Modeling the Spectroscopy of the Lowest Excited Singlet State of *cis,trans*-1,3,5,7-Octatetraene: The Role of Symmetry Breaking and Vibronic Interactions

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The effects of the introduction of a cis linkage in the simplest polyenic chain containing both a cis and a trans bond on its spectroscopy are studied by using extensive ab initio calculations of the vibronically induced transition moments to the lowest excited singlet state and the first- and second-order vibronic coupling matrix elements between the lowest electronic states. It is shown that the effect of lowering the symmetry from C_{2h} to C_s is less important than that of vibronic coupling between the lower electronic states. As a result, the $S_1 \leftarrow S_0$ excitation spectrum is found to be dominated by bands arising from Herzberg−Teller borrowing. Support for this conclusion is found in the comparison of the theoretically predicted spectrum with excitation spectra in the solid state and by calculation of the first-order vibronic coupling matrix elements between S_1 and S_2. The well-known S_0−S_1 coupling, which leads to the frequency inversion of the completely in-phase C═C bond stretching vibration between the two states in all-trans polyenes, is shown to spread over several C═C bond stretching vibrations. Finally, it is found that the second-order S_1−S_2 couplings are not particularly affected in the isomerized molecule, in agreement with previous calculations that showed them in all-*trans*-octatetraene to be linked to stringlike behavior.

I. Introduction

Linear systems have the appeal of simplicity and elegance. When linearity arises in a geometric context because of atomic arrangements, chemists and physicists alike have often been able to use analytical models to obtain fundamental insight into the properties of such molecules. The models have shown a richness of facets reflecting the important roles that some linear chains play in biology and materials science. Foremost amongst linear systems are those derived from the CH substructure that appears in the light harvesting and the vision processes of living organisms and that are envisaged as one of the basic building blocks of future molecular electronics.[1,2]

For a long time, it was assumed that the lowest excited singlet state of polyenes derives from the intuitively expected HOMO → LUMO excitation, which, for all-trans polyenes of C_{2h} symmetry, leads to the strongly dipole-allowed ionic 1^1B_u state. Starting with the initial discovery by Hudson and Kohler[3] that in α,ω-diphenyl-1,3,5,7-octatetraene an excited singlet state could be observed with an excitation energy that was lower than that of the 1^1B_u state, it is now firmly established that in polyenes with three or more double bonds the first excited singlet state is the 2^1A_g valence state,[4,5] which is strictly dipole forbidden in all-trans polyenes. This state is characterized by the important role of electron correlation and can, in a zeroth-order picture, be described as a linear combination of the HOMO → LUMO + 1, HOMO − 1 → LUMO, and $(\mathrm{HOMO})^2 \rightarrow (\mathrm{LUMO})^2$ excitations.[6] Vibronic interactions emerge prominently in the spectroscopic properties of this 2^1A_g state. For example, vibronic coupling with the 1^1B_u state along vibrational coordinates of b_u symmetry induces one-photon transition intensity,[4,7] while vibronic coupling with the 1^1A_g ground state is responsible for the counterintuitive increase of the frequency of the completely in-phase C═C bond stretching vibration of a_g symmetry upon excitation.[7−9]

Carbon chemistry graces polyenic chains with an important degree of freedom, which is exploited by nature in retinoids to trigger the series of reactions that leads to the visual signal and in the synthesis of polyacetylene to polymerise acetylene, the possibility to form CC double bonds in either the cis or the trans configuration. Whilst there is no doubt that the most stable structures are associated with trans linkages, the presence of cis bonds deserves close scrutiny because of the role that metastable species containing them can play in a number of phenomena. Apart from the decrease of stability, introduction of a cis linkage usually has the nontrivial effect of diminishing the symmetry of the chain, which in turn, can make previously forbidden electronic transitions (weakly) allowed. One can therefore expect the existence of specific spectroscopic fingerprints of the less stable configuration. Because of the competition with various other effects, vibronic intensity borrowing comes to mind as the most relevant one, it is not entirely straightforward to predict the activity of a single cis junction on an all-trans chain.

In this work, we consider from a theoretical point of view the spectroscopy of the first excited singlet state of the simplest conjugated system in which both a cis and a trans C═C bond are present, namely *cis,trans*-1,3,5,7-octatetraene, and compare the results with those previously obtained for the all-trans

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isomer.[10,11] The comparison is then encouragingly extended to experimental results available from studies in a nonisolated phase.[12]

The presentation is organized as follows. In section II, the theoretical background and the details of calculations are given. Here, not only the generalities of the methods used are provided but they are also specialized to the case at hand. In section III, the vibronically induced intensities along with the first- and second-order vibronic couplings are discussed with the intent of furnishing a comprehensive view of *trans*,*trans*-1,3,5,7- and *cis*,*trans*-1,3,5,7-octatetraene.

II. Theoretical Background and Computational Details

Within the Born−Oppenheimer approximation, the transition dipole moment between the ground state $\psi_{\rm g}(\mathbf{r};\mathbf{Q})\chi_{\rm g}(\mathbf{Q})$ and an excited state $\psi_{\rm e}(\mathbf{r};\mathbf{Q})\chi_{\rm e}(\mathbf{Q})$ is given by $(\chi_{\rm e}(\mathbf{Q})|\langle\psi_{\rm e}(\mathbf{r};\mathbf{Q})|\mu(\mathbf{r})|\psi_{\rm g}(\mathbf{r};\mathbf{Q})\rangle\chi_{\rm g}\ \mathbf{Q}))$, in which $\psi_i(\mathbf{r};\mathbf{Q})$ denotes the electronic wavefunction of state i and $\chi_i(\mathbf{Q})$ its vibrational wavefunction, with $\mathbf{r}$ and $\mathbf{Q}$ being the set of electronic and nuclear coordinates, respectively. Generally, one defines the electronic transition moment as $\mathbf{M}_{\rm ge}(\mathbf{Q}) = \langle\psi_{\rm e}(\mathbf{r};\mathbf{Q})|\mu(\mathbf{r})|\psi_{\rm g}(\mathbf{r};\mathbf{Q})\rangle$. Within the Condon approximation, it is assumed that this electronic transition moment is independent of the nuclear coordinates and equal to the value at the equilibrium geometry of the ground state $\mathbf{M}_{\rm ge}(\bar{\mathbf{Q}}_{\rm g}) = \langle\psi_{\rm e}(\mathbf{r};\bar{\mathbf{Q}}_{\rm g})|\mu(\mathbf{r})|\psi_{\rm g}(\mathbf{r};\bar{\mathbf{Q}}_{\rm g})\rangle$, leading to an expression for the vibronic transition moment which reads

$$\mathbf{M}_{\rm ge} = \mathbf{M}_{\rm ge}(\bar{\mathbf{Q}}_{\rm g})(\chi_{\rm e}(\mathbf{Q})|\chi_{\rm g}(\mathbf{Q})) \qquad (1)$$

The Condon approximation thus predicts that the intensities of vibronic transitions are determined by the square of the vibrational overlap integrals and are only nonzero for transitions involving either totally symmetric modes or even numbers in the difference of quantum numbers between the initial and final state.

