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Buma, W.J.; Zerbetto, F.

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Vibronic activity in *trans,trans*-1,3,5,7 octatetraene: The $S_0 \rightarrow S_1$ spectrum

Wybren Jan Buma

Laboratory for Physical Chemistry, University of Amsterdam, Nieuwe Achtergracht 127,
1018 WS Amsterdam, The Netherlands

Francesco Zerbetto

Dipartimento di Chimica "G. Ciamician," Università di Bologna, V. F. Selmi 2, 40126 Bologna, Italy

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Various levels of configuration interaction are used to investigate the vibronic intensity pattern of the false origins of the $1^1A_g \rightarrow 2^1A_g$ transition of all-*trans* octatetraene. The vibronically induced mixing of the A_g with the B_u states is best simulated when polarization, i.e., d , functions are added to the basis set of atomic orbitals. Normal mode rotation upon electronic excitation plays an important role in the intensity distribution of the b_u false origins. The progressions of the totally symmetric modes built on the b_u bands is satisfactorily simulated at the CASSCF/6-31G* level. The calculations also show that the overtones of at least four out-of-plane modes should be present in the spectra whose assignment is tentatively proposed. Through comparison of the pure electronic intensities calculated for *cis-trans* octatetraene with the vibronically induced intensities of *trans-trans* octatetraene, it is found that the presence of a *cis* linkage induces a spectral perturbation similar to that of the most active b_u mode. © 1995 American Institute of Physics.

I. INTRODUCTION

The great interest in the vibrational and electronic properties of polyenes¹ arises from their highly versatile nature which casts them as prototypes of systems important in materials science² and in biological processes.³ In particular, *trans,trans*-1,3,5,7 octatetraene has provided a large amount of information on the short-time dynamical behavior of these unsaturated chains. In many of the processes in which a polyenic moiety is involved, the bulk of the activity is triggered through a complicated process that involves excitation to the $S_2(1^1B_u^+)$ state followed by radiationless deactivation to the $S_1(2^1A_g^-)$ state and ultimately medium-to-long-time dynamics to the ground state through steps that may include various isomerization reactions.

The nature of the electronic wave functions of the S_1 and S_2 states is by now well understood: to zeroth order, the $2^1A_g^-$ state is described, in a molecular orbital scheme, as a linear combination of three excitations (HOMO \rightarrow LUMO+1, HOMO-1 \rightarrow LUMO, HOMO,HOMO \rightarrow LUMO,LUMO) while the $1^1B_u^+$ state arises from the HOMO \rightarrow LUMO configuration.⁴ In a valence bond picture,⁵ S_1 is covalent in nature whereas S_2 has an ionic, diffuse character. The singly excited character and the ionicity of the S_2 wave function make the electronic transition from the ground state strongly allowed, while the $S_0 \rightarrow S_1$ electronic transition is by symmetry strictly dipole forbidden. Interestingly, as long as a C_2 axis exists in the molecule, symmetry does not allow the first two excited states of polyenes to interact and they remain separate.^{6,7} A simple and effective way to make the two lowest electronically excited states interact is a symmetry breakdown induced either by vibrational modes or by some kind of geometrical change. Because of the electronic wave function pseudoparity, i.e., their plus or minus signs, the interaction between S_1 and S_2 tends to be more effective when the molecule is distorted along CCC bending coordinates.⁸ Since the true 0-0 origin of the

$S_0 \rightarrow S_1$ spectrum is symmetry forbidden, the b_u fundamentals appear as false origins in the $1^1A_g \rightarrow 2^1A_g$ one-photon transition. Spectroscopic measurements in supersonic jet expansions have sufficient resolution to allow detection and accurate measurement of these false origins.⁹ They also enable one to disentangle part of the effects that usually operate in the excited state dynamics by exciting directly into the 2^1A_g manifold and thereby avoiding excitation to the 1^1B_u state.

To complement and to add further insight into these experiments, one can now perform quantum chemical calculations whose aim is twofold. On the one hand, one would like to simulate the experimentally observed vibronic pattern of frequencies and intensities to have a grasp of the basic vibronic or "electron-phonon" interactions in this model compound. In general, the amount of Duschinsky mixing and the possible presence of nonlinearity (second order Herzberg-Teller and non-Condon effect) are among the issues that one would want to explore. On the other hand, one would also like to extract from the results obtained by the simulations a better understanding of the interactions that occur between the different electronic states. Whilst appropriate weighing of these interactions may be rather awkward to determine experimentally, computational theory is naturally suited to accomplish their separation. In this paper, we use various levels of configuration interaction in combination with high quality force field calculations to study the $1^1A_g \rightarrow 2^1A_g$ vibronic transition of all-*trans* octatetraene. The rationale for this somewhat extensive set of calculations is to simulate the vibronic transitions and to achieve a realistic understanding of their nature. As such one must understand both the electronic and the vibrational part of the spectroscopic data.

The presentation is organized as follows: In the next section, we present the theoretical background and the computational details, and try to describe all the factors that we have attempted to assess. We then present the results of the calculations of the vibronically induced intensities and criti-

cally examine our results in the light of force field calculations which allow us to take the normal mode rotation into account. In order to estimate the validity of the force fields used in this work through an independent check calculations of the Franck–Condon intensities of the progressions of the totally symmetric vibrations will be discussed. Finally, the effect of symmetry breaking caused by introduction of a *cis* linkage is also considered.

II. THEORETICAL BACKGROUND AND COMPUTATIONAL DETAILS

Within the Born–Oppenheimer approximation, the $1^1A_g \rightarrow 2^1A_g$ polyenic transition is electronically forbidden, i.e.,

$$\mathbf{M}_{\text{ge}}^0(\bar{\mathbf{Q}}_g) = \int \psi_g^*(\mathbf{r}; \bar{\mathbf{Q}}_g) \mathbf{M} \psi_e(\mathbf{r}; \bar{\mathbf{Q}}_g) d\mathbf{r} = \mathbf{0}. \quad (1)$$

Following Herzberg and Teller,¹⁰ we can expand the electronic transition moment $\mathbf{M}_{\text{ge}}(\mathbf{Q})$ in a Taylor series of the normal coordinates centred at the equilibrium position of the ground state

$$\mathbf{M}_{\text{ge}} \approx \sum_p \mathbf{m}_{p,g} Q_{p,g}, \quad (2)$$

in which

$$\mathbf{m}_{p,g} = \left(\frac{\partial \mathbf{M}_{\text{ge}}}{\partial Q_{p,g}} \right)_{\bar{\mathbf{Q}}_g}. \quad (3)$$

The $\mathbf{0} \rightarrow \mathbf{1}_p$ transition dipole moments are now given by¹¹

$$\mathbf{M}_{\text{ge}}^{01p} = \sum_{p'} \mathbf{m}_{p',g}(\mathbf{0}_{p',g} | Q_{p',g} | \mathbf{1}_{p,e}), \quad (4)$$

where $|\mathbf{1}_{p,j}\rangle$ denotes the vibrational wave function of the vibrational state belonging to the j th electronic state in which the p th mode is in its first excited state and all other modes are in their ground state.

