On the structure of hot absorption spectra of polyatomic molecules: Solvent effect on the transition energy gap

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Hot absorption spectra of polyatomic molecules may exhibit a characteristic shoulder. Its origin and connection to the 0-0 transition energy gap has been established on the basis of a recently developed quantum-classical approach. We demonstrate that an accurate estimate of the transition energy can be obtained directly from experimental data. The method can be used to study the solvent influence on the energetics of electronic transitions. © *2009 American Institute of Physics.*
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Ultraviolet and visible (UV-vis) absorption spectra provide direct information about energetics of electronic transitions, which is of primary importance for the modeling and understanding of reaction dynamics. Usually, measurements of absorption/fluorescence emission[1–3] are performed at low temperatures (crystals, supersonic jet expansion) to resolve the vibronic band progressions, thus obtaining extensive information about internal structure and transition energies of molecules. The calculation of electronic spectra in this case may be achieved by the Fermi golden rule approach,[4–7] where the intensity of the transition is given by the Franck–Condon (FC) overlaps of the initial nuclear wave functions with the corresponding vibrational wave function of the final electronic state, which generally requires evaluation of multidimensional integrals.

However, the vast majority of chemical and biological reactions take place in solution at moderate to high temperatures. The corresponding hot UV-vis absorption spectra are not only temperature broadened, but also affected by the surrounding media,[8–10] and may contain hot bands originating from FC forbidden transitions.[11] The number of FC integrals necessary to describe hot absorption spectra sharply increases with increasing temperature, and therefore, the quantum number of the low-frequency modes, thus making the quantum Fermi golden rule approach inapplicable.

Recently we suggested a new quantum-classical approach[12] to model nonadiabatic transitions in polyatomic molecules, which can be extended to the *ab initio* simulation of UV-vis absorption spectra. Assuming fast equilibration in the phase spaces of electron potential energy surfaces (PESs) to the temperature of the surrounding media compared to the time scale of light-induced transition, and vanishing power of the absorbed light (linear response regime), the stationary absorption power can be written as

$$P_{\text{abs}}(t) = \hbar(\langle \text{Im}[\Omega(q)W(q)\eta^{(1)}(q,t)]\rangle_q$$
$$+ \langle \text{Im}[\Omega(q)W(q)\eta^{(2)}(q,t)]\rangle_q)\gamma(\omega), \qquad (1)$$

where

$$\gamma(\omega) = 1 + \tanh\left(\frac{\hbar\omega + \varepsilon}{2k_BT}\right) \qquad (2)$$

is the frequency dependent factor with

$$\varepsilon = -k_BT \ln(Z_1/Z_2) \qquad (3)$$

being the change in the free energy due to the transition, expressed via the statistical sums $Z_{1,2}$ of the corresponding PESs indicated by the subscript. Here $\hbar$ and k_B are Planck's and Boltzmann's constants, respectively, whereas T is the temperature of the surrounding media.

The structure of Eq. (1) deserves additional discussion. Two terms in brackets on the right hand side are closely related to the evolution of the quantum phase of the transition, $\hbar\Omega(q)$ is the vertical energy splitting between the PESs at a given point of phase space q, $W(q)$ is the coupling term and represents itself scalar product between the vectors of the electric field amplitude and of the transition dipole moment of the molecule, whereas the auxiliary functions $\eta^{(1,2)}(q,t)$ contain complete information about quantum coherence and memory effects, and obey

$$\frac{\partial \eta^{(1,2)}(q,t)}{\partial t} = i(\Omega(q) - \omega)\eta^{(1,2)}(q,t) + iW(q,t)/\hbar$$
$$+ \mathcal{L}_q^{(1,2)}\eta^{(1,2)}(q,t), \qquad (4)$$

where ω is the frequency of the absorbed light, and $\mathcal{L}_q^{(1,2)}$ is the linear functional operator describing evolution in the phase space of the first or the second PES indicated by the superscript. Finally, $\langle\ldots\rangle_q$ in Eq. (1) denotes phase space average, which can be performed using *ab initio* molecular dynamics methods, similar to Ref. 12.