For all-trans polyenes of C_{2h} symmetry, the vibrationless $2^1A_g \leftarrow 1^1A_g$ one-photon transition is symmetry forbidden. To account for the fact that the transition can nevertheless be observed, albeit built upon false origins, non-Condon terms need to be invoked, which derive from the $\mathbf{Q}$ dependence of the electronic transition moment. This $\mathbf{Q}$ dependence can be incorporated into the electronic transition moment by expanding it, following Herzberg and Teller,[13] in a Taylor series of the ground-state normal coordinates centred at the equilibrium geometry of the ground state

$$\mathbf{M}_{\rm ge}(\mathbf{Q}) \approx \mathbf{M}_{\rm ge}(\bar{\mathbf{Q}}_{\rm g}) + \sum_p \left(\frac{\partial \mathbf{M}(\mathbf{Q})}{\partial Q_{\rm p,g}}\right)_{\bar{\rm Q}_{\rm g}} Q_{\rm p,g} = \mathbf{M}_{\rm ge}(\bar{\mathbf{Q}}_{\rm g}) + \sum_p \mathbf{m}_{\rm p,g} Q_{\rm p,g} \qquad (2)$$

The $1_{p,\rm e} \leftarrow 0_{\rm g}$ vibronic transition moments are now given by

$$\mathbf{M}_{\rm ge}{}^{01_p} = \mathbf{M}_{\rm ge}(\bar{\mathbf{Q}}_{\rm g})(1_{p,\rm e}|0_{\rm g}) + \sum_{p'} \mathbf{m}_{p',\rm g}(1_{p,\rm e}|Q_{p',\rm g}|0_{\rm g}) \qquad (3)$$

where $|1_{p,\rm e})$ denotes the vibrational wavefunction of the vibrational state belonging to the excited state in which mode p is in its first excited state and all other modes are in their ground state. For the $2^1A_g \leftarrow 1^1A_g$ one-photon transition in all-trans polyenes, $\mathbf{M}_{\rm ge}(\bar{\mathbf{Q}}_{\rm g})$ is zero and the excitation spectrum is built upon false origins whose intensities are determined by an electronic factor in the form of the derivatives of the electronic transition moment $\mathbf{m}_{p',\rm g}$ and a vibrational factor, which in the harmonic approximation can be expressed as[14]

$$(1_{p,\rm e}|Q_{p',\rm g}|0_{\rm g}) = \left(\frac{\hbar}{2\omega_{p',\rm g}}\right)^{1/2}(1_{p,\rm e}|1_{p',\rm g}) \qquad (4)$$

From another point of view, one could say that the intensities of the false origins in all-trans polyenes arise from the mixing of electronic states under the influence of the vibrational motions. Once the symmetry lowering due to the vibrational motion along, for example, mode $Q_{\rm k}$ is included, the wavefunctions of the electronic states can be described through perturbation theory as linear combinations of the electronic states at the equilibrium geometry

$$\psi_i(\mathbf{r};\mathbf{Q}) \approx \psi_i(\mathbf{r};\bar{\mathbf{Q}}_{\rm g}) + \sum_{j\neq i} \frac{\left\langle \psi_i(\mathbf{r};\bar{\mathbf{Q}}_{\rm g}) \middle| \left(\frac{\partial {\rm H}_{\rm e}(\mathbf{r};\mathbf{Q})}{\partial Q_k}\right)_{\bar{\mathbf{Q}}_{\rm g}} \middle| \psi_j(\mathbf{r};\bar{\mathbf{Q}}_{\rm g}) \right\rangle}{E_i(\bar{\mathbf{Q}}_{\rm g}) - E_j(\bar{\mathbf{Q}}_{\rm g})} Q_{\rm k}\psi_j(\mathbf{r};\bar{\mathbf{Q}}_{\rm g}) \qquad (5)$$

The experimental observation that for all-trans polyenes the one-photon excitation and emission spectra of the 2^1A_g state are built upon false origins of b_u symmetry shows that in these cases vibronic intensity is induced by vibronic interactions with states of B_u symmetry. While vibronic coupling via non-totally symmetric b_u modes is necessary to explain the observation of the $2^1A_g \leftarrow 1^1A_g$ one-photon transition, vibronic coupling via totally symmetric a_g modes has been found crucial to rationalize the frequency increase of the completely in-phase C═C bond stretching vibration upon excitation from the ground state to the first excited state. Calculations of the appropriate adiabatic vibronic coupling matrix elements[8]

$$V_{ij}^k = \left\langle \psi_i(\mathbf{r};\bar{\mathbf{Q}}_{\rm g}) \middle| \left(\frac{\partial H_{\rm e}(\mathbf{r};\mathbf{Q})}{\partial Q_k}\right)_{\bar{\mathbf{Q}}_{\rm g}} \middle| \psi_j(\mathbf{r};\bar{\mathbf{Q}}_{\rm g}) \right\rangle \qquad (6a)$$

and corresponding nonadiabatic vibronic coupling matrix elements[11,15,16]

$$T_{ij}^k = \left\langle \psi_i(\mathbf{r};\bar{\mathbf{Q}}_{\rm g}) \middle| \frac{\partial}{\partial Q_k} \middle| \psi_j(\mathbf{r};\bar{\mathbf{Q}}_{\rm g}) \right\rangle_{\bar{\mathbf{Q}}_{\rm g}} = \frac{V_{ij}^k}{\Delta E_{ij}} \qquad (6b)$$

have shown that the vibronic intensity in the $2^1A_g \leftarrow 1^1A_g$ one-photon transition predominantly derives from the vibronic interaction between the 2^1A_g state and the one-photon dipole-allowed 1^1B_u, state, while vibronic coupling of the 1^1A_g and 2^1A_g states is responsible for the frequency inversion of the completely in-phase C═C bond stretching vibration of a_g symmetry in the ground and excited states.

The expansions used in eqs 2 and 5 have been truncated to first order, since higher-order corrections are in general expected to be significantly smaller and not necessary to explain the salient features in the experimental spectra. All-*trans*-octatetraene is at odds with such expectations.[11] Calculations of second-order vibronically induced intensities of out-of-plane a_u and b_g combination bands in the $2^1A_g \leftarrow 1^1A_g$ excitation spectrum and calculations of the second-order vibronic coupling matrix elements

$$T^{kl}_{2^1A_g,1^1B_u} = \left(\left\langle 2^1A_g \middle| \left(\frac{\partial}{\partial Q_k^{a_u}}\right)\left(\frac{\partial}{\partial Q_l^{b_g}}\right) \middle| 1^1B_u \right\rangle\right)_{\bar{\mathbf{Q}}_{\rm g}} \qquad (7)$$

TABLE 1: CASSCF/6-31G* Vibrational Frequencies (cm^{-1}) for the Ground (S_0) and First Excited Singlet States (S_1) of *cis,trans*-Octatetraene Scaled Uniformly by a Factor of 0.9 for the a′ Vibrations and Unscaled for the a″ Vibrations[a]

a′	S_0	S_1	a″	S_0	S_1
ν_{33}	93	104	ν_{48}	66	70
ν_{32}	207	222	ν_{47}	122	95
ν_{31}	325	316	ν_{46}	174	164
ν_{30}	400	387	ν_{45}	221	259
ν_{29}	476	473	ν_{44}	409	332
ν_{28}	648	639	ν_{43}	639	364
ν_{27}	874	865	ν_{42}	681	377
ν_{26}	919	917	ν_{41}	806	461
ν_{25}	1022	976	ν_{40}	841	472
ν_{24}	1118	984	ν_{39}	856	728
ν_{23}	1165	1087	ν_{38}	860	790
ν_{22}	1226	1165	ν_{37}	977	799
ν_{21}	1262	1210	ν_{36}	1015	874
ν_{20}	1274	1250	ν_{35}	1046	959
ν_{19}	1276	1264	ν_{34}	1061	977
ν_{18}	1302	1313			
ν_{17}	1364	1333			
ν_{16}	1414	1353			
ν_{15}	1454	1461			
ν_{14}	1526	1482			
ν_{13}	1575	1500			
ν_{12}	1605	1588			
ν_{11}	1608	1817			

[a] CH stretching modes are excluded.

clearly demonstrated the importance of second-order coupling terms and provided evidence for stringlike behavior in this molecule.