Equation (4) shows that the calculation of the vibronically induced intensities amounts to the evaluation of two terms: calculation of the derivatives $\mathbf{m}_{p',g}$ and calculation of the integrals over the vibrational wave functions. The calculations of the derivatives $\mathbf{m}_{p',g}$ have been performed in a doubly harmonic adiabatic scheme by simply displacing the molecular geometry along each individual b_u coordinate by a very small amount, usually 0.1 a.m.u.^{1/2} Å. The calculations are doubly harmonic because they rely on normal modes and assume that the induced dipole moment functions are linear with the geometry displacement (Condon approximation). Results of a study in which the relative intensities of the vibronically induced false origins in the $S_0(1^1A_g) \rightarrow S_1(1^1B_{2u})$ transition in benzene were calculated with a configuration interactions of singles in the same scheme were very successful¹² and give reason to believe that this doubly harmonic approach may also be applied in the present study.

In this work we have used eight different levels of calculation to calculate the derivatives of the transition moments and to study the interplay of various effects upon the vibronically induced b_u false origins of the $1^1A_g \rightarrow 2^1A_g$

excitation spectrum of all-*trans* octatetraene. The purpose of this rather extensive approach is to try and disentangle the various effects that enter the description of the vibronically induced transition moments. Such effects can be ascribed to two different causes. The first is physical in nature, the second is of computational character and we have actually subdivided it further into two (*vide infra*). In a broader sense, they are all related to the “basis sets” used throughout the calculations: by “basis sets” one can obviously refer both to the basis set of atomic orbitals, i.e., its size, contraction scheme, and whether or not higher angular momenta orbitals are included, and to the basis set of molecular orbitals used in the CI calculations, i.e., σ vs π molecular orbitals. The first effect that one would like to explore is the influence of correlation of σ and π electrons. Different calculations that include either the σ orbitals or that are limited to the space of only the π orbitals can help to assess the relevance of this issue. The second effect is also related to the molecular orbitals and can be described as the investigation of the consequences of the inclusion of some electronic correlation in the orbitals used in the CI calculations: as such, the use of CASSCF instead of RHF orbitals can provide some indications about it. The third is the influence on the results of the quality of the atomic orbital basis set.

In the calculations basically three different atomic orbital Gaussian basis sets have been employed: the $(9s5p|4s)$ basis contracted according to Dunning and Hay¹³ to the $[3s2p|2s]$ valence double zeta basis, to which we will refer from now on as the DH basis, the $(9s5p|4s)$ basis contracted according to Dunning to the $[4s2p|2s]$ full double zeta valence basis,¹⁴ augmented with a d function with an exponent of 0.75 on the carbon atoms when the case arose, referred to as the DV and DV* bases, and the very popular 6-31G* basis set.¹⁵ Calculations with the first two basis sets were performed to investigate the influence of the contraction scheme and the influence of higher angular momenta orbitals, the third basis set was used to assess the extent of the influence of the atomic exponents on the results.

Although various levels of theory can be used, we resorted to the following types of calculations:

(1) The DV basis set was used to perform self-consistent field (SCF) calculations of the ground state MOs. The basis of 100 MOs was truncated for the subsequent multireference single and double excitation configuration interaction (MRDCI) calculations by freezing the lowest 16 σ orbitals and discarding the highest 31 σ virtual orbitals. Such a scheme resulted in CI calculations with an active space of 9 σ and 4 π doubly occupied molecular orbitals and 28 σ^* and 12 π^* virtual orbitals. In the CI calculations a set of 35 reference configurations was used. It consisted of those configurations whose coefficients in the CI expansion of any of the three lower electronic states, namely, 1^1A_g , 2^1A_g , or 1^1B_u , were larger, in absolute value, than 0.05. From this set, single and double excitations were generated and included in the CI calculations using an energy threshold of 5 μ hartree. This resulted in CI expansions that varied in size between 20 000 and 23 000 configurations. These CI expansions were subsequently used to calculate all the derivatives of the transition moments with respect to the b_u normal co-

ordinates except for the CH stretching vibrations. This set of calculations assesses the accuracy of a nearly standard level of theory which includes σ and π electron correlation.

(2) The SCF calculations of the ground state MO were performed with the DV* basis set and were followed by MRDCI calculations whose MO active space consisted of four doubly occupied π orbitals and $12\pi^*$ virtual orbitals. The reference set of 51 configurations was determined by the same criterion used in calculation (1). Selection of the configurations using an energy threshold of 5 n hartree led to CI expansions of 23 000 to 27 000 configurations. This set of calculations assesses the importance of neglecting σ electron correlation with a rather large basis set which includes d orbitals.

(3) This set of calculations is similar to (2) but has an active space of 9σ , 4π , $29\sigma^*$, and $12\pi^*$ molecular orbitals resulting in 51 reference configurations and CI expansions of 21 000 to 24 000 configurations employing an energy threshold of 5 μ hartree. This set of calculations can be the standard against which one can assess the previous two calculations.

(4) The SCF orbitals of the ground state were calculated with the 6-31G* basis set. The CI calculations were performed with an active space of 9σ , 4π , $27\sigma^*$, and $12\pi^*$ MO using 41 reference configurations and the usual energy threshold of 5 μ hartree. The CI expansions had, on average, 26 000 configurations. This set of calculations uses a basis set rather similar to the previous one although not as flexible and may serve to investigate the influence of the choice of the atomic orbital exponents.

(5) The 6-31G* basis set was used to calculate the SCF MOs of the ground state. In the subsequent CI calculations, we performed a full-CI calculation in the space of 4π and $4\pi^*$ orbitals (1764 configurations), instead of the MRDCI approach adopted in the previous four sets. These calculations served to investigate the role of the π^* orbitals that were not taken into account in this calculation but were employed in the first four calculations and to assess the difference between using SCF MOs and CASSCF MOs used in calculations (6), (7), and (8).

(6) The DH basis was used to generate the CASSCF MOs of the ground state in the full-CI space of the 4π and $4\pi^*$ orbitals (1764 configurations). The subsequent CI calculations based upon these orbitals used the 153 singly and doubly excited configurations in the $4\pi-4\pi^*$ space with the ground state configuration used as the reference function. This is the simplest calculation one can probably think of using CASSCF level of theory.

(7) This set of calculations is similar to (6) but uses a full CI in the space of the 4π and $4\pi^*$ orbitals (1764 configurations) and can be thought of as one step up in complexity from (6).

(8) The molecular orbitals of (6) were used in a CI calculation with all single and double excitations generated by the 9σ , 4π , $8\sigma^*$, $4\pi^*$ active space (6531 configurations) using the ground state as the reference function. This set of calculations can also be considered a standard, in analogy with those of (3).

For sake of simplicity, we shall use the same numbering given above in the discussion and in the tables. The first four

types of calculations were performed with the Wuppertal–Bonn MRDCI package¹⁶ as implemented in the GAMESS-UK¹⁷ suite of programs, for the last four types of calculations the GAMESS-DAKOTA package¹⁸ has been employed.

