Franck–Condon Modeling of the Structure of the $1A_g-1B_u$ Electronic Transition of α,ω Diphenylpolyenes

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Abstract: The Franck–Condon structure of the lowest lying intense electronic transition, $1A_g-1B_u$, of diphenylbutadiene, diphenylhexatriene, and diphenyloctatetraene is investigated through model calculations. Because of the relatively low resolution of the spectra available and to avoid a possible bias in the simulation, the Franck–Condon parameters are calculated *ab initio* through a simple and general approach that can be applied to fairly large molecules. A transferable scaling procedure is used to improve the agreement between computational theory and experiment. The calculated $1A_g-1B_u$ vibroelectronic spectra of the three molecules agree well with the experiment. The modeling allows a better insight into the effects of the one-electron dipole allowed excitation in α,ω diphenylpolyenes which are found to differ from pure polyenes of the same chain length in the low-frequency region.

Introduction

Over the last few years, the vibrational and electronic properties of polyenic systems have elicited great interest.[1] Such an interest is caused by their intrinsic properties and by their role as models for more complicated systems in materials science[2] and in biochemistry.[3] In many of the processes in which a polyenic moiety is involved, the activity is triggered by the excitation to the $S_2(1B_u)$ electronic state. Its wave function consists mainly of the configuration arising from the single excitation from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO).[4] Such a wave function differs greatly from that of $S_1(2A_g)$ which is formed by a linear combination of three excitations and, in C_{2h} symmetry, is also of different symmetry. Interestingly, as long as a C_2 axis exists in the molecule, symmetry does not allow $S_1(2A_g)$ and $S_2(1B_u)$ to interact electronically and the difficulties associated with the description of their respective wave functions are kept separate. In the vacuum and in nonpolar solvents, α,ω diphenylpolyenes share with their purely polyenic counterpart the same ordering and symmetry for S_1 and S_2. At odds with polyenes, they show a high fluorescence quantum yield that mkes them excellent probes for biological systems.[5] Because of the similarities between the electronic states of polyenes and diphenylpolyenes, it is of interest to understand how and why they differ. It should be mentioned that while the $1A_g-2A_g$ spectra of diphenylpolyenes can be obtained with high vibrational resolution, the $1A_g-1B_u$ spectra show only a scarcely resolved vibronic envelope that is usually assigned to the Franck–Condon progressions of the C–C single bond stretch vibration and the C=C double bond stretch vibration. This assignment mainly follows that of polyenes. However, while in the case of polyenes there is a great deal of experimental and computational evidence for such an assignment, this is not entirely true for diphenylpolyenes. A more thorough analysis of the $1A_g-1B_u$ transition is therefore in order. To avoid a possible bias in the analysis, I calculated *ab initio* the input parameters to use in the Franck–Condon model calculations. The MO calculations were performed with the Gaussian92 series of programs.[6] The ground state was treated at the Hartree–Fock level using the 6-31G* basis set.[7] The $1B_u$ state calculations were performed, with the same basis set of atomic orbitals, at the Configuration Interaction Singles level.[8] In general, some caution should be exerted using this level of theory for the excited states of α,ω diphenylpolyenes. Such a caution, however, should be limited to the cases where the $2A_g$ wave function does come into play or whenever there are processes that in a MO scheme cannot be described by a wave function of singly excited configurations. Thus, although the present procedure may not be adequate to study some of the reactivity of polyenic systems, it can certainly be used to calculate the absorption spectrum of the three molecules at hand both because of their symmetry and because the $1A_g-1B_u$ spectra as such do not entail bond formation or rupture.

Because of the dimension of the molecules investigated, the excited state *ab initio* calculation of the Franck–Condon parameters does pose some computational problems and I use a non-standard approach. This method drastically reduces the intensiveness of the calculation. Its possible shortcomings and merits are discussed.

