective bleaching experiments described below, we know that the complex structure of the red band system in Fig. 2(B) is due to the presence of *all-trans* OT^+ in (at least) five different sites of the Ar matrix. Note, however, that these sites [vibronic origins labeled *a* through *e* in Fig. 2(B)] are not uniformly garrisoned in the course of the

photochemical formation of *t* from the other observed rotamers: while the height of peaks *b* and *e* increase only slightly, shoulder *a* and peak *d* grow markedly, indicating that the latter two sites are preferentially populated in this process. The site-selective photolyses described in the following section will yield more detailed insight into this matter.

Broadband (5 nm FWHM) irradiation at 447 nm leads to almost complete bleaching of all *t* absorptions and the reappearance of *s* through *o* with their corresponding red absorptions [Fig. 2(C)]. Apart from this, a group of small peaks remains around 400 nm . These do not show up in the spectra of OT^+ generated from cyclic isomers¹⁴ and since they are completely insensitive to all operations described below we conclude that they are due to a stable neutral radical or closed-shell ionic byproduct of OT^+ irradiation.

Although it may appear at first sight as though the species responsible for bands *o* through *s* are formed *simulta-*

neously from *t*, this proves not to be the case. This becomes evident upon prolonged photolysis at 447 nm whereupon bands *o*, *p*, and *s* continue to increase while *q* and *r* decrease. Evidently, a series of consecutive reactions which will be studied individually below leads to the slow establishment of a photostationary state involving all observed OT⁺ rotamers.

B. Selective bleaching of different OT⁺ rotamers

1. Observations

In our previous study on the ring opening of 1,3,5-cyclooctatriene cations,¹⁴ we had attempted to establish relationships between the blue and red band systems of the different resulting OT⁺ rotamers and gain some insight into their interconversions by selective bleaching of individual bands in the 500–455 nm (20 000–22 000 cm⁻¹) spectral region. This attempt had met with limited success, partially due to the relatively broad irradiation bandwidth (typically 3–5 nm) and partially due to a pronounced spread in λ_{\max} for certain rotamers occupying different matrix sites which resulted in broad features in the difference spectra. We therefore decided to reinvestigate this problem by applying our new narrow-bandwidth irradiation technique to OT⁺ samples obtained directly from neutral OT, thus hoping for a simpler site structure.

Figure 3 displays the collective results of this study, starting with the sample of Fig. 2(C) whose spectrum is replotted on a wave number scale in the top trace (A). Bands *o* through *s* were individually bleached by a series of consecutive 0.5 nm FWHM photolyses, moving in small increments through each absorption band and collecting the resulting difference spectra²³ until a change in band structure indicated that a new photoreaction had begun to occur. At this point, the previously obtained (similarly looking) difference spectra were added up to give the traces displayed in Figs. 3(B)–3(F). Note that these do not necessarily represent the results of complete bleaching of each rotamer because secondary photoreactions induced by irradiation into a vibrational progression of another than the "targeted" rotamer (for example a photoproduct of the latter) sometimes led to pronounced changes in the appearance of the difference spectra prior to completion of a given series. In order to minimize such interferences, all absorptions lying at lower energies (down to 20 000 cm⁻¹) than those of the next targeted rotamer were exhaustively bleached before the following series was initiated. This measure also proved to be necessary for the observation of distinct interconversions between individual rotamers (see below).

As can be seen, the above described procedure led to a set of very informative results: not only do the relationships between the blue and the red band systems of the different species (see Table I) stand forth very clearly but in addition, very selective interconversions between individual OT⁺ rotamers can be observed. Thus, photolysis of species *o* results in almost exclusive formation of *q* [Fig. 3(B)] which does, however, only partially revert to the former and mainly crosses over to *t* upon photolysis [Fig. 3(D)]. On the other hand, species *p* and *r* are apparently involved in a reversible

TABLE I. EA peak positions of different OT⁺ rotamers.^a

Species	<i>D</i> ₁		<i>D</i> ₂	
	nm	cm ⁻¹	nm	cm ⁻¹
<i>o</i>	756.6	13 062	498.2	20 072
	746.0	+ 343	488.0	+ 420
	741.0	+ 433	475.4	+ 963
<i>p</i>	740.0	13 514	487.4	20 517
	668.2	+ 1 450	476.6	+ 465
			466.0	+ 942
<i>q</i> ^b	777.4	12 863	473.6	21 115
	722.4	+ 975	464.0	+ 435
	653.2	(+ 2 495)		
<i>r</i>	770.2	12 984	462.6	21 617
	713.0	+ 1 042	454.0	+ 410
	693.0	+ 1 446		
	655.8	(+ 2 310)		
	643.0	(+ 2 568)		
<i>s</i>	760.6	13 147	457.0	21 882
	740.4	+ 360	449.4	+ 370
	706.4	+ 1 010		
	656.0	+ 1 430		