Apart from the description of electronic state wave functions, the other key factor in the simulation are the vibrational integrals $(\mathbf{0}_{p',g}|\mathbf{Q}_{p',g}|\mathbf{1}_{p,g})$. These integrals can be calculated as¹⁹

$$(\mathbf{0}_{p',g}|\mathbf{Q}_{p',g}|\mathbf{1}_{p,g}) = \left(\frac{\hbar}{2\omega_{p',g}}\right)^{1/2} (\mathbf{1}_{p',g}|\mathbf{1}_{p,e}). \quad (5)$$

Initially, we set out using ground state normal coordinates that had been obtained for another purpose.⁷ Since they were used successfully in the simulation of the $1^1A_g \rightarrow 1^1B_u$ spectrum, one can expect that these normal coordinates can be a good starting point for the present study, if the Duschinsky effect upon electronic excitation to the 2^1A_g state is small. Under such conditions and the further assumption that the frequencies in ground and excited states remain the same, the vibrational part of the induced transition dipole moment can easily be calculated according to Eq. (5) and is found to be equal to $(\hbar/2\omega_{p',g})^{0.5}$.

However, when the normal modes and their frequencies change considerably upon excitation, the vibrational integrals $(\mathbf{1}_{p',g}|\mathbf{1}_{p,e})$ needs to be calculated explicitly. To establish the extent of these phenomena and to account for the mode scrambling upon excitation, it was necessary to calculate the 2^1A_g force field. Such a calculation was carried out at the CASSCF (8π electrons in 8 active π orbitals) level with the 6-31G* basis set of atomic orbitals. In order to avoid spurious mode rotations introduced by the different levels of theory, the S_0 force field was also calculated at the same level of theory and the in-plane normal modes were found to differ negligibly from the ones used in the calculations. After careful bookkeeping of all the signs of the molecular wave functions, it was possible to recalculate the induced transition dipole moments taking into account the effect of Duschinsky rotation and frequency changes. To this purpose a program was written on the basis of the theory developed in Ref. 20 to calculate the vibrational integrals given in Eq. (5).

Apart from the relative intensities of the false origins, it is also of interest to study the relative intensities of the progressions of totally symmetric modes built upon the false origins. The availability of the S_0 and S_1 force fields also allowed the calculation of these components of the excitation spectrum of octatetraene.

As a final step and to extend our understanding of polyenes in general and octatetraene in particular, we calculated the transition moment for the $S_0 \rightarrow S_1$ transition in *cis-trans* octatetraene. In this isomer the *direct* transition, i.e., the transition between the vibrationless levels of S_0 and S_1 , is allowed. Calculations of this transition moment have been performed at the optimized geometry determined previously for the ground state.⁷ The purpose of this final set of calculations is to put on an *ab initio* theoretical basis the comparison of symmetry breaking induced by vibrations or geometry changes.

TABLE I. Calculated and scaled frequencies of the normal modes in all-*trans* octatetraene. In brackets are given the frequencies resulting from the scaling procedure described in the text.

	a_g				a_u				
	$1\ ^1A_g$		$2\ ^1A_g$		$1\ ^1A_g$		$2\ ^1A_g$		
	Calc.	Used ^a	Calc.	Used ^b	Calc.	Used ^a	Calc.	Used ^c	
ν_{17}	249(247)	242	209(211)	210	ν_{25}	55(82)	55 ^d	48(75)	44
ν_{16}	352(339)	342	355(342)	336	ν_{24}	171(194)	181	139(163)	147
ν_{15}	573(537)	538	562(527)	530	ν_{23}	222(244)	245	272(293)	271
ν_{14}	1034(948)	956	1032(946)	965	ν_{22}	642(652)	629	330(348)	329
ν_{13}	1197(1094)	1136	1127(1031)	1080	ν_{21}	818(822)	840	455(470)	475
ν_{12}	1290(1177)	1179	1318(1202)	1225	ν_{20}	853(856)	900	793(798)	790
ν_{11}	1407(1282)	1281	1369(1248)	1276	ν_{19}	1018(1016)	960	875(878)	842
ν_{10}	1423(1296)	1291	1410(1284)	1280	ν_{18}	1070(1067)	1011	981(981)	928
ν_9	1448(1318)	1299	1435(1307)	1284					
ν_8	1603(1457)	1423	1620(1472)	1445 ^c					
ν_7	1755(1593)	1608	1649(1499)	1509					
ν_6	1785(1619)	1617	2041(1849)	1798					
	b_g				b_u				
	$1\ ^1A_g$		$2\ ^1A_g$		$1\ ^1A_g$		$2\ ^1A_g$		
	Calc.	Used ^a	Calc.	Used ^c	Calc.	Used ^a	Calc.	Used ^b	
ν_{32}	144(168)	164	161(185)	177	ν_{48}	91(106)	96	75(92)	76
ν_{31}	346(364)	343	262(283)	271	ν_{47}	413(394)	390	380(364)	440
ν_{30}	671(680)	722	280(301)	297	ν_{46}	605(565)	565	596(557)	523
ν_{29}	848(852)	877	455(470)	484	ν_{45}	1005(923)	940	993(912)	952
ν_{28}	855(858)	896	758(764)	739	ν_{44}	1236(1129)	1139	1094(1002)	1044
ν_{27}	981(981)	958	798(803)	814	ν_{43}	1363(1242)	1229	1238(1131)	1138 ^c
ν_{26}	1054(1051)	1080	964(965)	984	ν_{42}	1409(1284)	1280	1352(1233)	1230 ^c
					ν_{41}	1454(1306)	1303	1401(1276)	1268 ^c
					ν_{40}	1570(1427)	1405	1503(1368)	1363 ^c
					ν_{39}	1709(1552)	1569	1635(1485)	1554
					ν_{38}	1791(1625)	1632	1770(1606)	1591

^aExperimental frequencies (Ref. 21).^bExperimental frequencies (Ref. 9).^cCalculated using Duschinsky matrix (see the text).^dFrequency used as calculated.

III. RESULTS AND DISCUSSION

In C_{2h} symmetry, the 0–0 vibronic transition of the $1\ ^1A_g \rightarrow 2\ ^1A_g$ spectrum of all-*trans* octatetraene is strictly one-photon dipole forbidden and cannot be observed. The onset of the spectrum is therefore a false-origin band due to the lowest frequency b_u mode.⁹ This band is the most prominent one in the spectrum and is followed, at higher energies, by other bands of b_u symmetry. Upon this set of false origins, progressions of totally symmetric modes are built. Further bands may arise because of second order Herzberg–Teller coupling, Fermi resonances, and frequency distortions between the two electronic states involved in the transition. In this work, however, we focus mainly on the nature of the false origins, the mechanisms by which they arise and how one can simulate them. Also the intensities of the totally symmetric progressions are calculated and some discussion is provided.

