Calculation of vibronic spectrum of a molecule undergoing excited state intramolecular proton transfer by the time-dependent method

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Absorption spectrum of an isolated molecule of 2-(2'-hydroxyphenyl)benzoxazole is calculated by the time-dependent path integral approach. 2-(2'-hydroxyphenyl)benzoxazole is a compound that undergoes the excited state intramolecular proton transfer. Despite the potential energy surface in the first excited state demonstrates shallow minimum for the enol structure of the molecule the calculations in harmonic approximation predicts well the frequencies of the maxima observed in the solution at room temperature. At the same time the relative intensities of the maxima are reproduced rather semi-quantitative. The Duschinsky rotation takes place for a large number of normal vibrations.

Experimentally observed absorption spectra of organic molecules originate from transitions between ground and excited electronic states. The molecule in the ground and excited electronic states demonstrates a large number of energy levels caused by vibrational motion of the nuclei. In the Born-Oppenheimer approximation motion of the electrons and nuclei can be separated assuming that there is a large difference in time scales between changes of the electronic and nuclear coordinates. In this case the total wave function is expressed as a product of nuclear and electronic wave functions [1-3]:

$$\Psi(\boldsymbol{r},\boldsymbol{R}) = \psi(\boldsymbol{r},\boldsymbol{R})\Phi(\boldsymbol{R}), \tag{1}$$

where $\psi(\boldsymbol{r},\boldsymbol{R})$ – electronic wave function; $\Phi(\boldsymbol{R})$ – nuclear wave function; $\boldsymbol{r}$ and $\boldsymbol{R}$ – coordinates of the electrons and nuclei. In the harmonic approximation the nuclear wave function is a product of eigenfunctions of one-dimensional harmonic oscillators which correspond to the normal vibrations:

$$\Phi(R) = \prod_j \chi_j(Q_j), \tag{2}$$

where Q_j – normal coordinate of molecular vibrations.

The rate of energy absorption by a molecule under the transition from the state i to the state f is defined by the expression [3]

$$k_{if}(\omega) = \frac{4\pi^2\omega}{3} |\langle \Psi_i | \mu | \Psi_f \rangle|^2 \, \delta(E_i - E_f - \hbar\omega). \tag{3}$$

The electric dipole moment μ can be separated into an electronic part μ^e and nuclear part μ^n, and $\mu_{if} = \langle \psi_i | \mu^e | \psi_f \rangle$. Then $\langle \Psi_i | \mu | \Psi_f \rangle = \langle \Phi_i | \mu_{if} | \Phi_f \rangle$ [3]. Absorption spectrum can be calculated as the sum over states [2]

$$k(\omega) = \sum_{if} \rho_i k_{if}(\omega), \tag{4}$$

where ρ_i – the Boltzmann population of initial state i at temperature T.

If the dipole matrix element of the electronic transition μ_{if} slightly depends on the nuclear coordinates then the Taylor series expansion by normal coordinates is applied:

$$\mu_{if}(Q) = \mu_{if0} + \sum_j \frac{\partial \mu_{if}}{\partial Q_j} |_{Q=0} Q_j + ... \tag{5}$$

The term μ_{if0} corresponds to the Franck–Condon approximation, the sum of the first order – to the Herzberg–Teller approximation.

Normal coordinates of the initial and final states relates by Duschinsky linear transformation [1,2]:

$$Q = JQ' + K, \tag{6}$$

where Q – normal coordinates in the initial state; Q' normal coordinates in the final state; J – the Duschinsky matrix; K – shift vector.

The time-independent approach where k_{if} are calculated for different pairs of initial and final states implies very large numbers of transitions to be included into calculations [3]. The time-dependent method [1,2] uses Fourier transform representation of the Dirac δ-function

$$\delta(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} dt. \qquad (7)$$

Then

$$k(\omega) = \frac{4\pi^2 \omega}{3} \sum_{if} \rho_i \langle \Phi_i | \boldsymbol{\mu}_{if} | \Phi_f \rangle \langle \Phi_f | \boldsymbol{\mu}_{if} * | \Phi_i \rangle \int e^{i(E_f - E_i - \omega)t} dt. \quad (8)$$