In the present study, we consider *cis,trans*-l,3,5,7-octatetraene. Compared to all-*trans* polyenes, the 1^1A_g, 2^1A_g, and 1^1B_u states are now transformed into the $1^1A'$, $2^1A'$, and $3^1A'$ states, while the a_g and b_u in-plane vibrations and the a_u and b_g out-of-plane vibrations become of a′ and a″ symmetry. Because of the absence of inversion symmetry, the S_1 ($2^1A'$) ← S_0 ($1^1A'$) transition is symmetry allowed. Apart from the direct transition moment $\mathbf{M}_{ge}(\bar{\mathbf{Q}}_g)$ (see eq 2), the electronic nature of the transition makes it likely that the non-Condon terms $\mathbf{m}_{p,g}$ induced by totally symmetric a′ modes still contribute significantly to the total vibronic transition moment $\mathbf{M}_{ge}(\mathbf{Q})$. In that case, not only the vibronic intensity of the $1_{p,e} \leftarrow 0_g$ transitions is affected by the non-Condon terms (see eq 3) but also the dipole moment of the $0_e \leftarrow 0_g$ transition is modified and, in the harmonic approximation, is given by

$$\mathbf{M}_{ge}^{00} = \mathbf{M}_{ge}(\bar{\mathbf{Q}}_g)(0_e|0_g) + \sum_{p'} \mathbf{m}_{p',g}\left(\frac{\hbar}{2\omega_{p',g}}\right)^{1/2}(0_e|1_{p',g}) \quad (8)$$

Evaluation of the various terms entering eqs 3 and 8 has been performed using the GAMESS-DAKOTA package[17] in a way similar to our previous work on all-*trans*-octatetraene.[10,11] The starting points of the calculations are the force fields of the $1^1A'$ and $2^1A'$ states, which have been obtained at the CASSCF (eight π electrons in eight active π orbitals) level employing the 6-31G* basis set of atomic orbitals.[18] The vibrational frequencies resulting from these calculations are reported in Table 1. In contrast to all-*trans*-octatetraene, experimental information on the vibrational frequencies in these two states is rather scarce. For all-*trans*-octatetraene, agreement between experimental and theoretical frequencies could be obtained by scaling the frequencies of in-plane a′ vibrations with a factor of 0.9, while the frequencies of the out-of-plane a″ vibrations did not need to be scaled.[10] We have consequently chosen to apply these scaling factors here as well. It should be stressed, however, that, although the vibrational frequencies appear explicitly in eqs 3 and 7, the results as presented below are not very susceptible to the choice of frequencies. Vibrational overlap integrals appearing in eqs 3 and 8 have been calculated using an in-house written program on the basis of the theory developed in ref 19.

The derivatives $\mathbf{m}_{p,g}$ have been calculated numerically. To this purpose, the $2^1A' \leftarrow 1^1A'$ transition moment was determined for molecular geometries displaced along each individual a′ coordinate using a step size of $\Delta Q_p = 0.1$ amu$^{1/2}$ Å. Transition moments were calculated employing full-CI calculations in the space of four π and four π^* ground state 6-31G* SCF MOs (1764 configurations).

Nonadiabatic first-order vibronic coupling matrix elements via a′ vibrations have been calculated for coupling of the S_1 ($2^1A'$) and S_2 ($3^1A'$) states ($\langle 2^1A'|\partial/\partial Q_p^{a'}|3^1A'\rangle$) and of the S_0 ($1^1A'$) and $S_1(2^1A')$ states ($\langle 1^1A'|\partial/\partial Q_{p'}^{a'}|2^1A'\rangle$). These couplings have been obtained by numerical differentiation of the electronic wavefunctions on the basis of the theory developed in ref 20 using a step size of $\Delta Q_p = 0.1$ amu$^{1/2}$ Å. The accuracy of such calculations can be checked by comparison of each matrix element with its transpose, since the condition that the CI wavefunctions $\psi_i(\mathbf{r};\mathbf{Q})$ and $\psi_j(\mathbf{r};\mathbf{Q})$ are orthogonal for all values of $\mathbf{Q}$ implies that

$$\left\langle \psi_i(\mathbf{r};\mathbf{Q}) \middle| \frac{\partial \psi_j(\mathbf{r};\mathbf{Q})}{\partial Q_p} \right\rangle = -\left\langle \frac{\partial \psi_i(\mathbf{r};\mathbf{Q})}{\partial Q_p} \middle| \psi_j(\mathbf{r};\mathbf{Q}) \right\rangle \quad (9)$$

Numerical differentiation has also been employed to calculate second-order nonadiabatic coupling elements via combinations of a″ vibrations. Here, numerical stability was obtained for step sizes of $\Delta Q_k = \Delta Q_l = 0.025$ amu$^{1/2}$ Å for second derivatives of the form $\partial^2/(\partial Q_k^{a''}\partial Q_l^{a''})$ and a step size of $\Delta Q_k = 0.05$ amu$^{1/2}$ Å for second derivatives of the form $\partial^2/\partial Q_k^{a''2}$. These second derivatives are in principle not antisymmetric in the state indices; instead, it can be shown that the orthogonality condition of the CI wavefunctions leads to

$$\left\langle \psi_i \middle| \frac{\partial^2 \psi_j}{\partial Q_k \partial Q_l} \right\rangle = -\left\langle \frac{\partial^2 \psi_i}{\partial Q_k \partial Q_l} \middle| \psi_j \right\rangle - \left\langle \frac{\partial \psi_i}{\partial Q_k} \middle| \frac{\partial \psi_j}{\partial Q_l} \right\rangle - \left\langle \frac{\partial \psi_i}{\partial Q_l} \middle| \frac{\partial \psi_j}{\partial Q_k} \right\rangle \quad (10)$$

which, by insertion of the resolution of the identity, can be rewritten into

$$\left\langle \psi_i \middle| \frac{\partial^2 \psi_j}{\partial Q_k \partial Q_l} \right\rangle = -\left\langle \frac{\partial^2 \psi_i}{\partial Q_k \partial Q_l} \middle| \psi_j \right\rangle - \sum_n \left[\left\langle \psi_i \middle| \frac{\partial \psi_n}{\partial Q_k} \right\rangle \left\langle \psi_j \middle| \frac{\partial \psi_n}{\partial Q_l} \right\rangle + \left\langle \psi_i \middle| \frac{\partial \psi_n}{\partial Q_l} \right\rangle \left\langle \psi_j \middle| \frac{\partial \psi_n}{\partial Q_k} \right\rangle \right] \quad (11)$$

For the matrix elements considered here, i.e., coupling of the $2^1A'$ and $3^1A'$ states via combinations of a″ vibrations, symmetry requirements dictate that only first-order couplings of the $2^1A'$ and $3^1A'$ states with states of A″ symmetry contribute to the second term in eq 11. Since the latter states do not derive from $\pi\pi^*$ excitations, it is reasonable to expect that they will be small, and, consequently, that the considered second derivatives will still be approximately antisymmetric in the state indices. The results presented below indeed confirm this picture.