As a prerequisite to the calculation of the spectral intensity pattern, one needs to assess the correspondence between the normal modes of the two electronic states involved in the transition. Although a more detailed description of the amount and the implications of the normal mode rotation is

presented when the calculated intensities are given, we show in Table I the calculated frequencies for the $1\ ^1A_g$ and $2\ ^1A_g$ states, and the frequencies used in the calculations of the vibronically induced transition moments. The frequencies were either taken from the experimental literature^{9,21} or, when not determined experimentally, obtained by two scaling procedures. In the first scheme, we performed two separate linear regressions on the experimental ground state frequencies of the in-plane modes and the out-of-plane modes as a function of the calculated frequency. The parameters derived from these regressions were subsequently used to scale the excited state frequencies of the in- and out-of-plane modes. Although the scaled frequencies obtained in this way match the experimental frequencies very nicely (see Table I), it appears that some of the low-frequency modes have predicted values that seem rather large. We therefore chose a second approach in which scaling factors are calculated for each of the ground state normal vibrations as $s_i = h\nu_i(\text{expt.})/h\nu_i(\text{calc.})$. Scaling factors for the excited state frequencies were subsequently obtained by rotation of the ground state scaling factors with the Duschinsky matrix. The differences between the two approaches are minimal al-

TABLE II. Calculated relative intensities of the b_u false origins of the $S_0 \rightarrow S_1$ spectrum of all-*trans* octatetraene (S_0 modes, see the text).

	Calculated ^a								Expt. ^b	Expt. ^c
	1	2	3	4	5	6	7	8		
ν_{48}	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0(341)	100.0
ν_{47}	1.7	2.3	3.3	6.8	2.3	7.7	3.4	9.9	11.0(322)	11.6
ν_{46}	0.1	3.6	2.4	1.6	1.7	2.0	0.5	3.0	11.6(318)	12.4
ν_{45}	1.2	0.4	0.8	2.6	0.6	0.4	1.3	0.5	5.1(240)	7.2
ν_{44}	4.3	0.3	0.7	0.1	0.2	0.0	1.0	0.2	3.2(220)	5.0
ν_{43}	1.3	1.7	0.1	1.8	2.1	0.2	1.0	0.3		
ν_{42}	46.3	15.7	18.8	7.7	15.9	23.8	27.1	24.8		
ν_{41}	5.1	0.3	7.5	0.6	0.4	8.4	8.4	7.6		
ν_{40}	2.5	0.2	0.0	0.2	0.3	3.7	3.3	2.6		
ν_{39}	19.4	3.8	11.7	7.8	3.5	0.5	0.2	0.2	10.4(173)	20.5
ν_{38}	99.0	36.7	72.1	76.6	34.7	4.7	3.7	1.8	18.7(171)	37.3

^aThe intensity of mode ν_{48} is always taken as 100; the description of the eight different calculations can be found in the text.

^bAs assigned in Ref. 9. The lifetime in ns is given in brackets.

^cThe experimental value of Ref. 9 scaled by the ratio of the lifetimes (see the text).

though the low-frequency modes now seem to have lower frequencies and have consequently been selected for the calculations of the vibrational integrals. We hasten to notice, however, that the results that will be presented below are not very susceptible to the choice of frequencies.

In the following, we shall try to refer to the progressive frequency numbering in each state rather than making the one to one correspondence between the vibrations whose order may have been changed by excitation.

A. Vibronic intensities without normal modes scrambling

For sake of simplicity, the simplest picture that one can use to disentangle the vibronic structure of an electronic spectrum assumes that the normal modes and frequencies are the same in the two states involved in the transition. With this assumption, the calculated relative intensities are shown in Table II where they are compared with the experimental results reported in Ref. 9. In this table both the experimental and the calculated data are given as relative intensities with respect to the ν_{48} false origin. To put our results in a better perspective, we also provide the experimental values scaled by the ratio of the lifetime of ν_{48} and the lifetime of the inducing mode under consideration. This partly accounts for the nature of the experiment. We do not try to assess the influence of other possible effects such as, for instance, intramolecular vibrational relaxation, on the experimental intensities. In any event, one should bear in mind that the calculation refers to an absorption process while the experiment obtains a fluorescence excitation spectrum in which the intensities of the false origins are not only determined by the absorption process but also by the competition between emission and radiationless decay.

Before a detailed examination of the table is made, some general comments are in order: it appears that the overall agreement between theory and experiment is fair to good with the noticeable exception of the overestimate of the calculated intensities for ν_{42} and possibly ν_{41} . If one accounts for the 76.2 cm^{-1} shift of the true origin with respect to the

ν_{48} band, the fundamentals of ν_{42} and ν_{41} should fall between 1100 and 1200 cm^{-1} .⁹ In this region, no bands were assigned in Table I of Ref. 9, but inspection of Fig. 3 in the same work shows the presence of vibronic activity which can positively be assigned to these two modes. Even with this further assignment, it seems that all the present levels of configuration interaction *used in conjunction with S_0 normal modes* lead to an overestimate of the intensities in this region.

When the results of the various sets are compared, see, for example, sets 1 and 3 which differ only by the presence of d orbitals, it becomes evident that inclusion of d orbitals leads to better results. Similarly, comparison of set 2 with set 3 and of set 7 with set 8 shows that inclusion of σ orbitals in the CI improves the agreement with the experiment. The clearest difference between the calculations emerges when SCF MOs based calculations are compared with those which employ CASSCF MOs: In the latter case the intensity of ν_{38} is noticeably underestimated. Finally, we notice that comparison of the 6-31G* and the DV* based calculations surprisingly tend to favor slightly the 6-31G* basis set.

A more detailed comparison between experiment and calculations must consider the fact that the experimental results were obtained by fluorescence excitation spectroscopy. As such, they directly correspond to the present calculations inasmuch as the lifetime of each individual band is the same. By inspection of Table I in Ref. 9 whose results are summarized in the second last column of Table II of the present work, one can identify three regimes of lifetimes. To the first regime, which extends up to slightly above 500 cm^{-1} from the true origin (observed in two-photon excitation experiments⁹), belong the first three false origins, i.e., ν_{48} , ν_{47} , and ν_{46} . To the second regime, characterized by shorter lifetimes, belong ν_{45} and ν_{44} . The false origins of ν_{39} and ν_{38} have the shortest lifetimes amongst all the b_u fundamentals and belong to the third regime.

The ν_{48} , ν_{47} , and ν_{46} region

It is clear that the present choice of computational theory tends to underestimate the activities of ν_{47} and ν_{46} . The most

TABLE III. Duschinsky matrix for the b_u modes in the 1^1A_g and 2^1A_g states of all-*trans* octatetraene.

1^1A_g	2^1A_g	ν_{48}	ν_{47}	ν_{46}	ν_{45}	ν_{44}	ν_{43}	ν_{42}	ν_{41}	ν_{40}	ν_{39}	ν_{38}
ν_{48}	0.997	0.062	0.007	0.001	-0.006	-0.015	0.013	-0.016	-0.004	-0.001	0.001	
ν_{47}	-0.071	0.996	0.013	-0.008	0.042	-0.023	0.008	0.002	-0.009	0.004	-0.002	
ν_{46}	-0.002	0.017	0.995	-0.040	-0.067	-0.001	0.019	0.017	0.003	0.008	-0.048	
ν_{45}	0.003	0.023	0.006	0.903	-0.321	-0.005	0.120	0.167	-0.056	-0.006	-0.158	
ν_{44}	0.016	0.008	-0.016	-0.098	0.157	0.780	0.370	0.426	-0.007	-0.011	-0.212	
ν_{43}	0.014	-0.002	-0.016	-0.136	-0.037	-0.277	-0.440	0.836	-0.022	-0.056	-0.068	
ν_{42}	-0.012	0.001	-0.043	-0.230	-0.367	-0.378	0.738	0.218	0.164	-0.137	0.169	
ν_{41}	0.002	-0.037	0.040	0.110	0.563	-0.291	0.302	0.103	-0.675	0.141	0.051	
ν_{40}	0.008	-0.014	0.031	0.170	0.391	-0.121	0.097	0.125	0.616	0.613	0.136	
ν_{39}	0.005	-0.016	0.027	0.128	0.478	-0.186	0.067	-0.046	0.367	-0.680	-0.335	
ν_{38}	0.002	0.002	0.060	0.194	0.134	0.201	-0.072	0.116	0.038	-0.347	0.872	