^a See Fig. 2. Original spectral information is in nm (± 0.2 nm). Bold figures represent highest peak, figures with a "+" vibrational progression relative to origin of a given electronic transition. For the *t* rotamer, see Figs. 3 and 4.

^b See also Fig. 3.

photoreaction [Figs. 3(C) and 3(E)] which can be driven repeatedly with minimal loss of *p* + *r*. Only in the case of *s* [Fig. 3(F)] are the results somewhat ambiguous. Actually, this rotamer remains only in minute quantities after complete bleaching of *o* through *r* [most of the original absorption in Fig. 3(A) at this wavelength is due to vibrational progressions of *r* and *q*] and its photoreaction is less specific than those of the other rotamers. In fact, an absorption with λ_{\max} exactly between those of *p* and *q* is formed which may be due to a rotamer that is not present after ionization of OT or photolysis of *t* [Figs. 2(C) and 3(A)].

The results in Figs. 3(B)–3(F) can finally be used to analyze the red band system in Fig. 3(A) in terms of the contributions of OT⁺ rotamers *o*–*t*. Thereby it becomes evident that the fraction of *t* in the sample had initially been very small. Nevertheless, the spectrum obtained at the end of this series of photolyses is again identical to that in Fig. 2(B) (pure *t*) which indicates complete reversibility of all photoconversions among OT⁺ rotamers.

2. Assignments

It is tempting to try and establish a relationship between the above observations and the scheme of possible bond-rotation processes outlined in Fig. 1, in analogy to the earlier case of hexatriene⁺. There, we had assumed that selective and clean photoinduced interconversions did only occur between rotamers separated by a single bond-rotation process, an assumption which led to a consistent rationalization of the observed reaction pattern. If we carry this type of reasoning over to the present case then *q* must be adjacent to *t* (1d in Fig. 1), hence correspond to 1c, 1e, or 2d. Likewise, *p* and *r* form a pair linked by a single arrow and further evi-

