

Potential energy surfaces of short polyenes in the state T_1 : analysis of time resolved resonance Raman spectra.

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Abstract

The analysis of T_1 resonance Raman spectra of some conjugated compounds is discussed making use of semiempirical quantum chemical calculations. Information obtained about T_1 potential energy curve indicates that in short polyenes the perpendicular form is roughly degenerate with the trans isomer. Preliminary *ab initio* results on the T_1 vibrational force field of these compounds are reported.

1. INTRODUCTION

The understanding of photophysical and photochemical properties of molecules requires the knowledge of potential energy surfaces. The most important information is the location and the relative energy of saddle-points and of relative minima. Among these, the minima from which the decay to lower electronic states takes place, are of special importance.

Quantum chemical calculations can contribute to the understanding of photophysical properties by direct calculations of potential energy surfaces of relevant electronic states. The features of these surfaces identify the intermediates and the path followed in a specific deactivation process. However, in many practical problems, this direct approach is not sufficiently accurate to yield unambiguous results, because of the approximations embodied in the calculations. In these cases, a complementary approach combining calculations and time-resolved vibrational spectroscopy may be successful. In this approach, vibrational (infrared and/or resonance Raman) spectra are calculated for a number of minima in the excited state potential energy surface, which may correspond to photoreaction intermediates. Although different minima may have similar energy, they may have quite different calculated spectra. Thus, comparing calculated spectra with the spectrum actually obtained leads to the identification of the energy surface minimum that corresponds to the photoreaction intermediate. This often allows to determine the decay path and to obtain details of potential

energy surface. The increasing development of time-resolved vibrational spectroscopy in the time-scales ranging from micro- to picoseconds, renders this approach of wide applicability to several classes of compounds.

We have studied the cis-trans photoisomerization in the state T_1 of hexatriene, β -carotene and stilbene along these lines, interpreting transient resonance Raman (RR) spectra [1-6]. In all these cases the deactivation path is well identified and the purpose of the study is to determine which is the lowest energy geometric isomer or, in other words, which is the dominant form in the T_1 state after Boltzmann equilibration is reached.

2. CALCULATIONS

The quantum chemical calculation of resonance Raman spectra of transient species, like all the properties of excited states, is still a problem of considerable difficulty. Geometry optimization and vibrational frequencies of the lower state of the resonance transition (in this case T_1) need to be calculated at the ab initio or semiempirical level. At this stage, infrared intensities can be calculated without much difficulty. However, resonance Raman intensities require the calculation of the optimized geometry of the higher electronic state of the resonance transition, in our case an excited triplet T_n . In fact the most active modes are the totally-symmetric (TS) modes which gain their intensity via the Franck-Condon mechanism. The intensity of each TS band is determined by the change of equilibrium geometry upon the T_1 - T_n excitation, more precisely by their contribution to the T_1 - T_n displacement. If the exciting beam is in resonance with the 0-0 band of the T_1 - T_n transition, the intensity of a given vibrational band is proportional to its displacement parameter γ , which is defined as

$$\gamma = B^2 / 2 \quad (1)$$

where

$$B = 0.172 \, \omega^{1/2} (x_1 - x_n) m^{1/2} L_1$$

where ω and L_1 are the frequency and the normal coordinate in T_1 , m is the matrix of atomic masses and x_1 , x_n are the cartesian coordinate vectors defining the equilibrium geometry of T_1 and T_n , respectively. Further details of the procedure can be found in ref.[1].

Geometry optimization and vibrational frequencies of up to medium-sized molecules in their ground and lowest excited states can now be calculated at the ab initio level. However the reliability of these calculations for higher excited states has not been sufficiently tested. Therefore in our calculations we have extensively used semiempirical methods, in particular the QCFF/PI method [7]. We have begun to perform the same calculations at the ab initio level.

By changing the exciting laser frequency, the excited state in resonance with the excitation changes and thus also the RR spectrum changes. If the probed molecules are distributed among different isomers at equilibrium, changing the exciting frequency may also lead to changing the isomer that is the main responsible for the Raman spectrum. These features render the transient RR spectroscopy in principle more powerful than infrared spectroscopy. On the other hand, transient Raman spectra taken at a single excitation frequency are bound to give a biased view of the weights of different isomers in a thermally equilibrated system.