Equation (1) has a transparent physical meaning. The contribution to the rate of the nonadiabatic transitions between the PESs at a given point of phase space is proportional to the imaginary part of the product between the coupling and the auxiliary function. Similarly, the contribution to the rate of the energy absorption at the same point of phase space is equal to the rate of the transitions multiplied by the vertical energy splitting between the PESs.
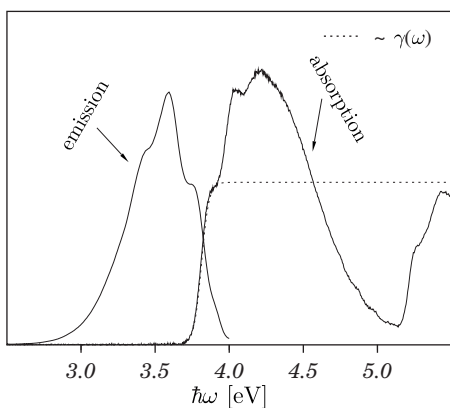
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FIG. 1. Fluorescence emission and absorption spectra of *trans*-stilbene dissolved in hexane at room temperature. The spectra were scaled to have similar amplitudes. The fit of the initial rise of the absorption spectrum by the stepwiselike function gamma, see Eq. (2), with the parameters $\epsilon = -3.81$ eV and $T = 293$ K, is shown by the dotted line.
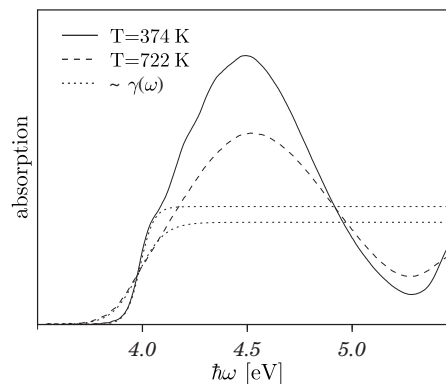

FIG. 2. Hot absorption spectra of *trans*-stilbene in gas phase taken at 374 K (solid line) and 722 K (dashed line). The corresponding fits of the initial rise by the frequency dependent factor $\gamma(\omega)$ with $\epsilon = 3.99$ eV are shown by the dotted lines.

A principal distinction between the suggested method and other quantum-classical approaches to nonadiabatic transitions is that the classical dynamics both along the ground and the excited PESs contribute to the evolution of the quantum phase, and therefore, to the absorption spectra, despite the fact that we consider transitions from the ground to the excited state. These two components have distinct maxima, corresponding to the absorption and emission ones, whereas a proper absorption spectrum part is separated out by the frequency dependent factor $\gamma(\omega)$, see Eqs. (1)–(3). At low temperatures these two parts are usually well separated spectrally. However, increasing the temperature, their overlap may become important and visible in the spectra. A vivid example of this kind is the absorption spectrum of *trans*-stilbene, dissolved in hexane at room temperature ($T = 293$ K), taken from the freely available PHOTOCHEMCAD database.[13] For the matter of convenience we also plot the fluorescence emission spectrum (excitation wavelength 290 nm), taken *ibidem*. The spectra were scaled to have similar amplitudes, see Fig. 1.

The absorption spectrum has a visible shoulder at its left side at an excitation energy of about 3.9 eV. A similar one exists in the emission spectrum, see Fig. 1. They appear because the two broad overlapping contributions in Eq. (1), discussed above, form a saddle between them. Besides, the width of this saddle at given temperature proves to be larger than the width of the stepwiselike factor $\gamma(\omega)$, see Eq. (2), which leads to the appearance of well visible shoulders in the spectra shown on Fig. 1. However it also means that the initial rise of the absorption spectrum has to be well described just by the functional dependence of $\gamma(\omega)$, and it is indeed perfectly fitted by Eq. (2) with $\epsilon = -3.81$ eV and $T = 293$ K, see Fig. 1. Among other things, it gives an accurate estimate of the free energy change upon photoexcitation including both 0-0 transition energy gap and the corresponding entropic part. The origin of shoulders in UV-vis absorption spectra may be different, see, e.g., Refs., 7 and 14 but in the case discussed above it seems to be due to the temperature broadening.