Theoretical Background

I have obtained an initial guess for the calculations of the Franck–Condon structure of the $1A_g-1B_u$ transition of diphenylbutadiene, DPB, diphenylhexatriene, DPH, and diphenyloctatetraene, DPO, by *ab initio* MO calculations. All S_0 calculations were performed at the Hartree–Fock level with the 6-31G* basis set.[7] The quantum chemical

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calculations for $1B_u$ were performed with the CIS (Configuration Interaction Singly excited configurations) procedure[8] implemented in the Gaussian92 program.[6] All the singly excited configurations were used in the calculation. The CIS level of theory cannot describe the $2A_g$ state whose wave function contains a large amount of doubly excited configurations. As long as a C_2 axis exists in the system, symmetry forbids the two states to interact electronically. An important feature of the present procedure is that all the singly excited configurations are included in the calculations.

The simulation of the Franck–Condon structure of the electronic spectra is performed along the lines of previous simulations which, however, used a more extensive set of quantum chemical calculations for the input parameters.[9] In short, harmonic oscillator is associated to each normal mode of vibration. The equilibrium position of the totally symmetric modes can, upon electronic excitation, undergo a displacement. It is the amount of this displacement, i.e., the change of bond lengths and bond angles, that governs the presence of bands due to a particular normal mode in the electronic spectra. For the Franck–Condon intensities of harmonic oscillators, a standard treatment is provided in a number of papers.[10] If, upon electronic excitation, there is no frequency variation and no normal mode rotation, the energy gradient with respect to the Cartesian coordinates, g, calculated for the final $1B_u$ state at the equilibrium position of S_0 is proportional to the displacement. To show this one must write the potential energy surface of the excited state both as a Taylor expansion

$$E = E_0 + gx + \frac{1}{2}xHx + \ldots \qquad (1)$$

and in dimensionless harmonic oscillator coordinates

$$E = E_0 + Bvq + \frac{1}{2}v^2q^2 + \ldots \qquad (2)$$

where E is the energy, g is the energy gradient with respect to the nuclear coordinates, x is a Cartesian displacement vector, H is the Hessian matrix, B is the vector of the displacements along the normal modes of the excited state potential energy surface with respect to the ground state surface, ν is the vibrational frequency, and q is the dimensionless coordinate of the harmonic oscillator. The relation between x and q is

$$q = \left(\frac{2\pi c\nu}{\hbar}\right)^{1/2} LM^{1/2}x \qquad (3)$$

where the constants π, c, and $\hbar$ have the usual meaning, L is the normal mode vector, and M is the $3N$ by $3N$ diagonal matrix of the atomic masses, with N number of atoms.

Equating the first-order terms in the eqs 1 and 2 and using eq 3 together with the proper conversion factors, one obtains

$$B = \frac{2408615}{\nu^{3/2}} gM^{-1/2}L \qquad (4)$$

where the frequency is in wavenumbers, the energy gradient is in hartree/Bohr, and the atomic masses are in atomic units.

Each spectral line calculated in the Franck–Condon simulation is then broadened by multiplying it by a Gaussian function,

$$G(\nu) = \frac{e^{-(\nu-\nu_0)^2/a^2}}{a\pi^{0.5}} \qquad (5)$$

where ν is the excitation wavenumber (in cm^{-1}), ν_0 is the calculated excitation wavenumber (in cm^{-1}), and a is a constant (in cm^{-1}) that accounts for the broadening, both homogeneous and inhomogeneous.

Table 1. Unscaled S_0 Totally Symmetric Vibrational Frequencies, cm^{-1}, and B Franck–Condon Parameters Calculated with the 6-31G* Basis Set