3. EXPERIMENTAL

In hexatriene as well as in other polyenes, the state T_1 cannot be prepared by direct excitation in the lowest B_u singlet state, because of the very small efficiency of the $S_1 \rightarrow T_1$ i.s.c. process. Thus the T_1 state is prepared by sensitization using acetone as sensitizer. The pump laser is an excimer laser emitting at the frequency of 308 nm. The probing laser is a dye laser, but only a single frequency was used. The pulse duration of the two lasers is 10-15 ns. The pump-probe delay is ca. 80 ns. The transient resonance Raman spectrum due to T_1 is obtained as the difference between the spectra taken after and before the pumping pulse.

4. RESULTS

4.1. Hexatriene and Methylhexatrienes

As it is wellknown, cis-trans photoisomerization of hexatriene occurs by twisting the central C=C double bond. Simple considerations based on orbital energies, such as the Woodward-Hoffmann rules, show that the T_1 potential energy curve for the torsion is roughly flat, at variance with the ground state potential energy curve which has a high barrier at the twisting angle of 90° . Thus the equilibration between different isomers is fast in the T_1 state. At the twisted geometry the energy gap between S_0 and T_1 is small, roughly a few tenths of eV, and thus the radiationless decay from T_1 is expected to occur at this geometry and to be fast in view of the energy gap law obeyed by radiationless transitions. This is confirmed by the measured lifetime of T_1 , 200 ns [2], which is much shorter than T_1 lifetimes of conjugated hydrocarbons without a torsional degree of freedom.

The question we wish to address is whether a deep minimum or, instead, a slight barrier is found on the T_1 potential energy curve at the twisted geometry. In other words, we wish to know whether the reaction intermediate, corresponding to a Boltzmann equilibrated mixture of trans, cis and twisted isomers, is represented predominantly by the planar or the twisted form.

Theoretical calculations of the T_1 potential energy curve lead to results that depend on the type and the details of the calculations. Calculated energies for the twisted geometry range from a minimum 6 kcal/mol deep to a barrier of 1 kcal/mol [8,9].

Transient and stationary electronic absorption spectra are too broad to be informative on this problem. On the contrary, time-resolved RR spectra, because of their rich structure, can allow the identification of the intermediate responsible of the spectrum. This assignment usually cannot be accomplished by an empirical discussion of the spectrum, but requires a quantitative analysis based on theoretical calculation of the Raman spectra of candidates species.

The T_1 resonance Raman spectra of trans and cis hexatrienes are identical [10] and this shows that molecules equilibrate along the torsional coordinate within the 100 ns pulse-probe delay. The common spectrum, taken at the probing frequency of 315 nm, is shown in Fig. 1 and consists of an intense band at 1570 cm^{-1} and four medium-intensity bands at 1270, 1234, 1200 and 1106 cm^{-1} .

To ascertain which isomeric form(s) contribute to this spectrum, we have computed the vibrational frequencies and their Raman intensities for three local minima of T_1 , located at the trans, twisted and cis geometry, respectively. We have calculated the manifold of triplet electronic states at each of the three geometries [1]: these states and their energies are reported in Fig. 2. A single T_n state is found to be associated with a high oscillator strength for the $T_1 \rightarrow T_n$ absorption, in each geometry, namely T_5 , located 4.3 eV (ca. 290 nm) above T_1 at planar geometries, and T_6 , at 5.5 eV (226 nm) at the twisted geometry. From a comparison of the experimentally observed $T_1 \rightarrow T_n$ transition energy (300 nm corresponding to 4.13 eV) [1] with the calculated ones, it appears that only the two planar forms contribute to the $T_1 \rightarrow T_n$ absorption at 315 nm. Consequently, using the excitation wavelength of 315 nm, the

