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Computer Chemistry

Ab Initio Calculations of Absorption Spectra of Large Molecules in Solution: Coumarin C153**

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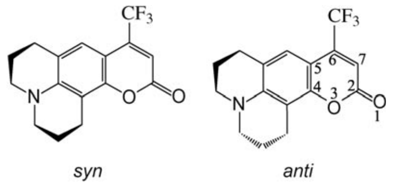
Electronic absorption spectra provide a wealth of information on the molecular properties of ground and excited electronic states, which are of paramount relevance in molecular, life, and materials sciences.[1] However, the interplay of many subtle effects in determining the overall spectral patterns calls for adequate interpretative tools, especially in condensed phases, where many fundamental features are often hidden within broad and structureless spectra.[2] In such scenarios, the development and validation of effective tools for the prediction and interpretation of vibrationally resolved spectra is extremely useful, and a number of significant advances have been made in the last few years.[3] However, until now it has only been possible to calculate vibrationally resolved absorption spectra in the gas phase.[4,5] This limitation is serious, as most chemical processes occur in solution and the related spectra are obtained under the same conditions. From a complementary point of view, absorption spectra are often recorded to investigate the interactions between a molecule and its environment, and part of these interactions is revealed by modifications of diagnostic molecular vibrations. Thus, being able to simulate complete absorption spectra in solution is very important.

Herein we propose a general quantum-mechanical tool that combines the most recent advances in density functional theory (DFT) and its time-dependent extension (TD-DFT)[6–9] with a proper treatment of bulk solvent effects, and a new effective method for calculating vibrational contributions. Provided that the gas-phase excited-state description is reliable, this method allows for the first time a full ab initio calculation of absorption spectra in solution, thus enabling a direct comparison of calculated results with experimental data for systems large enough to be of chemical, biological, or technological interest.

Because of the significantly different polarity of its ground and first excited electronic states and the large solvent shift of its absorption and emission spectra,[10] coumarin C153 (Scheme 1) has probably been the most used molecular probe for investigating solvation dynamics and understanding the microscopic basis of solvent effects,[11–17] thus making it the benchmark for theoretical solvation models. A quantitative prediction of solvent-induced spectral shifts of C153 by first-principle methods encounters difficulties related to the large dimensions, the lack of any symmetry, the presence of remarkable vibrational progressions for both low- and high-frequency modes, and the above-mentioned difference in polarity of the two lowest-energy electronic states. We show below that our new integrated computational tool leads to spectra closely resembling their experimental counterparts in two solvents (cyclohexane and dimethylsulfoxide (DMSO)) of different polarity, without resorting to any fitted parameter (apart from inhomogeneous broadening).



Scheme 1. The two conformers of C153.

The stick absorption spectrum from the electronic state $|e'\rangle$ to $|e\rangle$ is described by Equation (1) in which $\mu_{j',j} = \langle j'|\langle e'|\mu|e\rangle|j\rangle$ are the transition dipole moments of $|e'\rangle$ to $|e\rangle$, $|j'\rangle$, and $|j\rangle$ are the vibrational states and $E_{j'}$ and E_j the energies of the two states, and $p_{j'}$ is the Boltzmann population of the initial state $|j'\rangle$.[18] Our computational approach, described in detail in the Supporting Information), takes advantage of the recent feasibility of TD-DFT excited-state geometry optimizations for large systems thanks to the development of analytical gradients for both vacuum and solution,[8,9] which provide a reliable vibrational description in several systems.[5] However, as it can exploit any theoretical

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electronic method that allows for the calculation of excited-state first and second derivatives in the condensed phase (for example, CIS (Configuration Interaction Singles),[19] CASSCF (Complete Active Space Self Consistent Field)[20]), our method can be applied also to study processes for which TD-DFT has often failed (see the Supporting Information).

$$\sigma_{abs}(\omega) = \frac{4\pi^2\omega}{3c} \sum_{j',j} p_{j'} |\mu_{j',j}|^2 \delta(E_{j'} - E_j + \mathrm{h}\omega) \qquad (1)$$

Upon excitation from $|e'\rangle$ to $|e\rangle$, the solvent needs a finite time to respond to the solute change in charge density arising from the transition so that, depending on its relaxation times, a non-equilibrium ($\sigma_{\mathrm{abs}}^{\mathrm{neq}}$) or an equilibrium ($\sigma_{\mathrm{abs}}^{\mathrm{eq}}$)[21] regime for the calculation of the spectrum is more appropriate (see the Supporting Information). Both situations can be described in the frame of the so-called polarizable continuum model (PCM).[22–24]