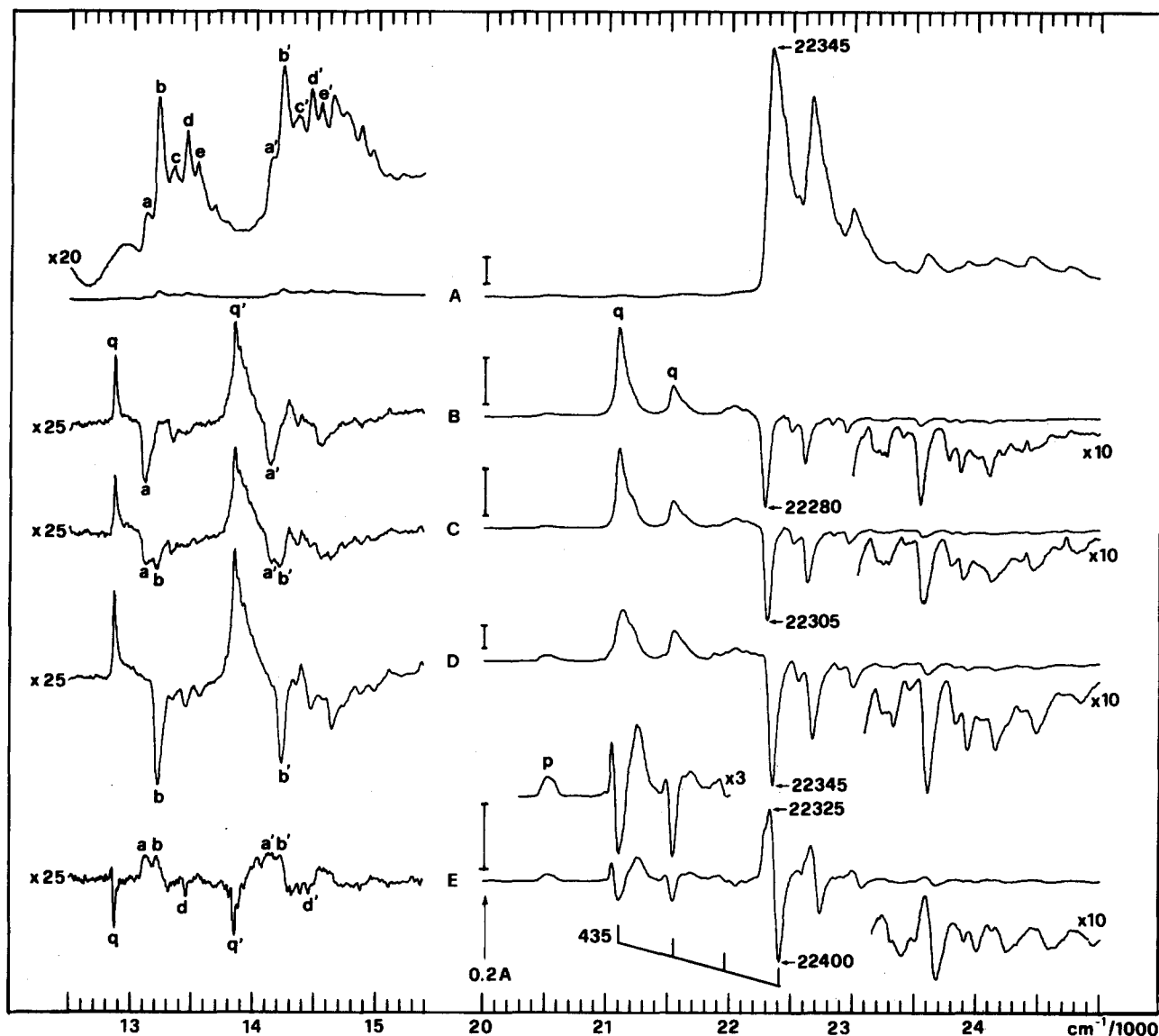


FIG. 4. Site-selective bleaching of all-*trans* OT⁺ [*t*, spectrum (A)]. *a*–*e* denote the vibrational origins, *a'*–*e'* the dominant 1010 cm^{−1} progressions of *t* in five different sites. The range between 15 and 20 cm^{−1}/1000 is not displayed because it contains no useful spectral information. Absolute scales for the high-energy parts of the spectra are indicated by vertical bars (0.2A) and are also applicable to the low-energy part after 25-fold expansion. Procedure and assignments, see the text.

dence obtained from the site-selective photolyses described in the next section indicates that *r* can also be formed from *t*.²⁴ Species *o* can in turn not be too far removed from *q* because the latter rotamer is formed directly upon its photolysis and *o* is at least partially reformed from *q*. On the other hand, *o* is observed upon photolysis of ring-opened cyclooctatriene⁺¹⁴ which we had assigned to 3g in Fig. 1 and must hence lie in the neighborhood of this latter species. Finally, *s* which appears only in minute amounts is not clearly linked to any of the other species *o*–*r* and *t* and may actually represent the only indication of a passageway to another set of rotamers.

Unfortunately the above described set of “chemical” relationships proves insufficient to yield an unambiguous assignment of all absorptions in terms of the geometries depicted in Fig. 1. It would therefore be of great help if the shifts in λ_{\max} observed for the different OT⁺ rotamers could be used to support individual assignments. The EA spectra of different hexatriene⁺ rotamers indicate that the $D_0 \rightarrow D_2$ transi-

tion suffers a red shift in proportion to the number of cisoid configurations within the polyene cation framework.^{12(a)} However, no quantitative theoretical model of practical use is currently available which allows a reliable prediction of these spectral shifts and the variations in absorptivity between different polyene cation rotamers. PPP-CI, which has generally proved to be of great help in assigning and discussing EA spectra of planar π systems and their radical ions²⁵ is very insensitive to changes in long range interactions unless the resonance integrals are explicitly adjusted, for which no practically tested guidelines exist. Open-shell all valence CNDO²⁶ or NDDO based procedures²⁷ are presumably not much better in this respect because they treat the π system (which is alone relevant in the present context) in much the same way as the simpler PPP procedure and higher level calculations are unfeasible for practical reasons. We therefore have to content ourselves at present with staking out the ground (Fig. 1) on which the observed chemistry (Fig. 2) takes place and await future developments in theory

to aid in the quest for an unambiguous and consistent assignment.