III. Results and Discussion

A. Vibronically Induced Transition Intensities. Table 2 presents the results of the calculations on the vibronic transition

TABLE 2: Relative Intensities of the a′ Fundamentals in the $S_1 \leftarrow S_0$ Absorption Spectrum of *cis,trans*-Octatetraene Using the Condon Approximation (I_{FC}), in which Intensities are Proportional to the Franck−Condon Factors and, in the approximation, in which also the Non-Condon Terms $(\partial \mathbf{M}_{S_1\leftarrow S_0}/\partial q_i^{a'})_{\bar{Q}(S_0)}$ Are Taken into Account (I_{FC+NC})[e]

mode	$I_{FC}{}^a$ $(\nu_i^{a'})_0^1$	$\lvert(\partial \mathbf{M}_{S_1\leftarrow S_0}/\partial q_i^{a'})_{\bar{Q}(S_0)}\rvert$	$I_{FC+NC}{}^a$ $(\nu_i^{a'})_0^1$	freq[c]	exptl[d] freq	exptl[d] int
ν_{33}	16.2	0.048 38	209.0	104		
ν_{32}	31.6	0.062 94	513.8	222	213	20
ν_{31}	43.8	0.047 56	81.8	316	328	5
ν_{30}	4.4	0.058 98	531.8	387	393	25
ν_{29}	1.3	0.005 98	3.0	473	497	5
ν_{28}	3.2	0.062 15	498.0	639	657	10
ν_{27}	3.5	0.018 91	3.0	865		
ν_{26}	8.8	0.002 38	16.0	917		
ν_{25}	0.3	0.020 46	10.5	976		
ν_{24}	4.2	0.018 56	10.6	984		
ν_{23}	51.1	0.034 37	46.1	1087	1130	30
ν_{22}	4.1	0.025 39	28.4	1165		
ν_{21}	26.7	0.031 05	90.9	1210	1228	20
ν_{20}	5.4	0.005 06	170.5	1250		
ν_{19}	7.2	0.003 55	18.7	1264		
ν_{18}	17.8	0.003 69	73.2	1313	1323	15
ν_{17}	6.7	0.035 95	104.2	1333		
ν_{16}	7.9	0.014 47	14.1	1353		
ν_{15}	0.0	0.034 19	5.0	1461		
ν_{14}	4.3	0.009 49	3.4	1482		
ν_{13}	10.5	0.014 75	368.8	1500	1508	35
ν_{12}	4.0	0.015 47	.5	1588		
ν_{11}	288.9	0.021 35	333.9	1817	1723	95

[a] Intensities given relative to the 0_0^0 transition, whose intensity is taken as 100.0. Transition moment $\lvert\mathbf{M}_{S_1\leftarrow S_0}(\bar{\mathbf{Q}}(S_0))\rvert$ (see eq 3) is 0.037 73 e Bohr. [b] Intensities given relative to the 0_0^0 transition, whose intensity is taken as 100.0. Transition moment $\lvert\mathbf{M}^{00}_{S_1\leftarrow S_0}\rvert$ (see eq 8), corrected for non-Condon terms, is 0.021 93 e Bohr. [c] Calculated frequencies (cm^{-1}) in S_1 (see Table 1). [d] Frequencies (cm^{-1}) and intensities of transitions as observed in fluorescence excitation experiments on *cis,trans*-octatetraene in an *n*-hexane matrix at 4.2 K.[12] Frequencies and intensities are given with respect to the 0_0^0 transition, whose intensity has been taken as 100. [e] The non-Condon terms $(\partial \mathbf{M}_{S_1\leftarrow S_0}/\partial q_i^{a'})_{\bar{Q}(S_0)}$ (e Bohr) are given employing dimensionless vibrational coordinates $q_i^{a'}$.

TABLE 3: First-Order Vibronic Coupling Matrix Elements $\langle S_1|\partial/\partial q_i^{a'}|S_2\rangle$ and $\langle S_0|\partial/\partial q_i^{a'} S_1\rangle$ for Totally Symmetric Vibrations of *cis,trans*-Octatetraene Employing Dimensionless Vibrational Coordinates $q_i^{a'}$[a]

$q_{a'}^{i}$	$100\ \langle S_1\lvert\partial/\partial q_i^{a'}\rvert S_2\rangle$	$100\ \langle S_0\lvert\partial/\partial q_i^{a'}\rvert S_1\rangle$
ν_{33}	1.870(0)	0.039(0)
ν_{32}	2.137(0)	0.061(0)
ν_{31}	2.001(2)	0.085(0)
ν_{30}	2.260(1)	0.134(0)
ν_{29}	0.089(0)	0.230(0)
ν_{28}	2.970(2)	0.161(0)
ν_{27}	0.218(1)	0.510(1)
ν_{26}	0.442(1)	0.260(1)
ν_{25}	0.788(1)	0.716(0)
ν_{24}	1.033(0)	0.323(0)
ν_{23}	2.062(4)	0.980(2)
ν_{22}	0.504(10)	1.429(0)
ν_{21}	0.559(3)	0.489(0)
ν_{20}	4.320(18)	0.372(1)
ν_{19}	0.690(1)	0.071(0)
ν_{18}	1.555(21)	0.385(0)
ν_{17}	2.000(5)	0.063(0)
ν_{16}	0.976(16)	0.281(0)
ν_{15}	1.313(0)	0.076(0)
ν_{14}	2.134(4)	0.377(0)
ν_{13}	0.447(1)	0.897(2)
ν_{12}	8.526(28)	1.394(2)
ν_{11}	6.404(229)	2.257(1)

[a] Numbers in parentheses give the accuracy in the last digits of the calculated value.

dipole intensities of the $(\nu_i^{a'})_0^1$ transitions in the $S_1 \leftarrow S_0$ excitation spectrum of *cis,trans*-octatetraene, which have been calculated as $I_{i_0^1} = \mathbf{M}^{01_i}_{S_1\leftarrow S_0}|^2/\mathbf{M}^{00}_{S_1\leftarrow S_0}|^2$. When non-Condon effects are neglected, these intensities are simply proportional to the appropriate Franck−Condon factors (column I_{FC}). It is important to notice that these Franck−Condon factors are not only determined by geometry changes upon excitation but by normal mode rotations (Duschinsky mixing[21]) as well. In fact, the Duschinsky matrix calculated for the a′ normal coordinates (not given) shows that, apart from ν_{33} to ν_{28}, for which rotations of less than 10° occur, all other modes become heavily scrambled upon excitation, similar to what was observed for the in-plane a_g and b_u modes of all-*trans*-octatetraene.[10]