DPB		DPH		DPO	
ν	B	ν	B	ν	B
1881	1.373	1878	1.427	1874	1.423
1807	0.768	1823	0.482	1857	0.487
1778	0.232	1804	0.510	1806	0.499
1672	0.290	1774	0.199	1777	0.149
1619	0.177	1671	0.218	1671	0.177
1509	0.067	1614	0.176	1617	0.127
1469	0.391	1493	0.236	1520	0.073
1454	0.664	1467	0.067	1483	0.292
1351	0.466	1451	0.170	1464	0.104
1326	0.087	1419	0.631	1447	0.282
1307	0.489	1347	0.519	1388	0.442
1255	0.457	1317	0.072	1345	0.522
1200	0.501	1307	0.328	1320	0.108
1188	0.087	1259	0.706	1307	0.204
1132	0.057	1207	0.461	1267	0.874
1088	0.411	1189	0.020	1228	0.236
927	0.024	1131	0.017	1208	0.322
681	0.017	1088	0.305	1190	0.006
663	0.259	899	0.026	1131	0.011
508	0.013	681	0.074	1088	0.234
239	0.369	671	0.054	909	0.005
147	1.351	599	0.179	696	0.082
		366	0.108	680	0.049
		197	0.533	538	0.108
		103	1.213	513	0.010
				277	0.106
				169	0.629
				76	1.119

Results and Discussion

It is instructive to compare the calculated excitation energies with the available experimental data. The calculated vertical energies are 37 969 cm^{-1} for **DPB**, 36 054 cm^{-1} for DPH, and 34 554 cm^{-1} for DPO. To compare them with the energy of the onset of the 0–0 transition one should first subtract the Stokes' shift. In the present calculation, this is found to be 3750 cm^{-1} for DPB, 3676 cm^{-1} for DPH, and 3592 cm^{-1} for DPO. One should further subtract the difference in zero-point energies of the states involved in the transition. This quantity is not available. For hexatriene and octatetraene, the difference was found to further reduce the energy gap by more than 1000 cm^{-1}.[9f,g] It is safe to assume that a value of 1000–2000 cm^{-1} can be used in the present case. Experimental excitation energies for the 0–0 transition are available in vacuum or in the gas phase for DPB and DPH: they are 31 250 cm^{-1} [11] and 29 160 cm^{-1},[12] respectively. The present calculation therefore overestimates the $1A_g$–$1B_u$ gap by 2000–4000 cm^{-1}.

The approach I use to calculate the B Franck–Condon parameters is valid only for totally symmetric modes and as long as the only difference between the harmonic potential energy surfaces involved in the transition is the equilibrium position of the normal modes. Distortion, i.e., change of vibrational frequency, Duschinsky effect, i.e., rotation of normal modes, and intensity arising via non-totally-symmetric modes are not accounted for. In many instances this is not a serious limitation. Even in the case of experiments able to discern the presence of the aforementioned effects, such as resonance Raman excitation profiles and single vibronic level fluorescence,

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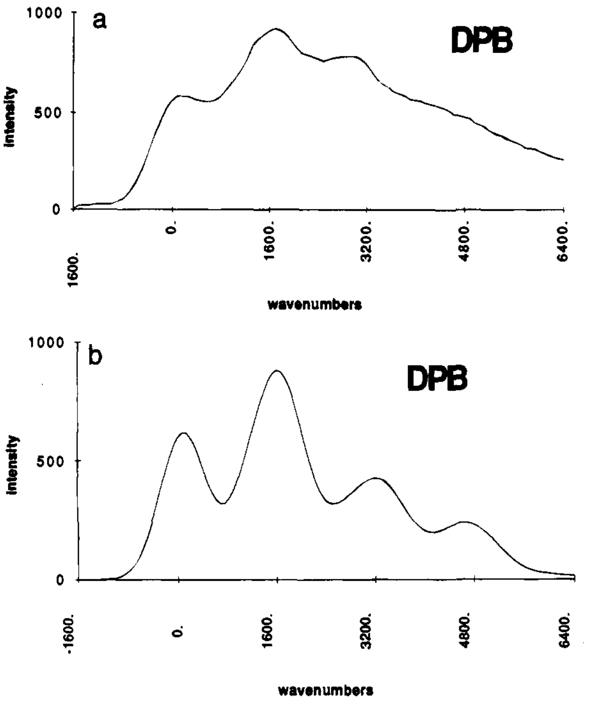

Figure 1. (a) Reference experimental spectrum of DPB adapted from data presented in Figure 3, ref 14. The spectrum was first scanned in and then digitized for replotting (see text). The intensity is now in arbitary units. (b) Scaled *ab initio* simulation (see text) of the $1A_g$–$1B_u$ spectrum of DPB. The vibronic line width is 500 cm^{-1}, and the intensity is in arbitrary units.

calculations with this procedure would give a reasonable initial guess for the analysis.