C. Site-selective photolyses

1. The *all-trans* rotamer

As noted above, the traces in Figs. 3(B)–3(F) always represent *sums* of difference spectra obtained in the course of a series of successive narrow-band photolyses, a form of presentation which proved necessary to obtain a satisfactory S/N ratio for the weak red band systems in all cases. What does, however, not become evident in this way is the fact that bleaching can actually be effected down to the level of *individual sites*. This is best illustrated on the example of the *all-trans* rotamer *t* whose red band system had been found to show a distinct site structure.¹⁴ Although we would have ideally liked to take advantage of this feature by effecting the photolyses in this frequency range, this approach proved to be too time consuming due to the sluggishness of the photo-reactions induced by excitation into the first excited state D_1 . Thus, the procedure described above was applied to the D_2 absorption of a sample of essentially pure *all-trans* OT⁺ [Fig. 4(A)].

The first changes were noticed when the monochromator was set at 449.5 nm ($22\,245\text{ cm}^{-1}$) where 90 min photolysis resulted in the difference spectrum shown in Fig. 4(B). Inspection of the expanded red band system reveals that only those *t* rotamers occupying site *a* were bleached in this process, with concomitant exclusive formation of rotamer *q* in what appears also to be essentially a single site (apparently *t* and *q* form a pair of rotamers related by a reversible photoisomerization similar to that observed above for *p* and *r*). After exhaustive photolysis at this wavelength, the monochromator setting was decreased by 0.5 nm where another 90 min photolysis gave difference spectrum (C) in Fig. 4. Although the train of downward-pointing peaks in the blue region is almost superimposable to that immediately above (apart from a general $\sim 25\text{ cm}^{-1}$ blue shift) the red band system shows that *two* sites (*a* and *b*) were simultaneously bleached under these conditions. Furthermore, the shoulder on the *q* band at $21\,000\text{ cm}^{-1}$ indicates that this rotamer is concomitantly formed in two different sites.

The most pronounced spectral changes were induced by subsequent irradiation at 448 nm [Fig. 4(D)] which led to the disappearance of the red absorption labeled *b*. The difference spectrum (D) shows that the origin of the blue band system now coincides exactly with the peak maximum in the original spectrum (A) and that the dominant site *b* is almost exclusively affected by this 448 nm photolysis (apart from a very small fraction of *c*). On the other hand, the broad shape of the $21\,000\text{ cm}^{-1}$ band of *q* indicates that this species is formed in different sites. Apart from this the intensity ratio of the two peaks between $21\,000$ and $22\,000\text{ cm}^{-1}$ has significantly decreased and a noticeable quantity of rotamer *p* is formed. The latter two observations may be related in that the increase in the $21\,450\text{ cm}^{-1}$ band intensity presumably indicates the formation of *r* which is in turn partially converted to *p* through irradiation into one of its vibrational progressions. Perhaps site *b* is better predisposed to favor *t* \rightarrow *r* conversion than site *a* which would explain the in-

crease in *r* formation in going from Fig. 3(B) to Fig. 3(D).

Upon 0.5 nm FWHM irradiation at $\lambda < 447.5\text{ nm}$ one begins to observe rather complex spectral changes, in particular a simultaneous increase and decrease of absorptions lying within the same band system. As an example, Fig. 4(E) shows the results of photolysis at 447 nm ($22\,370\text{ cm}^{-1}$). Although it looks at first sight as though a photochemical site interconversion of species *t* has taken place, we prefer an alternative explanation which also takes into account the simultaneous change in the $21\,000$ – $22\,000\text{ cm}^{-1}$ range: extrapolation of the 435 cm^{-1} vibrational interval observed in the second electronic transition *q* shows that the (presumably very weak) fourth progression peaks exactly at the wavelength of the present irradiation which will therefore result in *simultaneous* bleaching of *t* and *q*. More precisely, inspection of the changes in the red band system suggests that rotamer *t* in site *d* is bleached with concomitant formation of rotamer *q* (in at least two different sites as judged from the shape of the blue band system) while at the same time rotamer *t* is formed in sites *a* and *b* by photolysis of *q* in the site affected most strongly by 447 nm photolysis. Apparently, bleaching of rotamer *q* had been avoided during the previous photolyses between 449.5 and 448 nm where the absorbance of *q* goes through a minimum.

2. Other rotamers

Similar experiments can be done on all OT⁺ rotamers. As an example, two such series of photolyses on the interconvertible pair *p/r* are documented in Fig. 5.