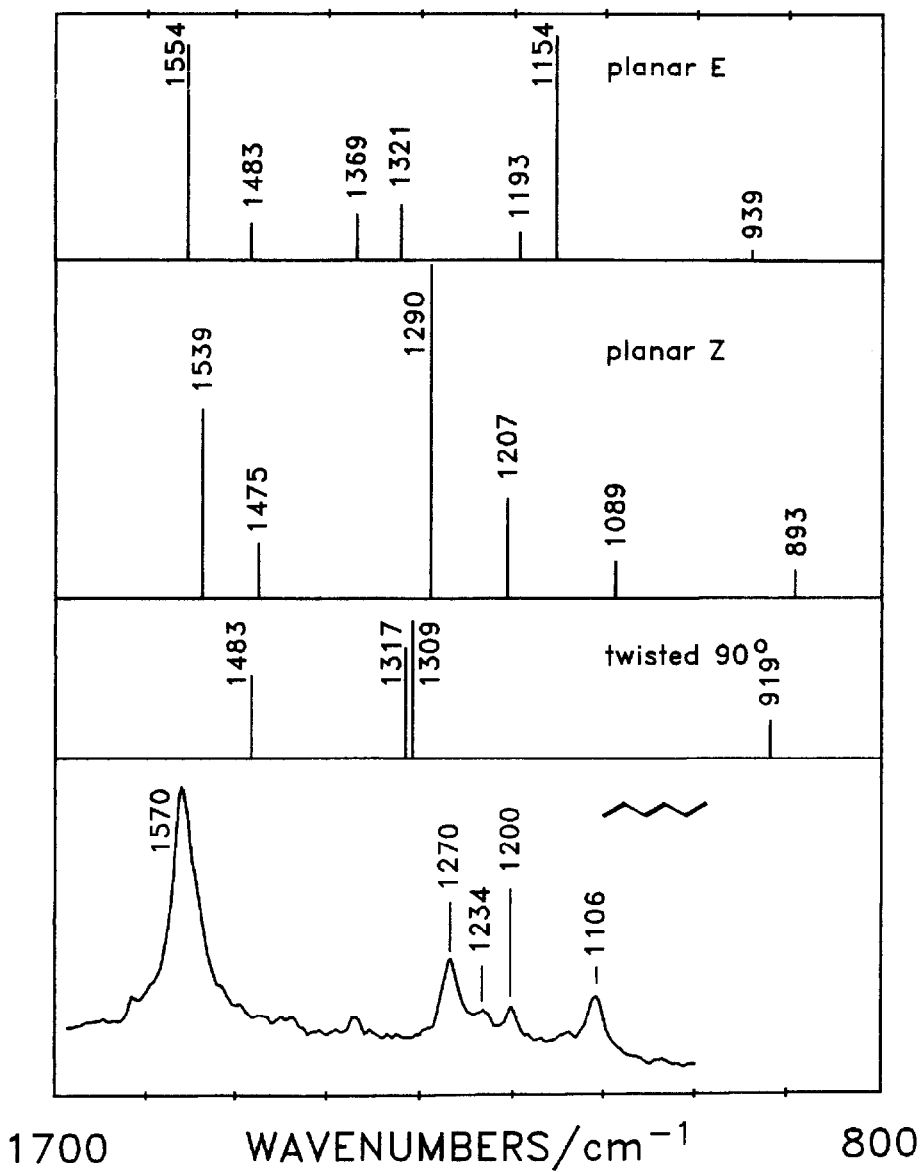


Figure 1. Calculated and observed resonance Raman spectra of hexatriene in the state T_1 ; calculated spectra are for the forms *trans*(E), *cis*(Z) and twisted.

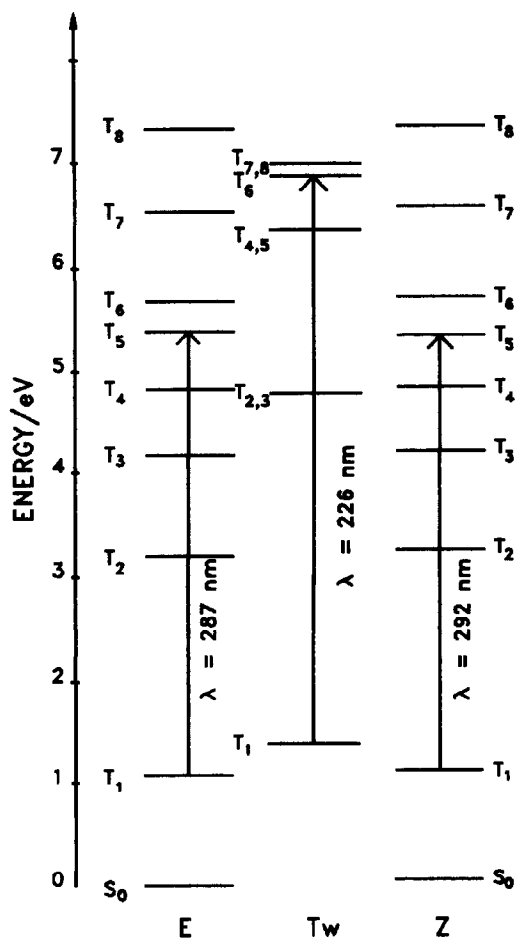


Figure 2. Calculated triplet energy levels of hexatriene in the trans(E), cis(Z) and twisted(Tw) forms and the most intense transitions from T₁.

resonance Raman enhancement apply to the planar forms, while the preresonance regime is appropriate to the Raman spectrum of the perpendicular form.

