A TIME-DEPENDENT STUDY OF ELECTRONIC SPECTROSCOPY OF 1, 3, 5-TRANS-HEXATRIENE MOLECULE

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Abstract: The electronic absorption spectrum, the relative Raman intensities upon 0-0 excitation, and the resonance Raman excitation profiles of trans-l, 3, 5-hexatriene in the region of the $1\,^1B_u \rightarrow 1\,^1A_g$ transition are analyzed on the basis of the structures and vibrational force fields obtained from ab initio molecular orbital (MO) calculations. Our implementation of the time-dependent theory for the fitting of experimental spectra and the simulation of model spectra as well as the quantum mechanical calculation of the model parameters is discussed. The implementation covers all electronic structure approaches which are able to deliver ground- and excited-state energies and transition dipole moments. As a test case we discuss the well-known case of the strongly allowed $1\,^1A_g \rightarrow 1\,^1B_u$ transition in 1, 3, 5- trans-hexatriene in detail using method ranging from simple single-reference treatments to elaborate multi-reference electronic structure approaches.

Keywords: DFT; Raman spectroscopy; Time-dependent; Franck-Condon principle

1. Introduction:

The structure and vibrational force field obtained for the ground electronic state by the simple Hartree-Fock method do not give an appropriate set of parameters for calculating the absorption spectrum and resonance Raman intensities. For 1, 3, 5- trans-hexatriene, the Franck -Condon analyses of the absorption spectra and the resonance Raman excitation profiles in the region of the $1\,^1B_u \rightarrow 1\,^1A_g$ transition have been performed. The Franck-Condon factors depend on the structural difference between the ground and excited electronic states. Therefore, a sufficiently correct estimate of the molecular structure in the ground electronic state is needed in order to obtain the structures in excited electronic states from Franck-Condon analyses. Similarly, the vibrational force field in the ground electronic state should be determined correctly. In general, the distribution of intensity within the spectra sensitively depends on the details of the ground- and excited-state potential energy surfaces (PES), transition dipole moment coordinate dependence, spin-orbit coupling, and nonadiabatic effects. Though the nonadiabatic effects have been found to be rather important in some cases, the Born-Oppenheimer (BO) adiabatic approximation appears to work satisfactorily for the description of various electronic spectra of molecules. In this case, the computational cost for the simultaneous prediction of ABS, fluorescence, and rR spectra is equal to that of a single excited-state geometry optimization step while the limitations of the short-time dynamics approximation are not taken into account

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2. Implementation:

We have used ORCA electronic structure package[1] for calculations However, the program has been designed with two goals in mind: (1) direct and simultaneous interpretation of experimental absorption (ABS), fluorescence, and rR spectra through either least square fitting or simulation procedures using displacements, transition moments, and broadening parameters as variables, and (2) simultaneous prediction of ABS/fluorescence band shapes as well as rR intensities and excitation profiles by any quantum chemical method that yields ground- and excited-state energies as well as electronic transition dipole moments. Thus, simulations procedures can be beneficially started from quantum chemical input data.

3. Computational details:

For all calculations reported in this paper the ORCA program [2] was used. Different methods have been used for the excited states calculation such as the CI method with single excitations (CIS), time-dependent density functional theory (TD-DFT) within the Tamm-Dancoff approximation (TD-DFT/TDA), multi-reference perturbation theory (MRPT), as well as multi-reference CI (MRCI) methods using TZVP Gaussian basis sets[3]. The influence of the basis set was tested by rerunning some of the calculations with the more extended TZVPP basis set which introduces $2d$ and $1f$ polarization sets on each heavy atom together with $2p$ and $1d$ sets on each hydrogen [4]. Excited-state displacements were calculated relative to the ground state equilibrium geometry located at the appropriate level of theory. Thus, for geometry optimization and frequency calculations the CIS excited-state calculations were combined with RHF. In a similar way the TD-DFT/TDA approach was tied to DFT ground-state calculations. The functionals BP86 [5, 6] and B3LYP [7, 8] were applied in the present study. The BP86 functional was chosen since it has shown excellent agreement between calculated harmonic frequencies and observed fundamental vibrational peaks [9].Therefore MRCI and MRPT methods have been probed for the calculation of the normal mode composition. Test calculations have not revealed any noticeable deviations of results if the normal mode compositions were obtained employing the functional B3LYP. HF frequency calculations have shown somewhat different normal mode compositions resulting in significant deterioration of some excited-state normal mode displacements.

4. Results and discussion for ($1\,^1A_g \rightarrow 1\,^1B_u$) transition of 1, 3, 5-trans-hexatriene:

The excited state of $1\,^1B_u$ has been the subject of important studies of theoretical and experimental aspects. Several methods QCFF/PI[10-12] ,the generalized valence bond method[13,14] ,the TD-DFT approach[15], the CASSCF based Methods[16] and the second-order perturbation approach on top a CASSCF wave function CASPT2[17,18,19] have been employed to calculate the low-lying excited states of THT , rR intensities have been predicted on the basis of CIS [20] and CASPT2 calculations with account of vibronic-coupling effects[19,21].The ground $1\,^1Ag$ state of the hexatriene molecule has the electronic configuration $(1a_u)^2$,$(1b_g)^2$, $(2au)^2$, $(2b_g)^0$ while the $1\,^1Bu$ excited state is well described by the leading configuration $(1a_u)^2$,$(1b_g)^2$, $(2a_u)^1$, $(2b_g)^1$. The $1\,^1Ag \rightarrow 1\,^1Bu$ transition is assigned to the intense dipole-allowed absorption band observed in the spectral region between 38000 and 50 000 cm−1. This band is characterized by a vibrational progression that occurs due to several FC active totally symmetric normal modes.