As in the above case, the species *lost* during consecutive 0.5 nm FWHM irradiations in 0.5 nm intervals show virtually identical but slightly displaced spectra for both the *p* \rightarrow *r* (left-hand side) and the *r* \rightarrow *p* conversion (right-hand side). On the other hand, the spectra of the species *formed* in these processes are less similar which indicates that the latter are produced in different sites, depending on which site of the starting rotamer is bleached (see especially the *r* \rightarrow *p* conversion). We also note that the peak labeled *s* is predominantly composed of vibrational progressions of rotamer *r* (although not entirely because one peak remains after complete bleaching of *r*, see also Fig. 3).

In conclusion of this series of experiments we wish to point out that even though up to 50 different narrow-band-width photolyses were carried out in the course of the bleaching of bands *o* through *s*, none of the corresponding difference spectra yielded firm evidence for the presence of any other than the initially visible rotamers. In spite of the sometimes considerable spread in λ_{max} for different matrix sites (see below), all data could be assembled into *six* groups of spectra showing very similar vibrational intervals and relative peak intensities (compare Figs. 3 and 4).

Finally, an intriguing observation concerns the wide spread in site sensitivity of the different rotamers and/or of their two EA bands. This sensitivity is most pronounced in the *all-trans* rotamer where the vibrational origins of the $D_0 \rightarrow D_1$ transition span a range of 420 cm^{-1} while this reduces to some 250 cm^{-1} in the $D_0 \rightarrow D_2$ transition. On the other hand, the first band of the *q* rotamer is completely insensitive to different sites which lead in turn to a ~ 300