The difference $E_f - E_i$ can be separated into difference between electronic states ΔE (adiabatic energy difference) and vibrational energy in the initial and final state. The values of vibrational energy are eigenvalues of corresponding vibrational Hamiltonians H and H' and $k(\omega)$ is expressed as

$$k(\omega) = \alpha \int Tr\left(\boldsymbol{\mu}_{if} e^{-iH'\tau'} \boldsymbol{\mu}_{if} * e^{-iH\tau} \right) e^{i\Delta Et} e^{-i\omega t} dt =$$

$$= \alpha \int \chi(t) e^{-i\omega t} dt = 2\alpha \operatorname{Re} \int_0^\infty \chi(t) e^{-i\omega t} dt \qquad , \qquad (9)$$

where $\chi(t)$ – correlation function, $\tau = \dfrac{1}{k_B T} - it$, $\tau' = it$.

The last expression can be calculated as discrete Fourier transform while correlation function is calculated analytically [1].

The temperature is included into calculations by the Boltzmann distribution. Broadening of the lines is included by the relation [1]:

$$k(\omega) = \alpha \int \chi(t) f(t) e^{-i\omega t} dt, \qquad (10)$$

where $f(t)$ – the function describing line shape.

2-(2'-hydroxyphenyl)benzoxazole (HBO) is a model compound for studying excited state intramolecular proton transfer. The preferable structure of the HBO molecule in the ground state is enol form (HBO) (Fig. 1a); in the first excited state the keto form (Fig. 1b) has lower energy. Calculations of minimum potential energy curves along OH stretching coordinate performed with density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods demonstrate that potential energy surfaces in the ground and first excited states are anharmonic and in the first excited state there is shallow minimum for the enol structure. The

calculated energy barrier between the enol and keto structures in the first excited state vanishes if zero-point vibrational energy obtained in harmonic approximation is taken into account [4].

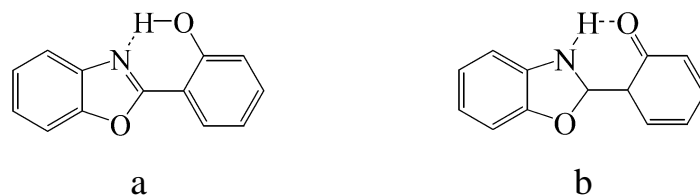a   b

Fig. 1. Enol (a) and keto (b) forms of the molecule of 2-(2'-hydroxyphenyl)benzoxazole (HBO).

The calculations were performed for an isolated molecule using the ORCA software package [1,5,6], the B3LYP functional [7], and def2-SVP basis set [8]. The vibrations were calculated in harmonic approximation using analytical second energy derivatives for the ground state and numerical ones with default parameters for the excited states. Vibronic structure of the absorption spectra was calculated with the adiabatic Hessian model and Duschinsky rotation in the Franck-Condon approximation. The spectrum was modeled assuming inhomogeneous broadening by Gaussian function with the full width at half maximum of 589 cm^{-1} (default value) and room temperature.

The calculated spectrum is shown in Fig. 2 along with the experimental spectrum measured in CCl_4 solution at room temperature. Increase in Fourier transform time by about 10 times does not change the calculated spectrum significantly so that the default value of 12000 atomic time units is sufficient for the modeling. The calculation of vertical transitions from the ground state S_0 shows that there is three transitions to the singlet S_1, S_2 and S_3 states in the range 25000–40000 cm^{-1} at 31200, 36050, 38250 cm^{-1}. The S_0–S_1 transition demonstrates much lower oscillator strength of 0.03 so that the S_0–S_1 and S_0–S_2 transitions are considered.

The largest values (dimensionless) of shift vector are found according to (6) in the state S_1 for the OH stretching mode, in-plane modes with calculated frequencies

