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Evidence of Stringlike Behavior in *all-trans*-Octatetraene

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The versatile nature of polyenes, $H(CH)_nH$, makes them prototypes of biologically active molecules and of polyacetylene, a polymer of fundamental importance in materials science. In the polymer, electron transport has long been modeled in terms of solitons which appear in the dynamics of a linear string of bodies.[1] In the pioneering model of polyacetylene,[2] the string was described by π electrons that were treated as quantized, with a tight binding scheme, whereas the σ electrons and nuclei were simulated by classical harmonic oscillators. No allowance was made for potential energy functions of bending and out-of-plane motions or for the hybridization of the carbon atoms that forms angles of ∼120°. Although the quasi-particles can appear in high-level calculations, the simplicity and success of the original model indisputably captures the fundamental aspects of the macroscopic phemomena, and the "experimental" detection of stringlike behavior in any polyene would sanction the generality of this ingenious scheme.

To detect the signature of stringlike behavior from experimental data, we selected *all-trans*-octatetraene, a highly studied polyene.[3−7] For alternant hydrocarbons,[8] such as octatetraene, a host of information can be obtained on the basis of pseudoparity quantum numbers.[9,10] Of interest for the detection of stringlike behavior is that pseudoparity considerations require that the vibronic interaction between electronic states of different pseudoparity be most effective for couplings *via* bending vibrations.[11] This requirement finds strong experimental support in the dipole-forbidden $S_0(1\ {}^1A_g^-) \rightarrow S_1(2\ {}^1A_g^-)$ spectrum of octatetraene where the most intense band is associated with the lowest-frequency in-plane bending vibration of CCC character.[4,6,7] This vibrational band owes its intensity to the coupling of $S_1(2\ {}^1A_g^-)$ with $S_2(1\ {}^1B_u^+)$.[11] Because of this context, it is natural to focus on bending motions of CCC character. If octatetraene were linear, a degenerate counterpart would be associated with each in-plane CCC bending mode. This counterpart is an out-of-plane CCC motion in the real molecule. Stringlike behavior would consequently imply similar roles for in- and out-of-plane motions of CCC character. When one considers the coupling of $S_1(2\ {}^1A_g^-)$ and $S_2(1\ {}^1B_u^+)$, the activity of out-of-plane motions would seem forbidden on symmetry arguments. In fact, the out-of-plane vibrations are divided into a_u and b_g symmetries and do not have the correct symmetry to mix the two states. But do they not? A combination of any two out-of-plane modes of different symmetry does indeed fulfill the symmetry requirements. Interestingly, if octatetraene becomes a string, the two electronic states still have different symmetries whereas only the a_u mode, becomes the counterpart of the b_u in-plane mode. In the real molecule, the remaining b_g mode can be seen as a helping vibration whose function merely is to "dress" the molecular deformation of octatetraene with the proper symmetry.

Table 1. First-Order Vibronic Coupling Matrix Elements $100\langle 2\ {}^1A_g^-|\partial/\partial Q_i|1\ {}^1B_y^+\rangle$ for b_u Vibrations (Dimensionless Coordinates *Q*) and Calculated Intensities[4] for the $S_0(1\ {}^1A_g^-) \rightarrow S_1(2\ {}^1A_g^-)$ Spectrum[a]

	matrix elements	inten		matrix elements	inten
ν_{48}	$\underline{2.734(1)}$	100.0	ν_{42}	2.701(46)	15.9
ν_{47}	$\underline{0.416(1)}$	2.3	ν_{41}	0.819(17)	0.4
ν_{46}	$\underline{0.480(1)}$	1.7	ν_{40}	2.877(24)	0.3
ν_{45}	2.037(5)	0.6	ν_{39}	1.724(75)	3.5
ν_{44}	2.770(13)	0.2	ν_{38}	13.335(423)	34.7
ν_{43}	3.293(1)	2.1			

[a] The couplings due to CCC bending vibrations are underlined. The numbers between brackets give the accuracy in the last digits of the calculated value. The intensities are given with respect to the intensity of ν_{48} which was taken as 100.0.