In the same table, the non-Condon parameters $\mathbf{m}_{p,g}$ are reported. These have been calculated employing dimensionless vibrational coordinates $q_{p,g} = (\omega_{p,g}/\hbar)^{1/2}Q_{p,g}$, with ω and $\hbar$ expressed in atomic units, and will henceforth be referred to as $\mathbf{m}_{p,g}(q)$. A rough feeling of their influence on the vibronic transition dipole intensities can be obtained when we assume that geometry changes and normal mode rotations are absent upon excitation. In that case, the vibrational overlap integrals appearing in eqs 3, 4, and 8 become either unity or zero and $I_{i_0^1}$, reduces to $|\mathbf{m}_{i,g}(q)|^2/2|\mathbf{M}_{S_1\leftarrow S_0}(\mathbf{Q}_{S_0})|^2$. Inspection of the non-Condon parameters then reveals that they lead to intensities that are similar to or even larger than the intensities calculated on the basis of the direct transition moment $\mathbf{M}_{S_1\leftarrow S_0}(\bar{\mathbf{Q}}_{S_0})$ only. We can consequently conclude already that the effects of symmetry breaking of the octatetraene skeleton introduced by the incorporation of a cis linkage do not overshadow the role of vibronic coupling in the $S_1 \leftarrow S_0$ excitation spectrum.

Proper evaluation of the vibrational overlap integrals in eqs 3, 4, and 8 leads to the intensities given in Table 2 under the column I_{FC+NC}. Here interference effects between Franck−Condon factors and the non-Condon contributions become clearly visible. On the one hand, they lead to a considerably reduced transition moment of the 0_0^0 transition; on the other hand, they result in a redistribution of the intensities of the $(\nu_i^{a'})_0^1$ transitions as compared to the intensities predicted on the basis of Franck−Condon factors or non-Condon contributions only. Interestingly, these calculations predict that the 0_0^0 transition does not carry the largest intensity and that vibronic coupling dominates the spectrum.

In contrast to all-*trans*-octatetraene, for which extensive REMPI[22] and fluorescence excitation and emission studies[23] on the molecule in the gas phase have been reported, the S_1 state of *cis,trans*-octatetraene has, as yet, only been investigated at 4.2 K in a fluorescence excitation and emission study of the molecule incorporated into an *n*-hexane matrix.[12] Table 2 contains tentative assignments of bands observed in this experimental study. These assignments should be considered with the appropriate caution. First, the experimental study concerns nonisolated molecules. Previous studies on the site dependence of the $2^1A_g \leftarrow 1^1A_g$ transition of all-*trans*-octatetraene substituted in a series of *n*-alkane matrices[24] have clearly demonstrated the sensitivity of the intensity of vibronic transitions and, in particular, the 0_0^0 transition on local perturbations; the transition is strictly forbidden in an *n*-octane host, but in other hosts both allowed and symmetry forbidden components are observed. Bearing in mind that we have concluded above that the $S_1 \leftarrow S_0$ transition in *cis,trans*-octatetraene is dominantly influenced by vibronic coupling and that the molecule is not expected to fit very well in an *n*-hexane matrix, we may expect a significant influence of local perturbations on the vibronic transition intensities. Secondly, the comparison of gas-phase studies on the $2^1A_g \leftarrow 1^1A_g$ transition of all-*trans*-octatetraene[23] with solid-state studies[25] has shown that a_g and b_u modes may exhibit considerable solvent shifts, indicating that their description is sensitive to changes in electronic structure upon solvation. Finally, gas-phase studies on all-*trans*-octatetraene have shown that the lifetime of vibronic levels in the excited state decreases significantly as the vibrational energy increases.[22,23] It is reasonable to assume that the same will hold for *cis*,*trans*-octatetraene and, as a consequence, that the intensities of higher energy vibronic bands in the fluorescence excitation spectrum will be decreased.

Despite these limitations, it is gratifying to find that predicted and observed spectra are in qualitative, and for some bands even quantitative, agreement under the assumption that the 0_0^0 transition should not be considered. Equally important to notice is that such an agreement is completely absent if it would be assumed that the $S_1 \leftarrow S_0$ transition is dominated by the direct transition moment $\mathbf{M}_{S_1 \leftarrow S_0}(\bar{\mathbf{Q}}_{S_0})$, in which case the intensities of the bands should be proportional to the Franck−Condon factors. This observation, considered in light of the results of our previous work on all-*trans*-octatetraene,[10] which showed that quantitative agreement between theoretically predicted and experimentally observed intensities of totally symmetric progressions could be obtained using the same methodology used here, allows us to conclude that the experimental excitation spectrum also carries the signature of a dominant role of vibronic coupling.

Of interest is now to compare the vibronic transition intensities in *cis*,*trans*-octatetraene with those in all-*trans*-octatetraene. In order to avoid any bias with respect to basis set and equilibrium geometry, we have recalculated the $\mathbf{m}_{p,g}(q)$ parameter for all-*trans*-octatetraene for the dominant inducing b_u mode ν_{48} ($\tilde{\nu}_{1^1A_g} = 96$ cm^{-1}; $\tilde{\nu}_{2^1A_g} = 76$ cm^{-1}) at the same level employed here for *cis*,*trans*-octatetraene, i.e., CASSCF equilibrium geometry and normal coordinates, and found that $\mathbf{m}_{48,g}(q)$ has a magnitude of 0.07678 e Bohr. Assuming the absence of geometry changes and normal mode rotations upon excitation (vide supra), this value implies that the intensity of the 0_0^0 transition in *cis*,*trans*-octatetraene would be about half that of the $(\nu_{48})_0^1$ transition in all-*trans*-octatetraene. At the same time, however, Table 2 shows that for *cis*,*trans*-octatetraene $\mathbf{m}_{p,g}(q)$ parameters are calculated that are nearly equal to $\mathbf{m}_{48,g}(q)$. As a result, vibronic transition intensities to fundamentals of dominant a′ modes are about the same as that of the $(\nu_{48})_0^1$ transition in all-*trans*-octatetraene. Vibronic coupling can therefore be concluded to be equally important for the $S_1 \leftarrow S_0$ transition in both isomers, although considerably more modes participate in *cis*,*trans*-octatetraene than in all-*trans*-octatetraene.