successful calculations are sets 4 and 8: a result that, in a sense, might have been expected since these calculations are the largest. Set 4 uses SCF MOs and 6-31G* atomic orbitals which also contain d functions; set 8 uses CASSCF MOs but does not have d functions. In both cases, the correlation encompasses both σ and π orbitals. Overall two points can be made: It appears that the d functions role can be mimicked by CASSCF MOs and perhaps more important is the consideration that the atomic orbitals description may play an important part in the description of the vibronic intensities since the calculations of set 3, which can be considered similar to those of set 4, are not as successful.

The ν_{45} - ν_{40} region

This region probably consists of two different regimes, the first containing ν_{45} and ν_{44} whose lifetimes are longer than 200 ns, the second, which starts around 1000 cm^{-1} , contains the fundamentals of ν_{43} , ν_{42} , ν_{41} , and ν_{40} which are characterized by lifetimes shorter than 200 ns. The false origins in the region below 1000 cm^{-1} are weak and it would be somewhat awkward to decide which calculation shows the best agreement. As mentioned above, the simulation of the intensities of the fundamentals of ν_{42} and ν_{41} presents difficulties. In the following, we shall show that inclusion of normal mode rotation improves the quality of the results considerably.

The ν_{39} - ν_{38} region

Experimentally, both bands are rather intense with ν_{38} the more intense one. Computationally, these two bands are very indicative of the fine effects one has to balance when simulating false origins intensities. It is instructive to see that for ν_{38} the calculated intensities vary over 2 orders of magnitude. The calculations of set 1 make it almost the most intense band, while CASSCF calculations (sets 6, 7, and 8) provide a description in which little or no intensity is predicted for this false origin. Overall it would seem that the calculations based upon SCF MOs lead to a somewhat better agreement of the intensities of both false origins with the experimental values.

B. The effect of mode scrambling onto the vibronic intensities

In the previous subsection, we have shown that a fair to good simulation of the relative intensities of the vibronically induced b_u bands in the $1^1A_g \rightarrow 2^1A_g$ spectrum of all-*trans* octatetraene can be obtained at several levels of theory. The question arises whether one can improve on the description obtained so far and if there is a physical, rather than computational, reason for part of the inevitable inaccuracies of the calculations. In principle, two phenomena need to be considered: The first is the possibility of normal mode rotation upon electronic excitation, the second is the possible presence of anharmonic effects which may affect both the normal mode picture itself and the vibronically induced transition dipole moment. In this work we have restricted ourselves to a doubly harmonic approximation, i.e., harmonic both in the vibrations and the dipole moments. We shall therefore consider only the effect of the rotation of the normal modes upon excitation to the 2^1A_g state. To account for this, one requires the 2^1A_g vibrational frequencies and normal modes. These were calculated at CASSCF level with 8π electrons in 8π orbitals using the 6-31G* basis set. The overlap of the S_1 normal mode matrix with the S_0 modes calculated previously and used in the calculations of the vibronically induced transition moments gave the Duschinsky, or normal mode scrambling, matrix. However, for sake of consistency, we thought it prudent to perform a similar CASSCF calculation also for the S_0 state in order to verify that the normal mode rotation calculated in this way was not caused by a change of the level of calculation. After this further computationally intensive calculation, it was rewarding to find that the two sets of in-plane modes of S_0 differed minimally.

The Duschinsky matrix obtained for the b_u modes with the CASSCF force fields of the 1^1A_g and 2^1A_g states is given in Table III. Since it is to be expected that the CASSCF force field will be the more accurate one, we have used this force field in further calculations in which the Duschinsky rotation was taken into account. To this purpose we have consequently projected the induced transition moments calculated with the original normal coordinates on the normal coordinates derived from the CASSCF calculation. Since the

TABLE IV. Calculated relative intensities of the b_u false origins of the $S_0 \rightarrow S_1$ spectrum of *all-trans* octatetraene (the calculations account for the Duschinsky effect, see the text).

	Calculated ^a								Expt. ^b	Expt. ^c
	1	2	3	4	5	6	7	8		
ν_{48}	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0(341)	100
ν_{47}	5.1	5.9	7.9	12.9	5.9	15.7	8.8	18.9	11.0(322)	11.6
ν_{46}	0.0	3.2	1.6	0.9	1.4	2.1	0.5	3.5	11.6(318)	12.4
ν_{45}	0.0	0.1	0.0	0.0	0.0	0.1	0.7	0.7	5.1(240)	7.2
ν_{44}	1.3	0.5	0.0	0.0	0.2	3.0	1.9	1.7	3.2(220)	5.0
ν_{43}	2.5	0.7	0.3	2.0	0.1	5.2	8.9	4.8		
ν_{42}	18.3	8.1	6.5	2.6	8.5	20.0	21.1	20.4		
ν_{41}	2.8	1.2	6.0	0.6	0.5	5.1	1.0	6.4		
ν_{40}	0.2	0.1	3.9	0.1	0.1	0.3	0.2	0.1		
ν_{39}	0.0	1.0	0.8	1.1	0.7	0.1	0.0	0.0	10.4(173)	20.5
ν_{38}	150.7	48.3	97.6	96.0	47.6	9.3	10.6	5.3	18.7(171)	37.3

^aThe intensity of mode ν_{48} is always taken as 100; the description of the eight different calculations can be found in the text.

^bAs assigned in Ref. 9. The lifetime in ns is given in brackets.

^cThe experimental value of Ref. 9 scaled by the ratio of the lifetimes (see the text).

vibronically induced transition dipole moments are obtained through wave functions which are calculated by diagonalization, it was necessary to painstakingly account for all the signs of such moments. Multiplication of the $(\mathbf{1}_{p',g} | \mathbf{1}_{p,e})$ matrix with the vector of the induced transition dipole moments furnished the results shown in Table IV. By inspection, one notices that the predicted intensity in the 1100–1200 cm^{-1} region is now decreased and that there is an overall improved agreement with the experimental trends. Here, for simplicity, we adopt the progressive labeling (the higher the b_u frequency, the lower its number) previously adopted for the 1^1A_g state. One can now examine in detail the three lifetime regimes.

The ν_{48} , ν_{47} , and ν_{46} region

Inclusion of the normal mode rotation improves the agreement between theory and experiment for the relative intensities of ν_{47}/ν_{48} although it has little or no effect on the ν_{46}/ν_{48} ratio. The improvement is brought about by a rather small rotation between the ν_{47} and ν_{48} normal modes. The corresponding matrix element is 0.06 which corresponds to a rotation of 3° . The same matrix element for ν_{46} and ν_{48} is calculated to be only 0.007. Obviously enough, a rotation similar in magnitude to that calculated for the two lowest frequency modes would bring theory and experiment in close agreement.