We have calculated the optimized geometries of the planar and perpendicular forms for the T_n ($n=5,6$) states of hexatriene [1]. As the resonance Raman scattering efficiency is dominated by the strongly allowed $T_1 \cdots T_n$ transition, the most active modes of vibration are the totally symmetric modes gaining their intensity from the Franck-Condon mechanism. The RR intensity is mainly governed by the displacements between the equilibrium geometries of T_1 and T_n ($n=5$ or 6). We have calculated the frequencies and dimensionless displacement parameters γ_i for the i -th totally symmetric mode. Under the given conditions the γ_i are expected to be approximately proportional to the RR intensity. The results for hexatriene are shown in Fig. 1 together with the experimental spectrum.

It is clear from Fig. 1 that the strongest observed band around 1570 cm^{-1} can only be assigned to planar forms. This agrees with the conclusion derived from triplet-triplet absorption measurements. Furthermore, it is plausible to assign the observed band at 1106 cm^{-1} to the calculated one at 1154 cm^{-1} . This seems to indicate that the planar trans form is the predominant one. However, it cannot be ruled out that the cis form contributes to the T_1 RR spectrum as well. On the contrary, there is no need to invoke the perpendicular form to explain the observed spectrum.

These results show that planar forms, which are responsible of the observed spectrum, are present with a substantial fraction in the thermally equilibrated T_1 state. It is not possible to exclude the presence of the perpendicular form, although its contribution to the Raman spectrum cannot be recognized: this is because the preresonance regime applies to the twisted form under the present experimental conditions. The efficiency of resonance scattering in the planar forms was estimated to be about 2000 times larger than that of preresonance scattering of the twisted form. This, together with the observed spectrum, is compatible with a trans-twisted form energy difference less than 2.7 kcal/mol . This conclusion is confirmed by the observation of T_1 lifetime and RR spectra at different temperatures [2]. Upon lowering the temperature to 183 K the RR spectrum remains unchanged except for the sharpening of vibrational bands. If the twisted species were at lower energy than the planar ones, a decrease of the intensity of the RR spectra would be expected due to the depopulation of planar forms. The T_1 decay was found to be an activated process with an activation energy of 0.7 kcal/mol . On this basis, the perpendicular geometry, from which the surface crossing to the ground state is expected to occur, is estimated to be 0.7 kcal/mol higher than the trans form, in agreement with results obtained from the analysis of T_1 RR spectra.

The transient RR spectra of a few deuterated derivatives of hexatriene have been studied and their analysis confirms the results obtained from the undeuterated hexatriene [1,2].

A number of methylated hexatrienes, 2-methyl-hexatriene, 3-methylhexatriene and 2,5-dimethyl-hexatriene in their cis and trans forms, have been studied in the same way [3,4]. The T_1 RR spectra of these compounds have been found to be due to planar isomers and it was deduced that trans and perpendicular forms are roughly at the same energy, as in hexatriene.

The methylation on the 2 and 5 positions increases the energy of the cis form with respect to the trans form, both in the ground and in the T_1 state; furthermore, the conformer predominant in the cis isomer, *tc*, is different than the conformer present in the trans isomer, *tt*. In these derivatives, the transient RR spectrum is due only to the trans isomer and the spectra obtained starting from the cis and trans species do not coincide. The latter observation is due to the different conformers in the two isomers and is a direct proof of the validity of the NEER principle in the T_1 state of hexatriene.

4.2. Tetramethylbutadiene.

Tetramethyl-butadiene is the smallest butadiene derivative for which vibrational information on the T_1 state is available. The T_1 lifetime is of the order of 50 ns [5]. The time-resolved resonance Raman spectrum shows a very intense band at 1620 cm^{-1} which has demonstrated the dominant contribution of a planar form to the RR spectrum [5]. However, the short

lifetime of T_1 suggests that the relative minimum at the twisted geometry, from which the decay to the ground state occurs, is at an energy very close to that of the trans minimum.