TABLE 4: Second-Order Vibronic Coupling Matrix Elements $^1/_2\langle S_1|\partial^2/\partial q_i^{a''2} S_2\rangle$ and $^1/_2\langle S_0|\partial^2/\partial q_i^{a''2}|S_1\rangle$ for Non-Totally Symmetric Vibrations of *cis*,*trans*-Octatetraene Employing Dimensionless Vibrational Coordinates $q_i^{a'}$[c]

$q_i^{a''}$	100 $^1/_2\langle S_1\|\partial^2/\partial q_i^{a''2}\|S_2\rangle$[a]		100 $^1/_2\langle S_0\|\partial^2/\partial q_i^{a''2}\|S_1\rangle$	
ν_{48}	0.237	(0.024)	0.160	(−0.172)
ν_{47}	0.113	(−0.061)	0.319	(−0.045)
ν_{46}	0.387	(0.078)	0.113	(0.026)
ν_{45}	**0.693**	(0.026)	0.082	(−0.059)
ν_{44}	0.041	(−0.028)	0.056	(0.029)
ν_{43}	0.128	(−0.036)	0.016	(0.008)
ν_{42}	0.112	(−0.003)	0.032	(0.005)
ν_{41}	0.244	(−0.047)	0.010	(0.017)
ν_{40}	0.311	(−0.021)	0.137	(0.063)
ν_{39}	0.096	(0.017)	0.083	(−0.045)
ν_{38}	0.100	(0.016)	0.177	(0.020)
ν_{37}	0.389	(−0.048)	0.377	(0.137)
ν_{36}	0.252	(−0.009)	**0.865**	(−0.242)
ν_{35}	0.229	(−0.285)	**0.722**	(−0.350)
ν_{34}	**3.323**	(−0.610)	**0.771**	(−0.417)

[a] Entries given in boldface are larger than $1/\sqrt{10}\langle S_1|\partial/\partial q_{33}|S_2\rangle$. [b] Entries given in boldface are larger than $1/\sqrt{10}\langle S_0\partial/\partial q_{11}|S_1\rangle$. [c] Numbers in parentheses give the values of the matrix elements $100\langle\partial S_1/\partial q_i^{a''}|\partial S_2/\partial q_i^{a''}\rangle$ and $100\langle\partial S_0/\partial q_i^{a''}|\partial S_1/\partial q_i^{a''}\rangle$.

B. First-Order Vibronic Coupling Matrix Elements. In the previous section, we have concluded that the $S_1 \leftarrow S_0$ transition of *cis*,*trans*-octatetraene is dominantly influenced by vibronic coupling along a′ modes. For all-*trans*-octatetraene semiempirical[8] and ab initio calculations[11] have demonstrated that this coupling can be traced back primarily to the coupling of S_1 with S_2 via b_u modes. We consequently expect the same to be true for *cis*,*trans*-octatetraene, an expectation by and large carried out by the first-order nonadiabatic vibronic coupling matrix elements along a′ modes given in Table 3. These modes now not only fulfil the role of the b_u vibrations in all-*trans* octatetraene but can also couple the first excited state with the ground state. Table 3 shows indeed that both couplings occur, although the majority of the modes can be termed as acting as "b_u" modes or "a_g" modes.

When we first consider the $\langle S_1|\partial/\partial q_i^{a'}|S_2\rangle$ matrix elements, we find that they are nearly equal in magnitude to the $\langle 2^1A_g|\partial/\partial q_i^{b_u}|1^1B_u\rangle$ matrix elements calculated for all-*trans*-octatetraene.[11] For example, for the most active mode in all-*trans*-octatetraene (ν_{48}), a coupling of 0.027 34 is obtained; here the lower frequency vibrations have similar values. It is clear, however, that while in all-*trans*-octatetraene ν_{48} is by far the dominant low-frequency mode in coupling S_1 with S_2, the activity is distributed over many more modes in *cis*,*trans*-octatetraene. Similar to the conclusions reached from our calculations on all-*trans*-octatetraene, Table 3 shows that the vibronically induced transition moments of the low-frequency a′ modes are predominantly determined by the S_1-S_2 couplings; e.g., for ν_{32}, a two-state model predicts an induced transition moment of 0.070 74 e Bohr, while direct calculation of the moment (Table 2) leads to a value of 0.062 94 e Bohr.

Coupling of the S_0 and S_1 states in all-trans polyenes occurs predominantly via the Franck−Condon active C═C stretching mode. For all-*trans*-octatetraene, it was found that the coupling induced via this mode (ν_6) by far surpasses the coupling induced by the other a_g C═C stretching mode ν_7 (0.0329[16] vs 0.0075[26]). Here, we see that the Franck−Condon active C═C stretching mode (ν_{11}) is also responsible for the largest coupling but that the other C═C stretching vibrations ν_{12} and ν_{13}, and to a lesser extent ν_{14}, now also carry a large part of the coupling. Although the Franck−Condon active C═C mode in *cis*,*trans*-octatetraene itself therefore couples the ground and excited state to a lesser extent than in all-*trans*-octatetraene, the sum of all C═C couplings is clearly larger in the former isomer 0.0493 vs 0.0404, which translates into 2040 vs 1619 cm^{-1} in terms of adiabatic couplings. Since this coupling is responsible for lowering the frequency of the C═C stretching modes in S_0, it is rewarding to notice that our calculations give rise to frequencies for the three highest frequency C═C stretching modes of all-*trans*-octatetraene (unscaled 1791, 1785, and 1755 cm^{-1} [10]), which are higher than those of the cis,trans molecule (unscaled 1787, 1783, and 1750 cm^{-1}), thereby implicitly confirming the consistency of the model used by us.

TABLE 5: Second-Order Vibronic Coupling Matrix Elements $\langle S_1|\partial^2/\partial q_i^{a''}\partial q_j^{a''}|S_2\rangle$ and $\langle S_0|\partial^2/\partial q_i^{a''}\partial q_j^{a''}|S_1\rangle$ for Non-Totally Symmetric Vibrations of *cis,trans*-Octatetraene Employing Pairs of Dimensionless Vibrational Coordinates $q_i^{a''}$ and $q_j^{a''}$[a]