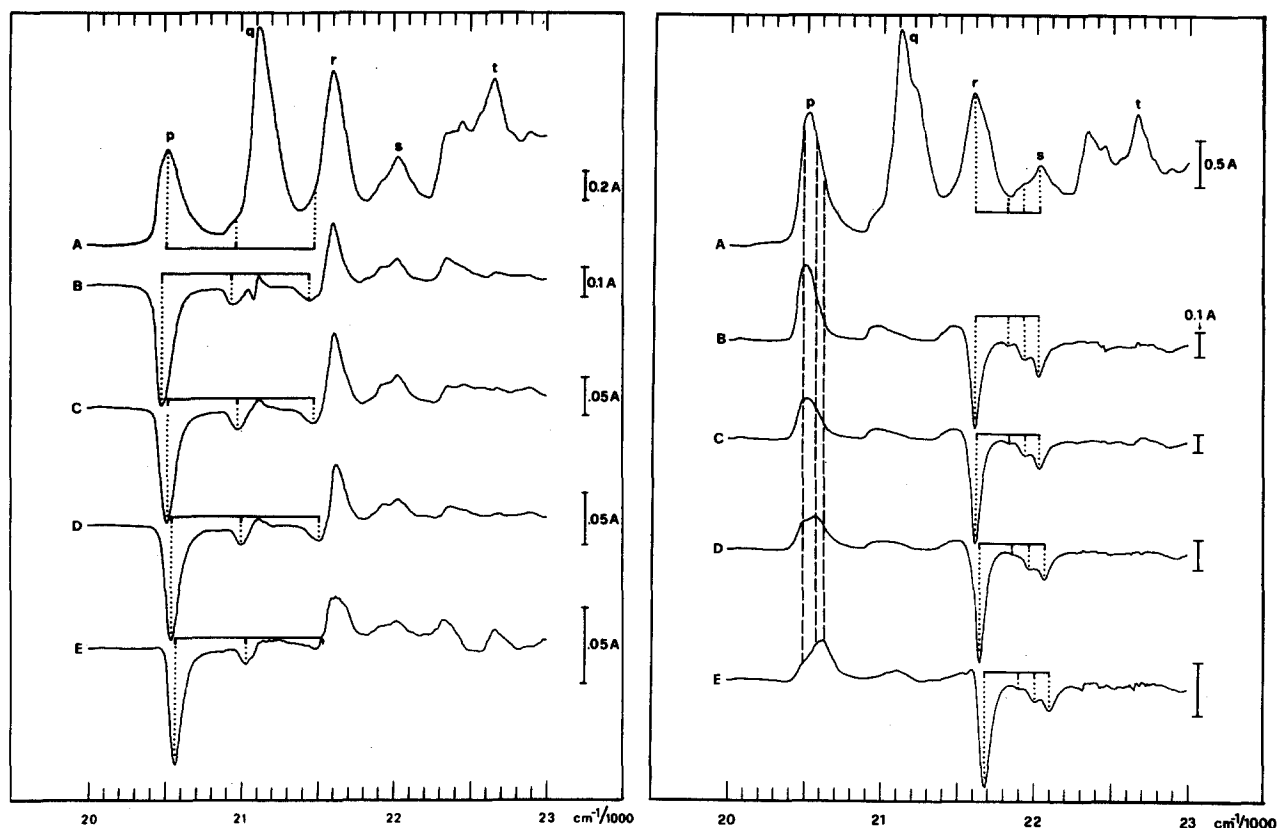


FIG. 5. Site-selective bleaching of *p* (left-hand side) and *r* (right-hand side). (A) is the starting spectrum, (B)–(E) are difference spectra for 0.5 nm FWHM bleaching in 0.5 nm intervals, going to higher energies. The dominant vibrational progressions of the bleached species are highlighted in order to visualize the progressive displacement of all peak maxima. Note also the shift in band maxima for the species formed upon photolysis (upward-pointing peaks).

cm^{-1} spread in λ_{max} for the second absorption. For the other rotamers, the $D_0 \rightarrow D_1$ transition is generally less affected if compared to the $D_0 \rightarrow D_2$ transition whose vibrational origins in the difference spectra cover a range of $\sim 200 \text{ cm}^{-1}$ as photolyses are carried out at progressively lower wavelengths. However, none of the EA bands except the first transition of the all-*trans* rotamer show distinct peaks with reproducible λ_{max} for different sites. This may be due to the fact that the Ar matrix provides a greater number of similarly shaped cavities for the more globular, partially *cis*-configured rotamers. Also, the resolution achieved by our present technique may be insufficient to resolve the closely spaced peaks associated with such similarly shaped matrix sites. On the other hand, a close inspection of the vibrational intervals for both band systems of the latter shows that they are identical within experimental uncertainty ($\pm 2 \text{ cm}^{-1}$ in the red, $\pm 5 \text{ cm}^{-1}$ in the blue band) for the different observed sites.

3. Vibrational analysis of the OT^+ spectrum

In their recent investigation, Dunkin *et al.*¹³ had attempted an analysis of the vibrational structure of OT^+ in the D_1 and D_2 states on the basis of spectra similar to that displayed in Fig. 2(A). This analysis was, however, severely hampered by the complicated site structure which occurs especially in the red band system. It was therefore desirable to try and disentangle this site structure in the hope of obtaining simpler spectra that are more easily amenable to vibrational analysis.

While it is often relatively easy to obtain emission spectra corresponding to M^+ occupying single sites in noble gas

matrices (selective excitation of a single site by laser light²⁸), these do not yield any detailed information on excited states (except of the first excitation energy). Conversely, the corresponding absorption (or excitation) spectra are more difficult to obtain. Bondybey *et al.* have recently obtained an excellent excitation spectrum of hexatriene⁺ in Ne by monitoring the fluorescence from a single site while scanning the excitation frequency,²⁹ but this approach is limited to the spectral range covered by tunable lasers and hampered by S/N problems. The present approach which consists in obtaining difference spectra for the bleaching of single sites (the absolute spectra often show only very small changes) therefore seems to be the most viable one for solving this problem.

This is well illustrated by Fig. 6 which shows an inverted and expanded plot of the downward pointing peaks in spectrum 4(D) which correspond to all-*trans* OT^+ in site *b* (the bands marked *x* belong to the spectrally adjacent site *c*). The complete band structure is readily interpreted in terms of four vibrations for the D_1 and three for the D_2 state. The numbers agree well with those obtained previously for an OT^+ sample originating from a cyclic precursor,¹⁴ although they are generally slightly higher. This effect is most pronounced for the train of peaks originating 1880 cm^{-1} above the $D_0 \rightarrow D_2$ 0–0 transition (Fig. 6), an interval which was only $1830\text{--}1855 \text{ cm}^{-1}$ in the samples originating from cyclic precursors (different site structure).