4.3. Stilbene.

The T_1 potential energy curve of stilbene was also studied by analysing its transient RR spectra. Comparing the observed with the calculated RR spectra it was demonstrated [6] that the species dominating the RR spectrum is the trans isomer. As in hexatriene, a substantial presence of the twisted form cannot be ruled out in the equilibrated triplet; actually this form must be at a comparable energy as indicated by the short T_1 lifetime.

A similar analysis has been performed on the T_1 RR spectra of β -carotene [11]. From the spectra, Hashimoto et al. [12], identified five species which they assigned to the planar trans, 7-cis,9-cis, 13-cis and 15-cis isomers. Calculations of the RR spectra for these isomers confirmed the assignment by Hashimoto et al. [12].

4.4. Ab initio calculations of T_1 force fields.

The analysis of RR spectra discussed above were based on QCFF/PI calculations. Although this method has shown to be accurate for hydrocarbons, it is obviously desirable to base the theoretical analysis on ab initio calculations, which are now becoming feasible in view of the increasing power of new computers. The use of this methods allows to extend this type of study to other systems for which no reliable semiempirical hamiltonians are available. We have performed ab initio calculations of the potential force field of hexatriene T_1 at the ROHF 6-31G level. [13] The unscaled and scaled vibrational frequencies (the scaling factors are the same used in the literature [14] for ground state frequencies) are reported in Table 1, in which for comparison, are listed also the QCFF/PI [1] and the experimental frequencies [2].

Table 1

Ab initio ROHF/6-31G, QCFF/PI and experimental vibrational frequencies (cm^{-1}) of hexatriene in the state T_1 .

ROHF		scaled ROHF	QCFF/PI	Exp.
1833	CCst	1588	1554	1574
1624	CH ₂ sciss	1455	1483	---
1516	CH ₂ rock	1345	1369	(1344)
1468	CHrock	1272	1321	1271
1284	CCst	1148	1193	1199
1156	CCst	1055	1154	1106
1027	CH ₂ rock	919	939	---
484	CCCbend	432	448	(432)
376	CCCbend	335	385	343
1741	CCst	1512	1243	---
1619	CH ₂ sciss	1450	1473	---
1482	CHrock	1289	1430	---
1419	CHrock	1239	1323	---
1162	CCst	1039	1139	---
1019	CH ₂ rock	922	963	---
604	CCCbend	538	599	(489)
162	CCCbend	144	177	---

From the data presented in Table 1 it appears that scaled ab initio frequencies are in agreement with the observed frequencies and the analysis of transient RR spectra based on the QCFF/PI hamiltonian is confirmed. Ab initio calculations of T_1 vibrational force field in stilbene is under way.

5. DISCUSSION AND CONCLUSIONS

From the examples discussed above it appears that theoretical methods are now sufficiently reliable to allow the assignment of vibrational frequencies in transient RR and infrared spectra and that it is possible to identify reaction intermediates by the analysis of their transient vibrational spectra. This provides a reliable tool for the study of the path of photochemical reactions.

Theoretical analysis shows that upon excitation to the state T_1 , the force constant matrix changes in such a way to modify not only vibrational frequencies, but also normal modes. Thus the excited states normal modes are described as a linear combination of ground state normal modes. This effect introduces a further change in frequencies. It follows that caution should be exercised in the empirical interpretations of transient spectra. In fact, it may be not correct to draw a one-to-one correspondence between ground state and excited state frequencies and it may be dangerous to associate on an empirical basis a change in one vibrational frequency with a specific structural effect.

From the experimental side, it would be desirable to study the T_1 RR spectra at several probing beam wavelengths, so as to confirm the indications obtained from a single exciting wavelength experiments and to obtain new information on the T_1 potential energy curve. Unfortunately, often it is not possible to decrease the probing wavelength at will because of the onset of ground state absorption. For example, in hexatriene the exciting wavelength cannot be tuned to reach the resonance with the $T_1 \rightarrow T_6$ transition of the perpendicular form for this reason. However, it is worthwhile in general to explore excitation profiles in the largest possible frequency range in order to pinpoint more accurately contributions to the transient RR spectrum by different electronic transitions and/or by different transient species.

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