The ν_{45} – ν_{40} region

In this region, a large intensity reorganization is introduced by normal mode mixing. Foremost is the decrease in the calculated intensities of ν_{42} and, to a lesser extent, ν_{41} in the calculations that use ground state SCF MOs. Interestingly, ν_{42} is strongly “rotated” in the 2^1A_g state and its overlap with its 1^1A_g counterpart is only 0.7. The scrambling involves all but the three lowest frequency modes, with coefficients ranging from 0.07 to 0.44.

The ν_{39} – ν_{38} region

The calculated intensities of the b_u false origins of the short lifetime region are computationally the most troublesome. These two modes undergo strong Duschinsky rotation which decreases the intensity of ν_{39} and increases the intensity of ν_{38} . This is not totally consistent with the analysis of the data reported by Petek *et al.*⁹

Despite some inaccuracies, the present set of calculations of the intensities of the b_u fundamentals in the $1^1A_g \rightarrow 2^1A_g$ spectrum of *all-trans* octatetraene can be considered satisfactory. One of the main results is the detection of the presence of strong Duschinsky mixing for the b_u modes upon excitation to the 2^1A_g state. Inclusion of this mode scrambling leads to an improved simulation of the spectrum.

C. The totally symmetric mode progressions

The question arises whether one can independently verify the accuracy of the rotation of the vibrational modes upon excitation. The calculation of the excited state geometry and force field that was required to assess the Duschinsky effect on the vibronically induced intensities also allows the calculation of the Franck–Condon component of the $1^1A_g \rightarrow 2^1A_g$ spectrum. A satisfactory simulation of the totally symmetric progressions would be strongly supportive of the accuracy of the force field calculations and, implicitly, of the amount of mode scrambling.

In Table V the calculated relative intensities of the first quanta of the progressions of the totally symmetric modes are shown together with their experimental counterparts. The experimental data are taken from the bands built on the ν_{48} false origin. We also provide the experimental values scaled by the ratio of the lifetime of the ν_{48} false origin divided by the lifetime of the first quantum of the totally symmetric mode under consideration. As before in the calculation of the relative intensities of the b_u false origins, this procedure partly accounts for the nature of the experiment. The influ-

TABLE V. Calculated relative intensities of the totally symmetric progressions of the $S_0 \rightarrow S_1$ spectrum of all-*trans* octatetraene. The reported experimental values are based on the progressions of the ν_{48} false origin.

	Calc. ^a	Expt. ^b	Expt. ^c
ν_{17}	5.8	3.5(337)	3.5
ν_{16}	47.9	55.2(337)	55.9
ν_{15}	3.5	3.7(314)	4.0
ν_{14}	10.8	4.3(242)	6.1
ν_{13}	21.3	8.9(212)	14.3
ν_{12}	75.8	45.4(235)	65.9
ν_{11}	0.0	8.4(203)	14.1
ν_{10}	43.3	4.9(201)	8.3
ν_9	1.3	2.5(197)	4.3
ν_8	9.0	0.0	
ν_7	12.1	8.8(169)	17.8
ν_6	273.6	92.0(145)	216.4

^aRelative intensities with respect to the false origin of mode ν_{48} taken as 100.

^bAs assigned in Ref. 9. The lifetime in ns is given in brackets.

^cThe experimental value of Ref. 9 scaled by the ratio of the lifetimes (see the text).

ence of possible further effects whose presence would effectively diminish the experimental signal is not considered.

A general comment is in order: upon scaling of the intensities by the ratios of the lifetimes, Table V shows a remarkable agreement between experiment and theory, which is in fact better than what has been calculated for the intensities of the false origins. The only disconcerting note is the intensity of ν_{10} which is apparently overestimated. However, one should notice that experimentally⁹ ν_{11} , ν_{10} , and ν_9 are located in a range of 8 cm^{-1} (1275.5, 1279.6, and 1283.8 cm^{-1}) and that they have only tentatively been assigned. In this context it is probably simpler to consider the three modes as strongly related and to be rather satisfied with the calculated intensity pattern, which in practice favours one of the three modes rather than spreading the activity over the three of them. To further support this notion, one can notice that, apart from the lowest frequency ones, all the totally symmetric modes are heavily scrambled upon excitation as can be concluded from Table VI where the Duschinsky matrix for the a_g modes is given.

TABLE VII. S_1 calculated frequencies and relative intensities of the most intense double quanta of the $S_0 \rightarrow S_1$ spectrum of all-*trans* octatetraene.

	Calc. freq. ^a	Calc. int.
a_u	271(543)	6.0
	475(949)	3.8
b_g	297(593)	7.9
	484(967)	4.0

^aIn brackets the frequency of the double quanta.

D. Further assignments

The computational picture obtained so far, by and large, concurs with the empirical spectral assignment of the $1^1A_g \rightarrow 2^1A_g$ spectrum of all-*trans* octatetraene proposed by Petek *et al.* The present calculations also allow to determine the presence of bands that have not been assigned or considered before, in particular double quanta of nontotally symmetric modes whose frequencies are greatly affected by electronic excitation. There are four such modes: two of a_u symmetry and two of b_g symmetry. The a_u modes concern the third and fifth lowest in frequency whilst the b_g modes concern the third and fourth lowest. In Table VII, we show the calculated S_1 frequencies and intensities for these transitions. Inspection of the Duschinsky matrix of the out-of-plane modes (Tables VIII and IX) readily shows that the origin of the frequency shift is found in the fact that the pristine S_0 modes are spread over several S_1 modes. Although the calculations show that these overtones should be present in the spectra, the assignment is complicated by the possibility that other bands of similar energy may arise as a result of second order Herzberg–Teller coupling. Such bands would be combination bands made up by one a_u quantum plus one b_g quantum. Somewhat tentatively, one can assign the double quanta of the third lowest frequencies a_u and b_g modes to the system of unassigned bands slightly above 530 cm^{-1} while the double quanta of the other two modes could be found in the system of unassigned bands around 870 cm^{-1} .

TABLE VI. Duschinsky matrix for the a_g modes in the 1^1A_g and 2^1A_g states of all-*trans* octatetraene.