1596 and 1387 cm^{-1} (modes in S_0). In the first excited state calculated frequencies of the corresponding normal vibrations with the largest elements of $\boldsymbol{J}$ are 1530 and 1404 cm^{-1}, however, the values are about 0.4.
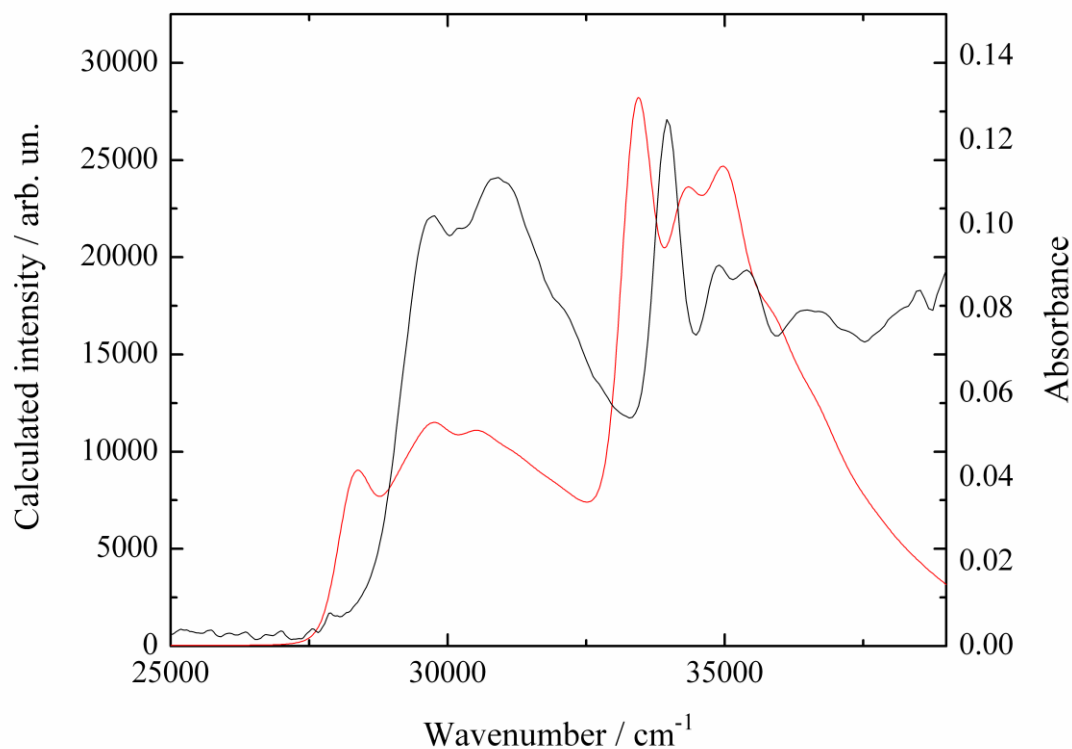

Fig. 2. Absorption spectrum of 2-(2'-hydroxyphenyl)benzoxazole (HBO) dissolved in CCl$_4$ (black line) and calculated spectrum (red line) of an isolated molecule.

27 out of 69 normal vibrations in the ground state demonstrate the largest elements of $\boldsymbol{J}$ matrix to be less than 0.7 in relation to the S_1 normal modes and 37 – in relation to the S_2 normal modes. Thus, consideration of the Duschinsky rotation is necessary for modeling the spectrum.

The absorption bands in the range 28000 – 33000 cm^{-1} is caused by the S_0–S_1 transition. In the experimental spectrum maxima are distinguished at about 29720, 30860 and a shoulder at 32150 cm^{-1}. In the calculated spectrum maxima are predicted at about 28360, 29780 and 30540 cm^{-1}. The differences are 1360, 1080 and 1610 cm^{-1} so that the systematic blue shift by 1300 cm^{-1} provides deviation of about 300 cm^{-1}.

The systematic deviation can be caused by inaccuracy of the calculated electronic transition energy and interaction with the solvent.

For the vibronic bands of the S_0–S_2 transition three sharp bands are observed at 33960, 34900 and 35400 cm^{-1}. The calculated values are 33450, 34490 and 34980 cm^{-1}. In this case deviations are less than those for the S_0–S_1 transition: 510, 410 and 580 cm^{-1}.

It should be noted that calculations provide rather semi-quantitative than accurate relative intensities of the spectral components (Fig. 2).

Despite anharmonicity of the potential energy surface in the first excited state of the molecule of HBO the absorption spectrum calculated with time-dependent approach and harmonic approximation for isolated molecule demonstrates good correspondence to spectrum measured in non-polar solution at room temperature predicting the frequencies of prominent bands. The method is found to be relevant for prediction of absorption spectra of compounds undergoing the excited state intramolecular proton transfer.

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