To determine the presence of stringlike behavior in octatetraene, one must therefore compare the coupling between $S_1(2\ {}^1A_g^-)$ and $S_2(1\ {}^1B_u^+)$ induced by CCC bending vibrations of b_u symmetry and by the combination of a_u and b_g CCC modes. Previously, we have employed quantum-chemical modeling to simulate the first-order vibronic activity in the $S_0(1\ {}^1A_g^-) \rightarrow S_1(2\ {}^1A_g^-)$ excitation spectrum of *all-trans*-octatetraene.[4,12] The calculated first-order vibronic couplings, are shown in Table 1. Notice that a two-state model gives excellent agreement with the full-scale calculations for the three CCC bending vibrations, ν_{48}, ν_{47}, and ν_{46}. For instance, for the induced transition moment of ν_{48} it predicts an induced moment of 0.0913 ea_0 versus 0.0851 ea_0 obtained in our previous calculations.[4] We can conclude that in case of the CCC bending modes the vibronically induced intensities are predominantly determined by the S_1-S_2 couplings, and that pseudoparity rules are almost perfectly obeyed.

The second-order couplings for combinations of out-of-plane modes are shown in Table 2. It is clear that the magnitudes of

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[12] Vibronically induced intensities of the b_u false origins were obtained by displacing the molecular geometry along the b_u normal coordinates. From the study of the influence of basis set, electron correlation, and Duschinsky mixing, it was concluded that calculations based on a 6-31G* basis, full-CI in the space of 4π and $4\pi^*$ ground state SCF MOs, and CASSCF/6-31G* force fields could simulate the experimental data satisfactorily.[4] The same numerical approach is used to obtain the mixing of the electronic states induced by the vibrational motions. A computer program was therefore written on the basis of the theory developed in ref 13 to calculate by numerical differentiation of the electronic wave functions the vibronic coupling matrix elements.[14] Calculation of the first-order couplings was performed using a step size of $\Delta Q_i = 0.1$ amu$^{1/2}$ Å, while numerical stability was obtained for second-order couplings with step sizes of $\Delta Q_j = \Delta Q_k = 0.025$ amu$^{1/2}$ Å. The accuracy of the calculations was checked by comparison of each matrix element with its transpose.

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Table 2. Second-Order Vibronic Coupling Matrix Elements 100 $\langle 2\ {}^1A_g^-|(\partial/\partial Q_j)(\partial/\partial Q_k)|2\ {}^1B_u^+\rangle$ for Combinations of a_u and b_g Vibrations Expressed in Dimensionless Coordinates Q^a

	ν_{32}	ν_{31}	ν_{30}	ν_{29}	ν_{28}	ν_{27}	ν_{26}
ν_{25}	0.545(50)	0.623(11)	1.019(44)	0.886(28)	0.446(3)	0.030(#)	0.460(47)
ν_{24}	0.033(17)	1.328(91)	0.313(17)	0.342(14)	0.601(6)	0.946(101)	0.167(76)
ν_{23}	0.041(19)	1.693(15)	1.307(17)	0.254(30)	0.432(15)	0.493(27)	0.383(73)
ν_{22}	0.559(27)	0.107(33)	0.341(94)	1.017(36)	1.198(35)	0.645(52)	0.968(5)
ν_{21}	0.948(5)	0.680(1)	1.369(64)	0.776(22)	1.289(4)	0.196(67)	0.400(50)
ν_{20}	0.158(9)	0.162(2)	0.680(39)	0.840(7)	0.030(15)	0.156(#)	0.793(164)
ν_{19}	0.504(61)	0.772(58)	0.537(3)	1.031(5)	0.008(#)	0.374(158)	1.514(127)
ν_{18}	0.811(45)	0.835(20)	0.591(5)	0.117(26)	1.074(35)	0.896(132)	1.351(292)

[a] The couplings due to CCC bending vibrations are underlined. The numbers in brackets give the accuracy of the last digits of the calculated value. Entries which have a numerical error larger than the value itself are indicated by #.

Table 3. Calculated Intensities of Second-Order Vibronic Coupling Induced 1 $^1A_g^-$ → 2 $^1A_g^-$ Transitions[a]