1^1A_g	2^1A_g	ν_{17}	ν_{16}	ν_{15}	ν_{14}	ν_{13}	ν_{12}	ν_{11}	ν_{10}	ν_9	ν_8	ν_7	ν_6
ν_{17}	0.998	0.019	0.016	-0.002	0.045	0.012	0.007	-0.008	0.011	0.000	-0.004	-0.001	
ν_{16}	0.025	0.998	-0.031	0.001	0.011	0.010	-0.003	-0.020	-0.003	0.003	-0.005	-0.036	
ν_{15}	-0.035	0.033	0.998	0.022	0.017	0.014	0.027	-0.006	0.006	-0.002	0.008	-0.012	
ν_{14}	0.014	0.001	-0.014	0.955	-0.198	0.068	0.090	-0.121	0.029	-0.086	-0.044	-0.094	
ν_{13}	-0.023	0.000	-0.028	0.022	0.615	0.399	0.597	0.142	-0.033	-0.198	-0.153	0.125	
ν_{12}	0.012	0.025	0.014	0.150	-0.033	0.181	-0.337	0.850	0.034	0.067	0.007	0.318	
ν_{11}	0.003	-0.014	0.001	-0.064	-0.067	0.831	-0.384	-0.339	-0.143	0.045	0.108	0.055	
ν_{10}	0.022	0.007	-0.001	-0.085	-0.515	0.114	0.484	0.184	-0.621	0.124	0.202	-0.019	
ν_9	0.003	0.007	-0.010	-0.119	-0.369	0.241	0.358	0.050	0.766	0.132	0.239	0.009	
ν_8	-0.010	-0.003	-0.002	0.092	0.141	0.000	0.078	-0.087	-0.013	0.924	-0.308	0.099	
ν_7	-0.012	-0.008	-0.015	0.131	0.396	-0.070	-0.042	0.055	-0.051	0.240	0.837	-0.233	
ν_6	0.001	0.030	0.006	0.069	-0.007	-0.180	0.057	-0.287	-0.029	-0.047	0.262	0.900	

TABLE VIII. Duschinsky matrix for the a_u modes in the 1^1A_g and 2^1A_g states of all-*trans* octatetraene.

1^1A_g	2^1A_g	ν_{25}	ν_{24}	ν_{23}	ν_{22}	ν_{21}	ν_{20}	ν_{19}	ν_{18}
ν_{25}	0.939	0.335	0.075	0.031	-0.011	0.012	-0.003	0.024	
ν_{24}	-0.310	0.890	-0.237	0.181	-0.001	-0.002	-0.008	0.131	
ν_{23}	0.082	-0.281	-0.266	0.850	-0.023	0.003	0.148	0.025	
ν_{22}	-0.084	0.074	0.652	0.195	0.510	0.101	0.461	0.291	
ν_{21}	-0.030	0.013	0.150	0.144	0.096	0.826	-0.500	-0.111	
ν_{20}	0.087	-0.082	-0.565	-0.217	0.791	0.070	0.019	0.029	
ν_{19}	0.018	0.007	-0.238	-0.216	-0.285	0.525	0.704	-0.104	
ν_{18}	0.039	-0.143	-0.159	-0.114	-0.209	0.151	-0.087	0.932	

E. Comparison between all-*trans* and *cis-trans* octatetraene

So far we have shown that the present levels of calculations are well capable of reproducing the main features of the $1^1A_g \rightarrow 2^1A_g$ excitation spectrum. A remaining point of interest concerns the effect of the other, geometrically trivial, symmetry breaking mechanism in polyenes, i.e., the introduction of a *cis* linkage whose effect is to lower the molecular symmetry to such an extent that the transition between the ground and first excited state becomes allowed. The comparison between the vibronically and geometrically induced mechanisms becomes even more of interest when the results of recent experiments are considered. Resonance enhanced multiphoton ionization (REMPI) studies on the *cis*- and *trans*-isomers of hexatriene²² surprisingly showed that for this polyene only the *cis*-isomer gives rise to a well-resolved excitation spectrum. For the *trans*-isomer no resonance enhancement could be detected. This observation was further confirmed by the fluorescence excitation studies of Petek *et al.*²³ At that time a possible explanation for the absence of resonance enhancement in the *trans* isomer seemed to be that the purely electronic transition moment of the *cis* isomer would be considerably larger than the vibronically induced transition moments of the *trans* isomer. Such an explanation seemed also to be supported by the results of previous fluorescence excitation studies on various isomers of octatetraene in the solid state,²⁴ which gave reason to believe that the $S_0 \rightarrow S_1$ transition moments of isomers without inversion centre were at least 1 order of magnitude larger than the induced transition moments in centrosymmetric isomers. On this basis the next set of REMPI experiments, in which the $S_0 \rightarrow S_1$ excitation spectrum of isolated octatetraene in the gas phase could be obtained for the first time,²⁵ were interpreted

to derive their resonance enhancement from the *cis-trans* isomer. The one- and, in particular, two-photon fluorescence excitation studies by Petek *et al.*⁹ performed subsequently showed, however, that the observed excitation spectrum should indeed be attributed to only the all-*trans* isomer. In these studies it was argued that it is the vibronic coupling with the S_2 state which is primarily responsible for the $S_0 \rightarrow S_1$ transition moment, and thus implicitly that the “double-excitation” electronic character of S_1 will dominate the transition moment, irrespective of the symmetry.

In order to address this issue we have calculated using levels 2, 3, 6, 7, and 8 the $S_0 \rightarrow S_1$ transition moment for the 0-0 transition moment in *cis-trans* octatetraene, an isomer for which the direct transition is symmetry allowed. In Table X the intensity obtained for this 0-0 transition is compared to the vibronically induced intensity calculated for the $\nu_{48}(b_u)$ false origin in the one-photon excitation spectrum of all-*trans*-octatetraene. These results show that both intensities are comparable and certainly of the same order of magnitude. It can therefore be concluded that, although symmetry breaking does indeed lead to a measurable transition moment, it does not induce a transition moment which exceeds the vibronically induced transition moments in the centrosymmetric isomer by orders of magnitude.

The intriguing question raised by these results is of course the role of vibronic coupling between the S_1 and S_2 states in isomers such as *cis-trans*-octatetraene, i.e., how do the vibronically induced transition moments in such an isomer compare with the direct transition moment? The results of studies, in which such questions will be addressed, will be the subject of two forthcoming papers,²⁶ in which we have investigated the vibronic coupling problem in *cis-trans* octatetraene and in *cis*- and *trans*-hexatriene. Preliminary re-

TABLE IX. Duschinsky matrix for the b_g modes in the 1^1A_g and 2^1A_g states of all-*trans* octatetraene.

1^1A_g	2^1A_g	ν_{32}	ν_{31}	ν_{30}	ν_{29}	ν_{29}	ν_{27}	ν_{26}
ν_{32}	0.828	-0.530	0.097	0.030	0.000	0.015	0.090	
ν_{31}	0.541	0.708	-0.387	0.038	-0.051	0.024	-0.241	
ν_{30}	0.068	0.211	0.672	0.518	0.306	-0.200	-0.316	
ν_{29}	-0.041	-0.109	-0.111	0.053	0.511	0.808	-0.247	
ν_{28}	-0.121	-0.242	-0.553	0.787	-0.026	-0.151	-0.008	
ν_{27}	0.029	0.023	-0.223	-0.187	0.785	-0.413	0.293	
ν_{26}	0.063	0.305	0.175	0.290	-0.026	0.326	0.826	

TABLE X. Comparison of the intensity of the $\nu_{48}(b_u)$ false origin in the $S_0 \rightarrow S_1$ spectrum of all-*trans* octatetraene and the intensity of the $S_0 \rightarrow S_1$ vibrationless transition of *cis-trans* octatetraene. Description of the various calculations can be found in the text.