The finding that this latter interval is much more strongly dependent on the environment than any of the others lends support to our earlier conjecture that it does not correspond to a vibronic progression (which would be difficult to

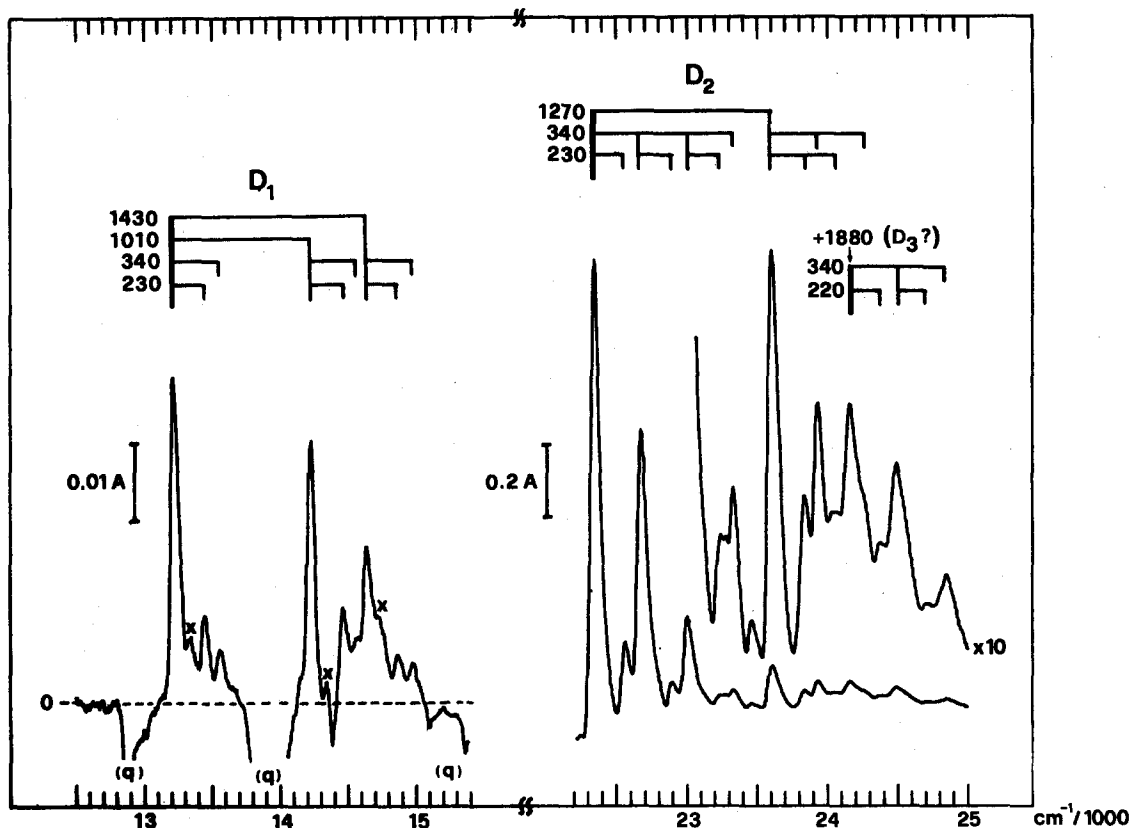


FIG. 6. Vibrational analysis of the $D_0 \rightarrow D_1$ and the $D_0 \rightarrow D_2$ transitions in all-*trans* OT⁺ (*t*) in site *b* (peaks labeled *x* correspond presumably to *t* in the spectrally adjacent site *c*). For a discussion of the possible $D_0 \rightarrow D_3$ transition (right-hand side), see the text.

rationalize anyway¹⁴) but represents the origin of the $D_0 \rightarrow D_3$ electronic transition which is expected at roughly this energy according to various semiempirical open-shell CI calculations.^{10,16} The fact that this transition is dipole forbidden in C_{2h} does not necessarily speak against such an assignment because the unsymmetric matrix environment could induce a slight distortion of the polyene cation's molecular frame. Alternatively, a polarization of π electrons by nearby counterions may be invoked to explain a small gain in intensity. Actually, the relative intensities within the group of peaks around 24 000 cm^{-1} is also found to vary with the precursor and/or the bleached site in accord with the above rationale.

One additional piece of information gained from the present experiments is the finding of a 340 cm^{-1} progression in D_1 which had previously been obscured by the strong first *q* absorption. In conjunction with the 1010 and the 1430 cm^{-1} vibrational intervals, this allows an assignment of some previously unexplained peaks in the $D_0 \rightarrow D_1$ transition.