Table 1 shows the calculated totally symmetric frequencies and *B* Franck–Condon parameters. Their straightforward use in the spectral simulation yields rather good agreement with experiment. To further improve the agreement, both the frequencies and the Franck–Condon parameters are scaled by a common 0.9 for all the molecules. Experimental excitation spectra are given for DPB in ref 11, for DPH in ref 12, and for DPO in ref 13. Absorption spectra of DPB and DPH are also given in ref 14. The calculated spectra can be compared with their experimental counterparts in Figures 1–3. The experimental spectra were adapted from the literature. First, they were scanned in and then digitized for replotting. For the sake of comparison, the onset of the electronic transition in the experimental and the calculated spectra was set to zero. Such a procedure is obviously very crude and the reader should go back to the original spectra for more details. In Figure 1, the experimental spectrum of DPB (Figure 3, ref 14) is given together with the ab initio calculated spectrum. In Figure 2, the experimental spectrum of DPH (Figure 2, ref 12) is shown together with the ab initio calculated spectrum. In Figure 3, the experimental spectrum of DPO (Figure 4, ref 13) is provided together with the ab initio calculated spectrum. An initial comment is in order: despite the rather different pattern of Franck–Condon factors for the three molecules (see Table 1), the simulation leads to remarkably similar spectra. This is in agreement with experiment and can be taken as a signal of the underlying complexity of these spectra which is washed out by the low resolution. One should notice that, in general, the available fluorescence excitation spectra differ rather markedly in resolution and at times the vibronic structure is not entirely discernible. One should also be aware of the fact that in this type of experiment, at higher energies, there may be a lack of intensity due to the sudden opening of nonradiative channels not available at lower energies.

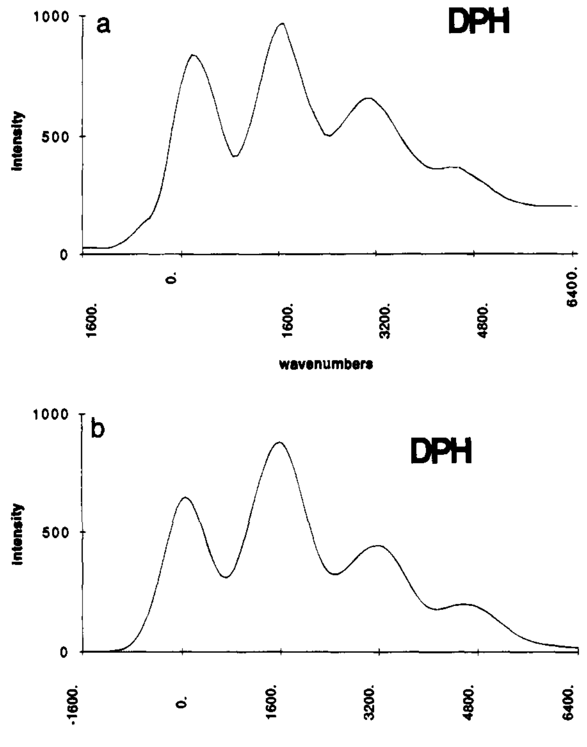

Figure 2. (a) Reference experimental spectrum of DPH adapted from data presented in Figure 2, ref 12. The spectrum was first scanned in and then digitized for replotting (see text). The intensity is now in arbitrary units. (b) Scaled *ab initio* simulation (see text) of the $1A_g$–$1B_u$ spectrum of DPH. The vibronic line width is 500 cm^{-1}, and the intensity is in arbitrary units.