Calculation	All- <i>trans</i> ^a ν_{48}	<i>Cis-trans</i> 0-0
2	100.0	72.6
3	100.0	142.0
6	100.0	106.1
7	100.0	89.9
8	100.0	91.6

^aThe intensity of mode ν_{48} is always taken as 100.

sults indicate that in *cis-trans* octatetraene the vibronically induced transition moments are comparable to the direct transition moment, but that in *cis*-hexatriene the vibronically induced transition moments are considerably larger than the direct transition moment, thereby lending support to the conclusion that vibronic coupling between the S_1 and S_2 states is a more effective pathway for the S_1 states state to obtain transition moment than symmetry breaking.

IV. CONCLUSIONS

All-*trans* octatetraene is a model compound whose vibronically resolved electronic spectrum has allowed the empirical assignment of a large number of vibrational bands of the $1^1A_g-2^1A_g$ spectrum. The 0-0 vibronic transition of the spectrum is strictly one-photon forbidden: as such the totally symmetric mode progressions are built on false origins of b_u symmetry. The quantum chemical simulation of the vibronic structure therefore requires two distinct types of calculations. In the calculation of the vibronically induced intensities, the mixing of the A_g states with B_u states must be described accurately. It is perhaps not too surprising that the best results are obtained when polarization function, i.e., d atomic orbitals, are added to the carbon atoms. In fact, this result can be explained if one considers that the electronic states, that are more effective in inducing intensity in the $1^1A_g-2^1A_g$ transition, are those that have a strong transition dipole moment with either one of the A_g states. The covalent nature of the A_g states makes transitions from them to ionic states such as, but not solely, the 1^1B_u state strongly allowed. As pointed out before,^{6,7} ionic states have a diffuse nature which makes their wave function extend far from the nuclei. In a scheme based on localized atomic orbitals, this phenomenon can be described either by orbitals whose exponent is small in absolute value or by orbitals with a high principal quantum number. Polarization functions fit this role.

The calculation of the Franck-Condon progressions uses CASSCF force fields. Once the nature of the experiment is partially accounted for by scaling the intensities with the experimental lifetimes, the simulations agree very well with the experiment. Implicitly, the accuracy of the calculations of the totally symmetric progressions strongly support the over-

all existence of a significant Duschinsky effect: in fact, we found that proper accounting of normal mode mixing is mandatory to improve the accuracy of the calculations of the intensities of the false origins. Frequency variations and mode scrambling also cause the appearance of four double-quanta bands that we have somewhat tentatively assigned in the experimental spectra. Calculations of the transition dipole moments induced by the introduction of a *cis* linkage in octatetraene show that the two symmetry breaking effects are of the same order of magnitude and not dramatically different as it was previously thought.

We are now planning to extend our investigation to other polyenic systems and to study the possible presence of non-linearity in the spectra of these molecules.

- ¹G. Orlandi, F. Zerbetto, and M. Z. Zgierski, *Chem. Rev.* **91**, 867 (1991), and references therein.
- ²*Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics*, edited by J. L. Bredas and R. R. Chance (Kluwer Academic, Dordrecht, 1990).
- ³R. R. Birge, *Annu. Rev. Phys. Chem.* **41**, 683 (1990).
- ⁴B. S. Hudson, B. E. Kohler, and K. Schulten, *Excited States*, edited by E. C. Lim, Vol. 6, 1 (1982).
- ⁵L. Salem and C. Rowland, *Angew. Chem.* **11**, 92 (1972); J. Michl, *J. Mol. Photochem.* **4**, 243 (1972).
- ⁶F. Zerbetto and M. Z. Zgierski, *J. Chem. Phys.* **98**, 4822 (1993).
- ⁷F. Zerbetto and M. Z. Zgierski, *J. Chem. Phys.* **101**, 1842 (1994).
- ⁸G. Orlandi and F. Zerbetto, *Chem. Phys. Lett.* **131**, 409 (1986).
- ⁹H. Petek, A. J. Bell, Y. S. Choi, K. Yoshihara, B. A. Tounge, and R. L. Christensen, *J. Chem. Phys.* **98**, 3777 (1993).
- ¹⁰G. Herzberg and E. Teller, *Z. Phys. Chem. (Leipzig) B* **21**, 410 (1933).
- ¹¹F. Zerbetto and M. Z. Zgierski, *Chem. Phys.* **127**, 17 (1988).
- ¹²G. Orlandi, P. Palmieri, R. Tarroni, F. Zerbetto, and M. Z. Zgierski, *J. Chem. Phys.* **100**, 2458 (1994).
- ¹³T. H. Dunning, Jr. and P. J. Hay, *Methods of Electronic Structure Theory*, edited by H. F. Shaefer III (Plenum, New York 1977), pp. 1-27.
- ¹⁴T. H. Dunning, Jr., *J. Chem. Phys.* **53**, 2823 (1970); **55**, 716 (1971).
- ¹⁵W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.* **56**, 2257 (1972); P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta* **28**, 213 (1973).
- ¹⁶R. J. Buenker, S. D. Peyerimhoff, and W. Butscher, *Mol. Phys.* **35**, 771 (1978); P. J. Bruna, S. D. Peyerimhoff, and R. J. Buenker, *Chem. Phys. Lett.* **72**, 278 (1980).
- ¹⁷GAMESS-UK is a package of *ab initio* programs written by M. F. Guest, J. H. van Lenthe, J. Kendrick, K. Schöffel, P. Sherwood, and R. J. Harrison, with contributions from R. D. Amos, R. J. Buenker, M. Dupuis, N. C. Handy, P. J. Knowles, V. Bonacic-Koutecky, W. von Niessen, V. R. Saunders, and A. Stone. The package is derived from the original GAMESS code due to M. Dupuis, D. Spangler, and J. Wendoloski, NRCC Software Catalog, Vol. 1, Program No. QG01 (GAMESS), 1980.
- ¹⁸M. W. Schmidt, K. K. Baldrige, J. A. Boatz, J. H. Hensen, S. Koseki, M. S. Gordon, K. A. Nguyen, T. L. Windus, and S. T. Elbert, *QCPE Bull.* **10**, 52 (1990).
- ¹⁹E. Bright Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).
- ²⁰E. V. Doktorov, I. A. Malkin, and V. I. Man'ko, *J. Mol. Spectrosc.* **64**, 302 (1977).
- ²¹H. Yoshida and M. Tasumi, *J. Chem. Phys.* **89**, 2803 (1988).
- ²²W. J. Buma, B. E. Kohler, and K. Song, *J. Chem. Phys.* **92**, 4622 (1990); **94**, 6367 (1991).
- ²³H. Petek, A. J. Bell, K. Yoshihara, and R. L. Christensen, *J. Chem. Phys.* **96**, 2412 (1992).
- ²⁴M. F. Granville, G. R. Holtom, and B. E. Kohler, *J. Chem. Phys.* **72**, 4671 (1980); M. F. Granville, B. E. Kohler, R. L. Christensen, and K. L. D'Amico, *ibid.* **70**, 593 (1979); B. E. Kohler and T. A. Spiglanin, *ibid.* **80**, 3091 (1984).
- ²⁵W. J. Buma, B. E. Kohler and T. Shaler, *J. Chem. Phys.* **96**, 399 (1992).
- ²⁶W. J. Buma and F. Zerbetto (unpublished).