Within this approach, the whole set of vibrational frequencies and normal modes of the molecule in solution can be obtained by analytical second derivatives of the ground state,[25] and by finite differences of analytical gradients for excited states. The last step to reproduce the spectrum is the calculation of the transition moments, $\mu_{j',j}$, which at the harmonic level is traced back to the evaluation of overlaps among vibrational states. Though this can be done analytically,[26,27] when dealing with large molecules without symmetry, the number of these states is huge. As a consequence, not only is a brute-force calculation out of question but also a simple selection of the final states lying in the energy range of the spectrum is not effective and leads to unaffordable costs (for C153 there are ca. 10^{17} possible transitions within 6000 cm^{-1} from the 0–0 transition, see the Supporting Information).[4a] Herein we present the results obtained by a new strategy, which is implemented in a modified version of the Gaussian program that allows an effective and automatic selection of the relevant overlaps to be calculated (see the Supporting Information for a description).[28]

The absorption spectrum of C153 is dominated by an allowed transition for which the Condon approximation (i.e., the transition dipole is independent of the nuclear coordinates) is fully adequate; moreover, the non-equilibrium regime is more appropriate as the faster nuclear response of DMSO (ca. 200 fs) is much slower than intramolecular dephasing (estimated to be ca. 30 fs,[12] see the Supporting Information). In the Supporting Information, we show that the gas-phase 0–0 transition energies, the oscillator strengths, and the shift in the dipole moment associated with the electronic transition derived by PBE0 and TD-PBE0 calculations for the almost-isoenergetic *syn* and *anti* isomers are in very good agreement with their experimental counterparts,[29,30] thus supporting the reliability of our computational approach. For example, the calculated values for the oscillator strengths match their experimental counterpart (0.37).[15]

Figure 1 a shows the calculated stick absorption spectrum for the *anti* isomer at 0 K in cyclohexane and its convolution with a Gaussian whose full width at half maximum (FWHM; 650 cm^{-1}) has been chosen to match the width of the main experimental bands. We checked that the spectrum is unaltered when calculated for 300 K, including all the 44 initial states with a Boltzmann population ≥ 0.4 of the ground-state population. Once convoluted, the spectra of the *syn* and *anti* isomers are virtually indistinguishable (see the Supporting Information), thus hereafter we will generically refer to them as the C153 spectrum. After the harmonic analysis has been performed, the new algorithm for the calculation of the spectrum is very efficient and gives a fully converged spectrum in around 13 min on a personal computer, after selecting 27×10^6 transitions out of about 10^{36} states in a very large range of 3 eV (see the Supporting Information for details).

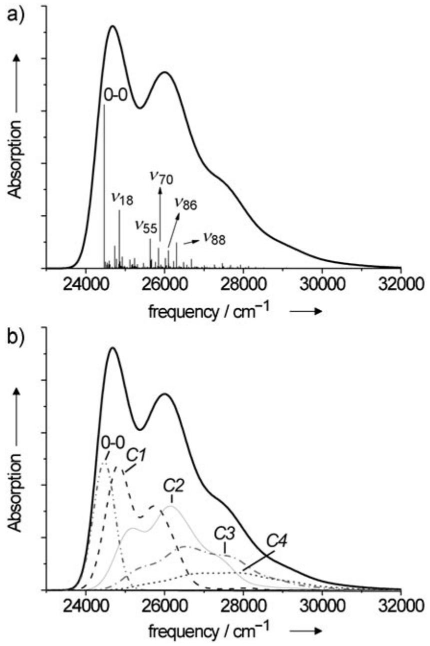

Figure 1. Calculated spectrum of C153 in cyclohexane: a) 0 K stick spectrum and its assignment (the main contributing bands all correspond to transitions with one quantum in a single oscillator, which is indicated as ν_n in the Figure) and its convolution with a Gaussian; b) decomposition of the spectrum (thick line) in its components, C_n which collect transitions to vibrational states of $|e\rangle$ with the same number *n* of simultaneously excited oscillators are considered.

The line shapes and positions of the calculated and experimental spectra are extremely similar: both spectra exhibit a two-peak structure with a spacing of approximately 1300 cm^{-1} between the peaks, and the absolute positions of the theoretical peaks are blue-shifted by just a few hundreds of cm^{-1} with respect to their experimental counterparts. All these features do not significantly depend on the choice of the convolution Gaussian and are well evidenced in Figure 2, in which, for better comparison, the calculated spectrum is artificially red-shifted by approximately 400 cm^{-1} (the same spectrum without the shift is given in the Supporting Information).