With regard to the previous vibrational analysis¹³ we note that the prominent 1010 cm^{-1} (red band) as well as the 340 and 1270 cm^{-1} progressions (blue band) were correctly identified on the basis of the multiple-site spectra although the numbers differ slightly. The postulated 220 cm^{-1} progression is also confirmed but its discovery was obviously due to the fortuitous coincidence between the latter and a (prominent) site interval in the multisite spectrum. The same holds also for the postulated 1230 cm^{-1} interval (1240

cm^{-1} in our case) which we prefer to assign to a combination of the 1010 and the 230 cm^{-1} vibrations. More importantly, the single-site spectra do not clearly support a 1640 cm^{-1} vibration in either the red or the blue band system although one might argue whether the weak nearby 1660 = 1430 + 230 (red band) or 1610 = 1270 + 340 cm^{-1} progressions (blue band) should be correspondingly assigned. Although it would be very interesting in the light of theoretical expectations³⁰ to compare the evolution of the OT framework stretching frequencies upon π excitation of the neutral and the radical cation, the present data do unfortunately not provide sufficiently secure grounds for this venture.

V. CONCLUSIONS

Narrow-bandwidth irradiation coupled with computer-assisted data work up to give digital difference spectra proved to be a valuable tool for the disentanglement of the complex spectra obtained after ionization of octatetraene (OT) in Ar matrices. A detailed analysis of many such difference spectra yielded no firm evidence for the presence of more than the initially observed six OT⁺ rotamers. Since the very same species are also observed after photolytic ring opening of isomeric 1,3,5-cyclooctatriene or bicyclo[4.2.0]octa-2,4-diene cations it must be concluded that they form a subset of preferentially formed OT⁺ rotamers within the full set of 20 possible (peri)-planar conformations. Various reversible photoinduced transformations among these six

rotamers were observed but without the help of a reliable quantitative theoretical model for the prediction of spectral shifts no definitive assignment of the spectra in terms of individual geometries could be made. An analysis of the strongly overlapping spectra was made possible through site-selective photoinduced transformations among the six rotamers. This analysis was particularly rewarding in the case of *all-trans* OT⁺, the only rotamer which shows a distinct and well-resolved site structure in the original (multisite) spectrum. Here, the single-site difference spectra revealed the onset of a third electronic transition within the vibrational progressions of the second. Furthermore, indirect site interconversions can be observed which occur by photoisomerization of *all-trans* OT⁺ in one site and simultaneous conversion of a product rotamer to give the former in a spectrally adjacent site.

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¹The term "polyene(s)" will be used to denote linear conjugated polyenes except where otherwise noted.

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¹⁷The number Z of possible periplanar rotamers of a polyene cation with $n + 4$ carbon atoms (or $n + 3$ bonds joining them) is given by the simple formula: $Z = 2^n + 2^{n/2}$. We are indebted to Professor R. Ineichen of our Mathematics Department for his help in working out this relationship.

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²¹For easier comparison we continue to use this somewhat arbitrary nomenclature introduced earlier (Ref. 13).

²²This bleaching must be effected in several steps, decreasing the irradiation bandwidth as one approaches the onset of the strong t absorption, because even very brief exposure of the sample to light with $\lambda < 450$ nm causes rapid reconversion of t to the other rotamers.

²³Note that this procedure gives different results than those obtained with the broader irradiation bandwidths used previously (compare Fig. 4 in Ref. 14). Although the combined FWHM for several successive narrow-bandwidth irradiations may exceed that of a single broad bandwidth irradiation, the cutoffs are much sharper in the former case and hence absorptions lying outside the targeted spectral range are less affected.

²⁴Since the reverse transformation (i.e., $r \rightarrow t$) is, however, not observed, we hesitate to attribute to r one of the three positions immediately adjacent to t in Fig. 1 (as opposed to q).

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³⁰Simple Hückel-type considerations [which are fully confirmed by higher-level calculations (Ref. 31)] show that either ionization or electronic excitation of OT leads to a decrease in π bond orders across the essential double bonds which should entail a decrease in the C=C stretching frequencies. This expectation (Ref. 31) is, however, not borne out by experiment in that the corresponding symmetric fundamental [1608 cm⁻¹ (Ref. 32)] remains virtually unchanged in OT⁺ [1610 cm⁻¹ (Ref. 33)] and increases upon excitation into the first {2 ¹A_g: 1755 cm⁻¹ [Refs. 4(d), and 8]} or the second {1 ¹B_u: 1640 cm⁻¹ [Refs. 4(b) and 4(c)]} excited state of OT. Since the π bond orders suffer further strong changes upon excitation of ionized OT, it would be interesting to see whether or not the symmetric framework stretching fundamentals change in accord with expectations in this case.

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