$(q^i_{a''},q^j_{a''})$	100 $\langle S_1|\partial/\partial q_{a''}{}^i\partial q_{a''}{}^j|S_2\rangle^a$		100 $\langle S_0|\partial/\partial q_{a''}{}^i\partial q_{a''}{}^i|S_1\rangle$		$(q^i_{a''},q^j_{a''})$	100 $\langle S_1|\partial/\partial q_{a''}{}^i\partial q_{a''}{}^j|S_2\rangle^a$		100 $\langle S_0|\partial/\partial q_{a''}{}^i\partial q_{a''}{}^j|S_1\rangle^b$	
(ν_{48},ν_{47})	0.557	(0.122)	0.054	(0.024)	(ν_{48},ν_{46})	0.043	(0.005)	0.042	(0.083)
(ν_{48},ν_{45})	0.371	(−0.071)	0.018	(0.195)	(ν_{48},ν_{44})	0.122	(−0.025)	0.046	(−0.139)
(ν_{48},ν_{43})	0.585	(0.127)	0.013	(−0.017)	(ν_{48},ν_{42})	0.429	(0.045)	0.181	(−0.057)
(ν_{48},ν_{41})	0.306	(0.082)	0.071	(0.012)	(ν_{48},ν_{40})	0.539	(0)	0.128	(0.056)
(ν_{48},ν_{39})	0.298	(0.057)	0.055	(−0.020)	(ν_{48},ν_{38})	0.147	(0.039)	0.047	(−0.017)
(ν_{48},ν_{37})	0.112	(0.031)	0.102	(0.081)	(ν_{48},ν_{36})	0.131	(0.025)	0.045	(−0.134)
(ν_{48},ν_{35})	0.261	(−0.027)	0.242	(−0.094)	(ν_{48},ν_{34})	**0.855**	(0.015)	0.030	(−0.104)
(ν_{47},ν_{46})	0.199	(0.044)	0.118	(0.193)	(ν_{47},ν_{45})	0.081	(−0.078)	0.352	(0.035)
(ν_{47},ν_{44})	0.183	(0.180)	0.007	(−0.135)	(ν_{47},ν_{43})	0.144	(−0.022)	0.047	(0.052)
(ν_{47},ν_{42})	0.168	(0.107)	0.134	(−0.015)	(ν_{47},ν_{41})	**0.630**	(−0.034)	0.141	(0.012)
(ν_{47},ν_{40})	0.546	(0.037)	0.083	(−0.042)	(ν_{47},ν_{39})	0.116	(0.049)	0.019	(0.023)
(ν_{47},ν_{38})	0.183	(0.148)	0.214	(0.134)	(ν_{47},ν_{37})	0.368	(0.077)	0.425	(0.191)
(ν_{47},ν_{36})	0.159	(−0.007)	0.405	(−0.178)	(ν_{47},ν_{35})	**0.687**	(0.056)	0.298	(−0.210)
(ν_{47},ν_{34})	0.337	(0.027)	0.355	(0.220)					
(ν_{46},ν_{45})	0.284	(0.258)	0.168	(−0.044)	(ν_{46},ν_{44})	**0.937**	(−0.090)	0.194	(0.041)
(ν_{46},ν_{43})	0.258	(−0.020)	0.058	(−0.122)	(ν_{46},ν_{42})	0.456	(−0.023)	0.034	(0.084)
(ν_{46},ν_{41})	0.252	(0.028)	0.013	(0.027)	(ν_{46},ν_{40})	0.311	(−0.032)	0.074	(0.160)
(ν_{46},ν_{39})	0.073	(0.037)	0.004	(−0.028)	(ν_{46},ν_{38})	0.092	(−0.007)	0.103	(0.070)
(ν_{46},ν_{37})	0.067	(−0.049)	0.329	(0.158)	(ν_{46},ν_{36})	0.135	(0.097)	0.260	(−0.062)
(ν_{46},ν_{35})	0.032	(−0.026)	0.039	(0.056)	(ν_{46},ν_{34})	0.329	(−0.047)	0.195	(0.033)
(ν_{45},ν_{44})	**0.707**	(0.006)	0.168	(−0.143)	(ν_{45},ν_{43})	0.208	(−0.035)	0.067	(−0.019)
(ν_{45},ν_{42})	0.465	(−0.010)	0.098	(−0.060)	(ν_{45},ν_{41})	**0.757**	(−0.020)	0.051	(0.022)
(ν_{45},ν_{40})	**1.163**	(−0.075)	0.081	(−0.005)	(ν_{45},ν_{39})	0.069	(−0.063)	0.058	(−0.052)
(ν_{45},ν_{38})	0.192	(0.052)	0.121	(0.042)	(ν_{45},ν_{37})	0.409	(−0.104)	0.232	(0.058)
(ν_{45},ν_{36})	0.480	(−0.023)	0.452	(−0.141)	(ν_{45},ν_{35})	0.114	(0.005)	0.407	(−0.234)
(ν_{45},ν_{34})	**1.643**	(−0.077)	0.621	(−0.127)					
(ν_{44},ν_{43})	0.233	(−0.007)	0.067	(0.020)	(ν_{44},ν_{42})	0.458	(−0.024)	0.004	(0.040)
(ν_{44},ν_{41})	**1.560**	(0.012)	0.016	(0.069)	(ν_{44},ν_{40})	0.115	(−0.003)	0.061	(0.038)
(ν_{44},ν_{39})	0.131	(−0.013)	0.005	(−0.008)	(ν_{44},ν_{38})	0.081	(0.013)	0.008	(0.028)
(ν_{44},ν_{37})	0.336	(−0.059)	0.017	(0.005)	(ν_{44},ν_{36})	**0.618**	(−0.129)	0.218	(−0.041)
(ν_{44},ν_{35})	0.218	(−0.124)	0.340	(−0.030)	(ν_{44},ν_{34})	**1.073**	(−0.190)	0.100	(−0.062)
(ν_{43},ν_{42})	0.191	(0.139)	0.055	(0.038)	(ν_{43},ν_{41})	0.211	(−0.015)	0.077	(−0.003)
(ν_{43},ν_{40})	0.567	(−0.080)	0.041	(0.078)	(ν_{43},ν_{39})	0.188	(−0.010)	0.034	(0.013)
(ν_{43},ν_{38})	0.226	(−0.015)	0.002	(0)	(ν_{43},ν_{37})	**0.813**	(−0.010)	0.088	(0.076)
(ν_{43},ν_{36})	0.374	(0.066)	0.392	(0.023)	(ν_{43},ν_{35})	0.359	(−0.095)	0.103	(0.098)
(ν_{43},ν_{34})	0.437	(−0.079)	0.200	(−0.019)					
(ν_{42},ν_{41})	**0.635**	(−0.165)	0.120	(0.022)	(ν_{42},ν_{40})	0.223	(−0.064)	0.064	(0.017)
(ν_{42},ν_{39})	0.176	(−0.025)	0.027	(−0.005)	(ν_{43},ν_{38})	0.267	(−0.004)	0.062	(0.030)
(ν_{42},ν_{37})	**0.762**	(−0.089)	0.246	(0.040)	(ν_{42},ν_{36})	**0.826**	(−0.203)	0.178	(−0.041)
(ν_{42},ν_{35})	0.053	i (0.003)	0.003	(0.146)	(ν_{42},ν_{34})	**1.298**	(−0.086)	0.282	(−0.009)
(ν_{41},ν_{40})	0.006	(0.016)	0.142	(0.021)	(ν_{41},ν_{39})	0.166	(−0.007)	0.021	(−0.020)
(ν_{41},ν_{38})	0.296	(−0.039)	0.075	(−0.001)	(ν_{41},ν_{37})	**1.238**	(0.102)	0.196	(0.113)
(ν_{41},ν_{36})	0.233	(0.038)	0.064	(−0.162)	(ν_{41},ν_{35})	**0.953**	(0.033)	0.372	(−0.073)
(ν_{41},ν_{34})	**1.190**	(−0.107)	0.004	(−0.183)					
(ν_{40},ν_{39})	0.177	(−0.009)	0.021	(0.027)	(ν_{40},ν_{38})	0.159	(−0.029)	0.005	(−0.003)
(ν_{40},ν_{37})	0.091	(−0.113)	0.288	(0.049)	(ν_{40},ν_{36})	**1.300**	(0.036)	0.006	(−0.199)
(ν_{40},ν_{35})	0.092	(−0.064)	0.237	(−0.121)	(ν_{40},ν_{34})	**1.034**	(0.016)	0.115	(−0.138)
(ν_{39},ν_{38})	0.036	(−0.002)	0.002	(−0.011)	(ν_{39},ν_{37})	0.164	(−0.002)	0.028	(0.055)
(ν_{39},ν_{36})	0.026	(0.011)	0.164	(−0.009)	(ν_{39},ν_{35})	0.240	(0.008)	0.116	(−0.056)
(ν_{39},ν_{34})	0.232	(0.024)	0.175	(−0.047)					
(ν_{38},ν_{37})	0.034	(−0.037)	0.199	(0.085)	(ν_{38},ν_{36})	0.095	(−0.007)	0.209	(−0.026)
(ν_{38},ν_{35})	0.053	(−0.031)	0.080	(−0.115)	(ν_{38},ν_{34})	0.052	(0.007)	0.167	(−0.059)
(ν_{37},ν_{36})	0.073	(−0.220)	0.103	(−0.112)	(ν_{37},ν_{35})	0.526	(−0.034)	0.203	(−0.219)
(ν_{37},ν_{34})	**1.785**	(−0.140)	0.174	(−0.052)					
(ν_{36},ν_{35})	**1.373**	(−0.085)	**1.605**	(−0.571)	(ν_{36},ν_{34})	**2.409**	(−0.471)	**1.523**	(−0.634)
(ν_{35},ν_{34})	**2.546**	(−0.147)	**1.684**	(−0.501)					