The first band (see Figure 1 b) is mainly due to the contribution of the 0–0 transition and of transitions (C_1) to states where a single vibrational mode is excited. Among these transitions, the highest band is due to the transition to a

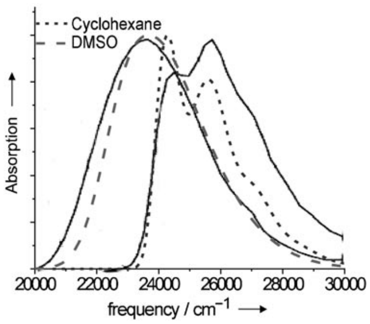

Figure 2. Calculated spectra of C153 in cyclohexane and in DMSO. Both spectra are shown red-shifted by 400 cm^{-1}. The experimental spectra (thick lines) are shown for comparison.

state with one quantum onto the vibrational mode ν_{18} with frequency 383 cm^{-1}, which corresponds to a complex cooperative motion of the rings with in-plane and out-of-plane components (see the Supporting Information). In full agreement with this result, a strong feature at 380 cm^{-1} is indeed found in the gas-phase-dispersed fluorescence spectrum.[31]

Interestingly the higher-energy second band is built up from contributions of both C_1 transitions and combination bands of two (C_2) and three (C_3) vibrational modes (see Figure 1b).

The only discrepancy between calculated and experimental spectra concerns the relative height of the two highest bands. The underestimation of the height of the blue-side band in our calculations is related to the presence of several transitions to C_2 and C_3 combination bands (whereas the red-side band is dominated by C_1 transitions, see Figure 1b), whose contribution would be increased by a more accurate account of anharmonicity (Supporting Information).

When simulating the spectrum in DMSO, we considered that the energetic effect of solvent fluctuations on the absorption spectra is much larger in polar solvents.[14] According to Horng et al.,[12] for C153 in DMSO, this effect can be simulated by a Gaussian convolution with a FWHM ≈ 1710 cm^{-1}; the results thus obtained are given in Figure 2 where, as in the case of cyclohexane, the calculated spectrum of C153 in DMSO is artificially red-shifted by 400 cm^{-1} (see the Supporting Information for assignments). It is apparent that the calculated and experimental band maxima are nearly coincident and that the asymmetric band of the experimental spectrum (more extended in the blue region of its maximum) is very well reproduced. This latter result supports the reliability of our computational approach as the asymmetry of the band is very sensitive to the underlying vibrational progression.

Finally, an inspection of Figure 2 indicates that a DMSO→cyclohexane solvent shift estimated from the calculated absorption spectra is only about 150 cm^{-1} smaller than its experimental counterpart.

In summary, the results we have presented show that our integrated procedure is able to predict the absorption spectra of C153, a large molecule in solution, with a high degree of accuracy (within a few hundred wavenumbers). Furthermore, the theoretical foundations of the proposed approach are conceptually easy, and the procedure is fully transferable to the simulation of fluorescence spectra and to the treatment of equilibrium/non-equilibrium regimes, thus making our method a powerful and flexible tool to investigate solvation dynamics for large systems of biological or technological interest, at least when coupled multiple-excited states are not involved. Our computational procedure is already interfaced with widely available computer programs, and thus is easily accessible to nonspecialists, which should increase fruitful crossovers between experiments and calculated and theoretical models.

Experimental Section

Computational procedure: We adopted DFT and TD-DFT methods, the standard 6-31G(d) basis set and the PBE0 hybrid functional.[29] In the PCM calculations, we used the dielectric constant at optical frequency $\varepsilon_{\mathrm{opt}}$ (2.179 for DMSO and 2.028 for cyclohexane) and the static dielectric constant ε (46.7 for DMSO and 2.023 for cyclohexane) in the non-equilibrium and equilibrium regime, respectively.

The Supporting Information includes technical details on the electronic and vibrational calculations, a description of the solvent, calculations of spectral intensities, and a discussion of the properties of the excited states. A table reporting geometric parameters of C153, a schematic drawing of the frontier orbitals and of the ν_{18}, ν_{55}, ν_{70}, and ν_{86} vibrational modes, and additional Figures of the spectra are also provided.

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