Because of the good agreement with experiment, a closer inspection of the results reported in Table 1 is warranted. There are three major sources of Franck–Condon intensity. In the high-frequency C=C double bond stretch region, the displacement and therefore the vibronic intensity is mainly concentrated on a single normal mode. This behavior seems quite general and is in accord with that observed and calculated for polyenes.[1,9f,g] For this region, the success of the present procedure depends on the fact that the S_0 and S_2 Franck–Condon active C=C vibrations have very similar frequencies. This coincidence is brought about by two distinct mechanisms. The first is that the S_0 frequency is lowered by vibronic coupling with the $2A_g$ state.[1] The second effect is that the S_2 frequency is also lowered by the excitation which transfers binding electron density from the double to the single bonds. These two mechanisms make the C=C frequencies in the two electronic states very similar.

In the C–C single bond stretch region, the situation is more confused. A number of modes carry a substantial displacement. This is confirmed for DPB by the Raman work[15] and would seem at odds with what happens in the case of polyenes. However, if one considers that the purely polyenic counterparts of these molecules are smaller and therefore have fewer vibrations, it is possible to ascribe this trend to small perturbations that spread the C–C stretch character among many vibrations. It is interesting to notice that an increase of the conjugation length leads to the reappearance of a dominantly

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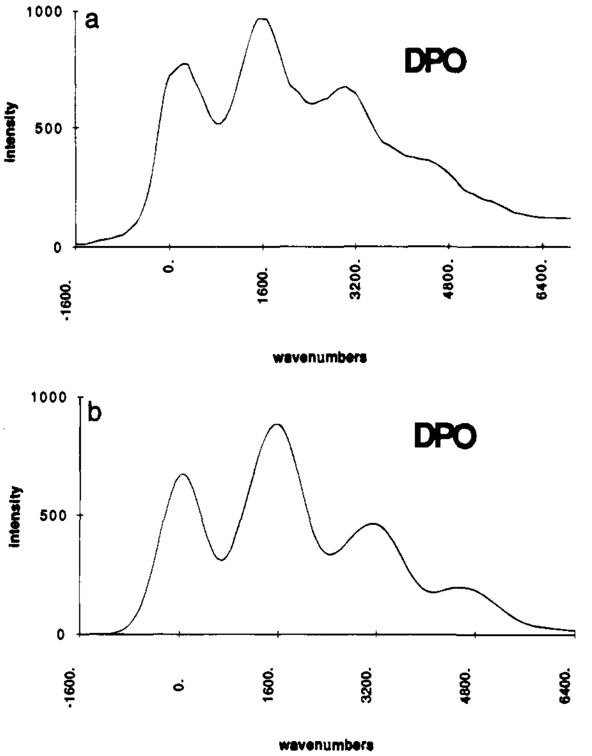

Figure 3. (a) Reference experimental spectrum of DPO adapted from data presented in Figure 4, ref 13. The spectrum was first scanned in and then digitized for replotting (see text). The intensity is now in arbitrary units. (b) Scaled *ab initio* simulation (see text) of the $1A_g$–$1B_u$ spectrum of DPO. The vibronic line width is 500 cm^{-1}, and the intensity is in arbitrary units.

displaced C–C mode: in DPO, which has the longest polyenic chain of the three molecules studied here, the 1267 cm^{-1} mode carries a Franck–Condon displacement of 0.874. In the same region, DPB has modes whose B parameters are around 0.5, while DPH has modes whose B parameters are around 0.5, while DPH has modes whose *B* parameters are of the order of 0.7.

