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Reminiscence of benzene in the spectroscopy of 1,3-benzodioxole: A computational study

Emanuela Emanuele, Fabrizia Negri *, Giorgio Orlandi *

Universita' di Bologna, Dipartimento di Chimica 'G. Ciamician', Via F. Selmi, 2, 40126 Bologna, Italy and INSTM, UdR Bologna, Italy

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Abstract

We present a theoretical investigation on the structure and spectroscopy of 1,3-benzodioxole. Ground state structure and vibrational frequencies are computed at several levels of theory ranging from density functional theory (DFT) to complete active space self consistent field (CASSCF) and are employed to provide a coherent assignment of IR and Raman spectra. In addition, excitation energies and transition dipole moments are estimated with the time dependent (TD) DFT approach and with configuration interaction calculations limited to single excitations (CIS). It is shown that the lowest excited singlet states correlate with those of benzene. Excited state equilibrium structures are obtained at CIS and at CASCCF levels. Optimized geometries, vibrational normal modes and frequencies computed for the ground and lowest excited states are employed to derive the parameters that govern the S_0–S_1 Franck–Condon (FC) activities in absorption and fluorescence spectra. The intensity of vibronically induced bands are estimated with the Herzberg–Teller approach. These parameters are used to identify correctly the most active modes in the single vibronic level (SVL) fluorescence spectra. The analysis of these spectra complements and completes the IR and Raman identification of ground state vibrational frequencies and provides evidence for substantial frequency changes upon S_0–S_1 excitation.

Keywords: Molecular spectroscopy; Vibronic structure; Excited states; Quantum chemistry

1. Introduction

1,3-Benzodioxole (BDO) has attracted a considerable attention for a number of years because it can serve as a model system for conformational studies of larger molecules [1–7]. This molecule, which is shown in Fig. 1, has an out-of-plane puckering vibration of the CH_2 group that is highly anharmonic and is characterized by a double-minimum potential, with a barrier to planarity of about 100 cm^{-1}. Furthermore, in BDO there is a second low-frequency mode, of the same symmetry as the puckering mode, namely the out-of-plane ring-flapping (or butterfly motion) of the penta-atomic ring with respect to the benzene ring [4,5]. The two modes are coupled and the vibrational levels arising from the combination of the two modes add complexity to the IR and Raman spectra and to 0–500 cm^{-1} section of the vibronic structure associated with electronic spectra. Many studies have been devoted to the elucidation of the vibronic structure due to these modes [4–7].

The harmonic and higher frequency modes in S_0 were studied by means of IR and Raman spectroscopy by Wieser and coworkers [2] and by Sakurai [6], but their assignments are not fully convincing and need to be reassessed. Hassan and Hollas [3] recorded for the first time the single vibronic level (SVL) fluorescence spectra emitted from the origin, from the 99 cm^{-1} and from the 204 cm^{-1} bands of the excitation spectrum. Similar SVL dispersed fluorescence spectra emitted from several vibronic levels of S_1 were recorded by Sakurai [6]. These spectra yield information that are mostly relevant to totally symmetric vibration frequencies.

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* Corresponding authors. Tel.: +39 051 2099471 72; fax: +39 051 2099456.

E-mail addresses: fabrizia.negri@unibo.it (F. Negri), giorgio.orlandi@unibo.it (G. Orlandi).

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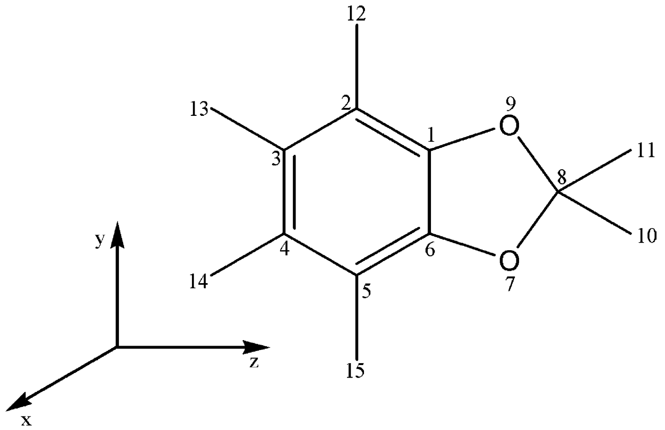

Fig. 1. Atom numbering of BDO and its orientation in the Cartesian coordinate system.