	ν_{32} **177**	ν_{31} **271**	ν_{30} **297**	ν_{29} **484**	ν_{28} **739**	ν_{27} **814**	ν_{26} **984**
ν_{25} **44**	0.2 (0.2)	0.4 (0.7)	0.1 (0.7)	0.5 (2.6)	3.9 (0.4) *702.2 (5.4)*	2.0 (0.4) *794.4 (1.8)*	0.1 (0.1)
ν_{24} **147**	2.4 (3.3) *246.8 (0.9)*	0.7 (2.0)	0.1 (0.7)	1.4 (10.2) *536.2 (4.7)*	0.0 (1.7) *817.5 (2.5)*	0.4 (0.1)	2.7 (0.8) *1061.0 (1.5)*
ν_{23} **271**	0.1 (0.2)	2.7 (24.5) *459.7 (1.5)*	4.8 (7.4) *519.2 (1.8)*	0.3 (1.3)	3.1 (0.3)	1.0 (1.3) *922.5 (2.1)*	1.2 (11.5) *1003.7 (1.4)*
ν_{22} **329**	5.4 (0.1) *446.7 (12.4)*	4.4 (0.3) *532.7 (1.6)*	14.2 (6.2) *534.3 (3.7)*	1.9 (0.3) *732.8 (2.4)*	5.8 (1.8) *970.2 (6.9)*	0.6 (2.7)	1.8 (7.6)
ν_{21} **475**	0.3 (4.1) *547.5 (1.2)*	0.5 (8.6)	1.8 (1.1)	17.0 (0.5) *870.5 (12.8)*	12.2 (4.3)	3.9 (2.9)	12.9 (0.5) *1415.7 (10.9)*
ν_{20} **790**	4.1 (1.2)	0.4 (0.2)	2.2 (2.7) *1003.7 (1.4)*	2.1 (0.2)	5.0 (21.1) *1477.8 (20.5)*	0.4 (8.2) *1498.7 (7.3)*	34.9 (3.2) *1670.9 (8.9)*
ν_{19} **842**	3.1 (1.3) *957.8 (3.3)*	0.8 (1.1)	1.5 (7.8) *1061.0 (1.5)*	0.3 (6.8)	3.5 (0.1) *1490.1 (6.3)*	0.1 (13.6)	52.7 (55.0) *1787.5 (18.9)*
ν_{18} **928**	0.1 (0.2)	0.0 (2.1)	0.4 (0.1)	1.1 (25.1)	10.1 (0.1)	37.5 (4.6) *1638.4 (2.5)*	13.9 (38.8) *1843.1 (13.8)*

[a] Intensities are given with respect to the calculated intensity of the $\nu_{48}(b_u)$ band taken as 100.0. The frequencies (in cm^{-1}) of the vibrations in the 2 $^1A_g^-$ state employed in the assignments are indicated with bold numbers and have been calculated in ref 4. The intensities without parentheses derive from a calculation in which Duschinsky mixing was taken into account; those given in parentheses represent intensities in the absence of Duschinsky mixing. In italics are given tentative assignments to bands observed in the excitation spectrum[6] together with the experimentally observed intensities, scaled[4] for the measured lifetime. Notice that the frequencies of the experimental bands are given with respect to the ν_{48} (b_u) vibronically induced origin in the one-photon excitation spectrum at 76 cm^{-1} from the true 0−0 transition.[6]

the mixing of the wave functions of the two lowest excited states of octatetraene induced by in- and out-of-plane vibrations are quite similar. *This similarity is, in general, not to be expected and is here taken to be indication of stringlike behavior in this molecule.* Although all first- and second-order couplings are reported, the comparison should only consider those that are underlined in Tables 1 and 2 because the associated vibrations have large CCC character.[15] According to pseudoparity considerations all the second-order perturbations can have similar values, an expectation by and large carried out by the present ab initio calculations.

The results can be further assessed by looking for the presence of second-order transitions in the high-resolution excitation spectrum of octatetraene.[6] Table 3 gives the intensities of the combination bands calculated in the presence or absence of Duschinsky mixing, the two values describe the "worst-case" range of intensities that we can expect for these bands. *Importantly, Table 3 also contains tentative assignments of bands observed in the experimental spectrum.*[16] This is the first ever assignment of second-order bands in the spectrum of octatetraene. Despite the somewhat tentative nature of our assignments, it is striking to observe that a large number of bands, which previously could not be assigned,[6] now fall into place. When the bands below ~900 cm^{-1} are considered, it is also observed that many of these combination bands have lifetimes that are shorter than those of neighboring bands. This observation corroborates their assignment to out-of-plane levels since it has been shown that out-of-plane modes lead to enhanced nonradiative decay with respect to in-plane modes.[19]

Calculation and comparison of first- and second-order couplings and the assignment of bands in the high-resolution spectrum of octatetraene is not only of relevance for the spectroscopy of this molecule. As discussed above, pseudoparity and topological arguments show that the two types of couplings should be the same if octatetraene were a string. Since the time scale of a vibroelectronic transition is in the (sub)-femtosecond regime, similar magnitudes for the first- and second-order couplings show that, at least on this time scale, octatetraene has stringlike behavior for which the newly assigned bands can be taken as markers. The extension of stringlike behavior to longer time scales is very attractive and supports the original model of a linearized polyene which was at the basis of the successful model used to explain the appearance of electron transport in polyacetylene.

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