α,ω diphenylpolyenes differ markedly from polyenes in the low-frequency CCC bend region. Below 200 cm^{-1}, the three α,ω diphenylpolyenes have a greatly Franck–Condon active 0–1 transition which has intensity close to that of the 0–0 transition. The three lowest frequency motions are similar and are mainly located on the phenyl groups. As such they have no counterpart in polyenes with the same length of the main chain. Such lowest frequency Franck–Condon active modes are given in Figure 4 for DPB, DPH, and DPO in order to obtain a qualitative understanding. By inspection of Table 1 and Figure 4, it is seen that two effects are observed with the increase of the length of the polyenic chain. The first is the decrease of the Franck–Condon activity. The second is that the nature of the active mode becomes more and more centered on the polyenic chain. These two trends, namely the decreased activity and the augmented polyenic nature, concur with one another. A final remark about this low-frequency vibronic transition is that, in the experimental spectra, it remains hidden by the large line width. This is therefore a new finding which appears to be general and shared by all diphenylpolyenes and should tend to disappear for very long polyenic chains.

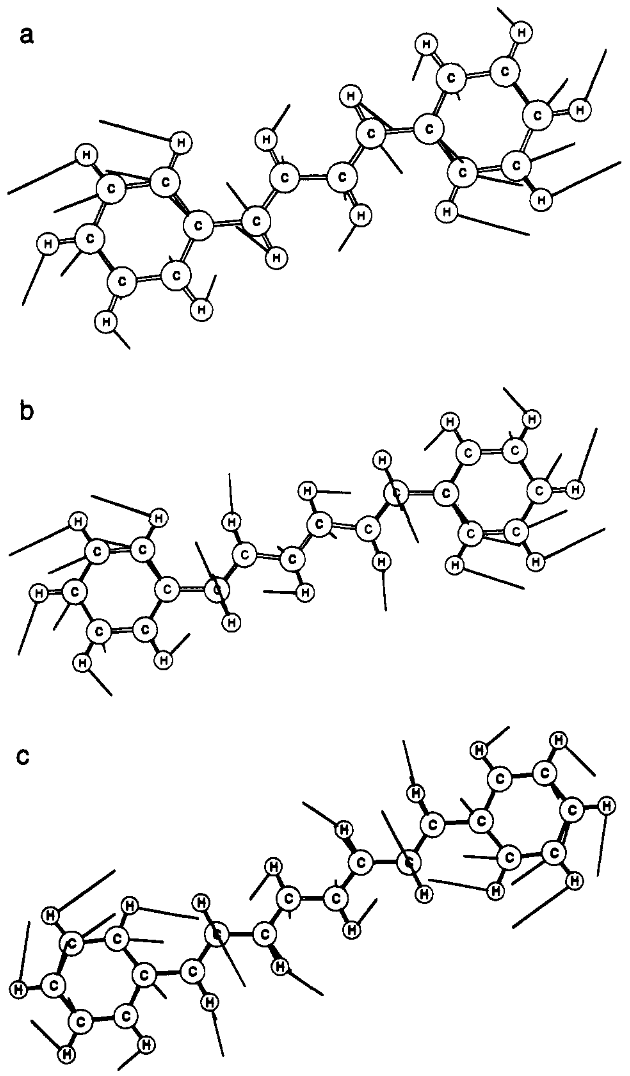

Figure 4. (a) The lowest frequency Franck–Condon active mode of DPB (calculated ν = 147 cm^{-1}). (b) The lowest frequency Franck–Condon active mode of DPH (calculated ν = 103 cm^{-1}). (c) The lowest frequency Franck–Condon active mode of DPO (calculated ν = 76 cm^{-1}).

Conclusions

I have simulated the $1A_g$–$1B_u$ spectra of the three shortest α,ω diphenylpolyenes. The excellent agreement between experiment and computational theory is obtained by starting from HF/6-31G* calculations for the ground state and a single point CIS/6-31G* energy gradient calculation for the electronically excited state. Although the present procedure does not yield information on the vibrational frequency changes upon excitation, it furnishes results that are of sufficient quality to acquire information hidden in the complexity of the spectra. To improve the agreement between theory and experiment, I have scaled the calculated frequencies and displacement parameters by a factor of 0.9. The scaling appears to be transferable in the series of α,ω diphenylpolyenes.

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