Our knowledge of the vibrational levels of S_1 is far less abundant. The most accurate work so far available is the high-resolution excitation spectrum in a supersonic jet in the region 0–550 cm^{-1} and a room temperature absorption spectrum in the same spectral range by Laane et al. [7]. Many of the observed vibronic bands are due to puckering and flapping vibronic levels and thus very little information is available about the other normal modes in S_1. Furthermore, the energies and the properties of the lowest excited electronic states are not well known and need to be clarified, in particular the possible interactions between S_1 and other excited states.

The ground state equilibrium structure of BDO was calculated with several methods [8]. The S_1 and S_0 vibrational frequencies were computed, but only a very limited selection of frequencies below 800 cm^{-1} was reported [7].

In view of the above considerations, we have performed a computational study to elucidate the nature and the properties of the lowest electronic states of BDO. We have also computed the S_0 vibrational frequencies and activities at several levels of theory and employed them to assign the experimental IR and Raman spectra. In addition, Franck–Condon (FC) activities and the efficiency of the intensity borrowing mechanism have been estimated to assign the vibrational structure of SVL fluorescence spectra.

We are not considering here the spectroscopic transitions involving the large amplitude motions, namely puckering and flapping, which have been discussed separately [9].

2. Computational details

The ground state equilibrium structure and vibrational frequencies of BDO were computed at HF level, with Density Functional Theory (DFT) using the B3LYP exchange-correlation functional [10], and with the complete active space self consistent field (CASSCF) method [11]. All the calculations were carried out with the 6-31G* basis set. The CASSCF calculations were carried out only in the C_{2v} point group and two active spaces were selected, namely 10 electrons in 8 orbitals (CASSCF(10,8)/6-31G*) and 12 electrons in 12 orbitals (CASSCF(12,12)/6-31G*). The first active space includes the 8 π orbitals (belonging to A_2 and B_1 irreducible representations of the C_{2v} point group) delocalized on the benzene ring and on the two oxygen atoms. The second active space includes four additional orbitals, namely one π orbital mostly localized on the C_8 carbon atom of the penta-atomic ring and three additional π orbitals delocalized over the entire system (overall, eight B_1 orbitals and four A_2 orbitals).

Vertical singlet excitation energies and transition dipole moments were computed with configuration interaction limited to single excitations (CIS) and with time dependent (TD) DFT using the B3LYP functional and the same 6-31G* basis set used for ground state calculations. Additional CIS/6-31G* calculations were carried out to optimize the S_1 and S_2 structures and to obtain S_1 vibrational frequencies, while the two CASSCF orbital spaces described above were employed to obtain the S_1 equilibrium structure and vibrational frequencies. The Gaussian98 suite of programs [12] was employed throughout except for the CASSCF calculations that were carried out with MOLCAS-5 [13].

The fundamental parameter that governs the FC activities of totally symmetric (TS) vibrations in electronic spectra is the displacement parameter B_i [14], which represents the projection of the geometry change upon excitation, onto normal vibrations of the ground state (fluorescence) or excited state (absorption):

$$B_i = \sqrt{\left(\frac{2\pi\omega_i}{h}\right)}[x_{S_n} - x_{S_m}]\sqrt{\mathbf{M}}\mathbf{L}_i^{S_m}, \qquad (1)$$

where $x_{S_{n,m}}$ is the $3N$ dimensional vector of the equilibrium Cartesian coordinates in the $S_{n,m}$ states, $\mathbf{M}$ is the $3N \times 3N$ diagonal matrix of the atomic masses, $\mathbf{L}_i^{S_m}$ is the $3N$ vector describing the normal coordinate $Q_i^{S_m}$ in terms of mass-weighted Cartesian coordinates and ω_i is its angular frequency.

In the harmonic approximation, the intensity of the vth member of a progression in the ith mode is [15]

$$(I_v)_i = \frac{e^{(-\gamma_i)}(\gamma_i)^v}{v!}, \qquad (2)$$

where $\gamma_i = \frac{1}{2}B_i^2$.

Beside TS modes, approximately harmonic non-totally symmetric (NTS) modes can contribute to the FC vibronic structure of electronic spectra, if their frequency variation upon electronic excitation is remarkable. The parameter governing the intensity of 0–v bands (v even) in the progression of NTS modes is

$$\xi_i = \frac{(v_i(S_0) - v_i(S_1))}{(v_i(S_0) + v_i(S_1))}, \qquad (3)$$

where $v_i(S_{0,1})$ is the vibrational frequency of the ith mode in the two electronic states. More specifically, it can be shown that the intensity ratio between the 0–2 band and the 0–0 band is [15],