[a] Entries given in boldface are larger than $1/\sqrt{10}\langle S_1|\partial/\partial q_{33}|S_2\rangle$. [b] Entries given in boldface are larger than $1/\sqrt{10}\langle S_0|\partial/\partial q_{11}|S_1\rangle$. [c] Numbers in parentheses give the values of the matrix elements $100[\langle\partial S_1/\partial q_i^{a''}|\,\partial S_2/\partial q_j^{a''}\rangle + \langle\partial S_1/\partial q_j^{a''}|\partial S_2/\partial q_i^{a''}\rangle]$ and $100[\langle\partial S_0/\partial q_i^{a''}|\partial S_1/\partial q_j^{a''}\rangle + \langle S_0/\partial q_j^{a''}|\partial S_1/\partial q_i^{a''}\rangle]$.

C. Second-Order Vibronic Coupling Matrix Elements. The calculated homogeneous and heterogeneous second-order matrix elements for vibronic coupling of the S_1 and S_2 states and of the S_0 and S_1 states via non-totally symmetric a″ vibrations are given in Tables 4 and 5, respectively. It is worth emphasizing that elementary considerations make one expect a priori that these second-order couplings are much smaller than the first-order ones. Such an expectation is strongly sustained by what is known for other organic molecules where second-order effects are rarely observed. Tables 4 and 5 conform to these anticipations with respect to the second-order couplings of the S_0 and S_1 states since it is observed that their values are in general an order of magnitude smaller than the first-order couplings.

When the coupling of S_1 with S_2 is considered, however, it is clear that the magnitudes of the mixing of the wavefunctions of the S_1 and S_2 state induced by in-plane first-order coupling and out-of-plane second-order coupling are quite similar. The presence of second-order activity with a magnitude comparable to the first-order one is rather exceptional and strongly implies that there must be an underlying physical reason. In our previous calculations on first- and second-order coupling in all-*trans*-octatetraene, a similar behavior was noticed.[11] There, it was argued that an elegant explanation could be found on the basis of pseudoparity considerations, which ultimately led to the conclusion that all-*trans*-octatetraene exhibited stringlike behavior; that is, in this molecule, electronic motion and its coupling with nuclear motion can be considered as occurring along a linear string of bodies. The present calculations confirm this picture and reinforce it; if octatetraene can be considered as a linear string of bodies, the introduction of a cis linkage should not give rise to any significant changes with respect to the all-trans isomer, in agreement with what we find here.

For all-*trans*-octatetraene, experimental evidence for the important role of second-order coupling could be found in the one-photon excitation spectrum of the 2^1A_g state; on the basis of our calculations, a large number of, till then, unassigned bands could be assigned.[11] For *cis*,*trans*-octatetraene, high-resolution gas-phase spectra are not available. Nevertheless, it is striking to observe that in the fluorescence excitation spectrum of the molecule in an *n*-hexane matrix a band of moderate intensity is present at 175 cm^{-1} from the 0_0^0 transition,[12] which, on the basis of calculated frequencies (Table 1) and second-order couplings, might well be assigned to the $(\nu_{48})_0^1(\nu_{47})_0^1$ transition.

Finally, we consider the matrix elements $\langle \partial S_1/\partial q_i^{a''} | \partial S_2/\partial q_i^{a''} \rangle$ and $\langle \partial S_0/\partial q_i^{a''} | \partial S_1/\partial q_i^{a''} \rangle$ and their heterogeneous counterparts. As was shown in section II, these matrix elements can be considered as being built up from the products of first-order couplings of S_0, S_1, and S_2 with states of A″ symmetry. Since the latter states derive from excitations other than $\pi\pi^*$ excitations, they are not expected to couple strongly to the ground and lower excited states. Tables 4 and 5 show indeed that these matrix elements can in most cases be neglected with respect to the second-order couplings, leading to the conclusion that for the couplings considered here approximate antisymmetry in the state indices is present.

IV. Conclusions

In the present work, ab initio calculations have been employed to investigate the spectroscopic effects of the introduction of a cis linkage into a polyenic chain. The calculations predict that the spectroscopy of the lowest excited singlet state of the simplest polyene containing both a cis and a trans linkage, *cis,trans*-octatetraene, is dominated by first-order vibronic coupling and not by the zeroth-order symmetry lowering. The calculated intensity of the 0_0^0 transition, which, in contrast to the same transition in all-*trans*-octatetraene, is symmetry allowed, is about half of the intensity of the nearest Herzberg–Teller induced bands. These bands, in turn, have intensities that are comparable to the intensity of the most active false origin of b_u symmetry in the spectrum of all-*trans*-octatetraene. The calculations have shown that the finer details of the intensity distribution over the various vibronic transitions are not exclusively determined by direct and vibronically induced transition moments but are dominantly influenced by geometry displacements and normal-mode rotation, which occurs upon excitation. Apart from the intensity of the 0_0^0 transition, the calculated $S_1 \leftarrow S_0$ excitation spectrum demonstrates an agreement with the experimental excitation spectrum that is quite satisfactory, especially when it is realized that the experimental spectrum has been obtained under nonisolated conditions. The comparison of the two spectra validates the conclusion that a possible fingerprint for the cis linkage may be found in the presence of many intense bands in the region below 650 cm^{-1}. Although further, more systematic work ought to be undertaken on this subject, this can be taken as a first step towards the identification of suitable fingerprints that can be important in tracking down the nature of the various transients in biological processes in which polyenic chains are involved.

The combination of a decreased symmetry and vibronic mixing is apparent in the S_0-S_1 coupling along C=C stretching modes as well. In the all-trans isomer, this interaction occurs essentially via one of the two C=C stretching mode; in the isomerized system, the interaction is distributed over three modes. The calculated first-order vibronic coupling matrix elements between S_1 and S_2 analogously show an increase in the number of participating modes with magnitudes that are as large as those previously found for all-*trans*-octatetraene.

The calculations have shown that higher order coupling effects play an important role in *cis*,*trans*-octatetraene, quite similar to what has been concluded for the all-trans species. In particular, second-order vibronic couplings between S_1 and S_2 have been found that are comparable to those previously obtained for all-*trans*-octatetraene. Since the mixing caused by these couplings is linked to the linear chain behavior of polyenes, which is not expected to differ substantially in the two isomers, this finding further validates our previous analysis.

It is hoped that our work will stimulate experiments that will record the excitation and emission spectra of *cis*,*trans*-octatetraene under isolated conditions, thereby extending the work and the memory of Bryan Kohler, who, in collaboration with Thomas Spiglanin, was the first to obtain the $S_1 \leftrightarrow S_0$ spectra of this classic molecule under nonisolated conditions.

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