The underlying chemical reason for the shifts is the significant CC bond order changes that occur upon excitation from a bonding π to an anti-bonding π^* orbital. Thus, the double bonds in the $1\,^1A_g$ state become more single-bond-like in the $1\,^1B_u$ state, and the single bonds in the $1\,^1A_g$ state become more double-bond-like in $1\,^1B_u$.[20] It was also found that for some normal modes one should invoke Duschinsky rotation in the excited state in order to fit the rR excitation profiles at high excitation energies[20,22] although the rR intensities turned out to be rather insensitive to the amount of normal mode rotation upon the excitation in the vicinity of 0-0 vibronic band[22].

5. Comparison of calculated and experimental absorption and resonance Raman spectra:

For illustration the method of spectral simulation we have the calculated absorption band shape of Raman bands of THT molecule. The simulations have been performed using the displacements obtained from the absorption and rR data .From our calculation we have seen that the B3LYP is more accurate than the other methods (Fig1.) and more closely to the experimental data in the range 3800-50000cm-1.

6. Conclusion:

In the present study we have performed a theoretical analysis of the absorption spectrum of trans-l ,3,5-hexatriene in the region of the $1\,^1B_u \rightarrow 1\,^1A_g$ transition. Since the Franck-Condon factors depend on the structural difference between the ground and excited electronic states and the Duschinsky rotation matrix, information on the structure and vibrational force field in the excited electronic state can be obtained by performing Franck-Condon analyses of absorption spectra and resonance Raman intensities.
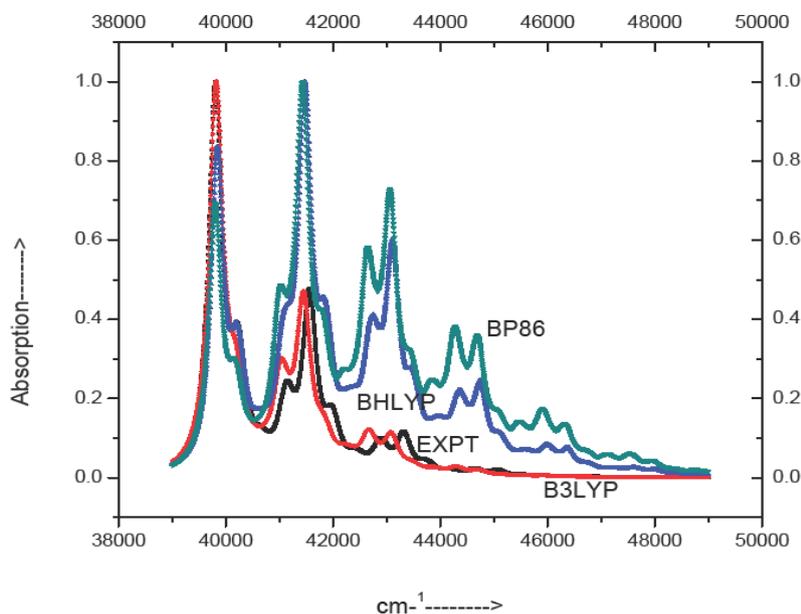
Figure 1: Experimental and calculated at the BHLYP/SV(P) ,BP86/SV(P) and B3LYP/SV(P) levels of theory absorption corresponding to $1\ ^1A_g \rightarrow 1\ ^1B_u$ transition in trans-1,3,5-hexatriene.

References:

[1] F. Neese, ORCA, an ab initio, density functional and semiempirical program package, University of Bonn, Bonn, Germany, 2007.
[2] F. Neese, J. Chem. Phys. 122, 034107, 2005.
[3] A. Schäfer, C. Huber, and R. Ahlrichs, J. Chem. Phys. 100, 5829, 1994.
[4] TURBOMOLE library: ftp://ftp.chemie.uni-karlsruhe.de/pub/basen.
[5] A. D. Becke, Phys. Rev. A 38, 3098, 1988.
[6] J. P. Perdew, Phys. Rev. B 33, 8822, 1986.
[7] A. D. Becke, J. Chem. Phys. 98, 5648, 1993.
[8] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B 37, 785, 1988.
[9] J. Neugebauer and B. A. Hess, J. Chem. Phys. 118, 7215, 2003.
[10] A. Warshel and M. Karplus, Chem. Phys. Lett. 17, 7, 1972.
[11] A. Warshel and M. Karplus, J. Am. Chem. Soc. 94, 5612, 1972.
[12] R. J. Hemley, A. C. Lasaga, V. Vaida, and M. Karplus, J. Chem. Phys.92, 945, 1988.
[13] M. A. C. Nascimento and W. A. Goddard III, Chem. Phys. Lett. 60, 197, 1979.
[14] M. A. C. Nascimento and W. A. Goddard III, Chem. Phys. 53, 265, 1980.
[15] J. Catalán and J. L. G. Paz, J. Chem. Phys. 124, 034306, 2006.
[16] M. Boggio-Pasqua, M. J. Bearpark, M. Klene, and M. A. Robb, J. Chem.Phys. 120, 7849, 2004.
[17] M. Nooijen, Int. J. Quantum Chem. 95, 768, 2003.
[18] L. Serrano-Andres, M. Merchan, I. Nebot-Gill, R. Lindh, and B. O. Roos,J. Chem. Phys. 98, 3151, 1993.
[19] C. Woywod, W. C. Livingood, and J. H. Frederick, J. Chem. Phys. 112, 613, 2000.
[20] H. Torii and M. Tasumi, J. Chem. Phys. 101, 4496, 1994.
[21] J. Neugebauer, E. J. Baerendes, and M. Nooijen, J. Phys. Chem. A 109, 1168, 2005.
[22] A. B. Myers and S. P. Crisanto, J. Phys. Chem. 93, 5079, 1989.