It is well known that surrounding media may considerably affect the energy splitting between distinct electronic states, the PES-specific dipole-dipole interaction with solvent molecules being one source of the influence. On the other hand, a direct measurement of the energy gap of 0-0 transition requires high resolution experiments usually performed at low temperatures, which can hardly be used to investigate solvent effects on the energetics of the electronic transitions. In the case of *trans*-stilbene, where we understand the origin of the shoulder, the accurate value of the transition free energy gap can directly be extracted from the hot absorption spectra as well. Indeed, applying the above procedure to the gas phase spectra shown on Fig. 2, where we expect no or little influence of the surrounding media, we obtain $\epsilon = 3.99$ eV, which is in excellent agreement with the value of 4.00 eV (310.23 nm), obtained for the jet-cooled molecule,[15] and for nonpolar benzene as the solvent,[16] where it is found to be 3.98 eV. Thus, one may conclude that hexane as the solvent reduces the splitting between the ground and the first excited state by 0.18 eV compared to the isolated or gas phase *trans*-stilbene.

Tyrosine, one of the 20 amino acids used by cells in protein synthesis, offers another example. A close look at the absorption spectrum[13] of tyrosine dissolved in water, shown in Fig. 3, reveals a characteristic shoulder, which is supposed
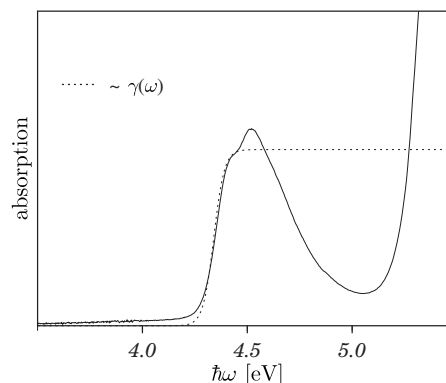

FIG. 3. The absorption spectrum of tyrosine dissolved in water at room temperature (solid line). The fit of the initial rise by $\gamma(\omega)$ with $\epsilon = 4.34$ eV and $T = 293$ K is shown by the dotted line.

to be of the same nature as for the *trans*-stilbene. Fitting of the initial rise of the spectrum with $\gamma(\omega)$ yields the transition free energy gap of 4.34 eV, and it is in a good agreement with the experimental values[17,18] of 286–288 nm (4.34–4.30 eV) obtained for tyrosine in RNase-S and RNase-A dissolved in water-glycerol mixture.

The accurate treatment of quantum phase is of fundamental importance for any *ab initio* quantum-classical approach to nonadiabatic transitions, as the spectral shape is very sensitive to the quantum phase. Note that neither mean-field[19,20] nor surface hopping[21,22] quantum-classical schemes can give satisfactory results when applied to the simulation of the line shape of UV-vis absorption spectra. In particular, quantum phase in mean-field approaches evolves on the averaged PES, which would give instead of spectrally shifted emission and absorption parts just an unphysical line in between. Similarly, surface hopping schemes estimate the dynamics of the populations but not the quantum phase, and therefore, *ab initio* simulation of UV-vis absorption spectra can hardly be done. On the other hand, the suggested quantum-classical approach is capable of *ab initio* modeling of both the population dynamics,[12] and the line shape of the absorption spectra. Its intrinsic feature, that in the quantum-classical approximation the classical dynamics both along the initial and the final PES contribute to the evolution of the quantum phase of transition, seems to be supported by experimental data. The method for direct extraction of the 0-0 transition energy gap from hot absorption spectra of some polyatomic molecules has been proposed. It gives an opportunity to study directly the solvent effects on the energetics of electronic transitions.

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