

Supplementary Material

for “Solute-Solvent Interactions Determine the Effect of External Electric Field on the Intensity of Molecular Absorption Spectra”

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In this Supplement we consider theoretically the effect of a condensed phase medium on the intensity of a molecular electronic absorption spectrum.

Intensities of electronic molecular spectra are described theoretically by transition dipole moments (TDM). The square of the TDM enters the Einstein coefficient for the spontaneous emission probability and the oscillator strength that determines the absorption intensity. The TDM is defined as

$$\bar{\mu}_{mjni} = \int \psi_{mj}^*(x, q) \bar{\mu}(x, q) \psi_{ni}(x, q) dx dq, \quad (1)$$

where $\bar{\mu}(x, q)$ is the molecular DM operator, and x and q are electronic and vibrational coordinates. The electron-vibrational wave-function can be written in the Born-Oppenheimer (BO) approximation as a product of the electronic and vibrational components

$$\psi_{ni}(x, q) = \psi_n^{el}(x, q) \psi_{ni}^{vibr}(q), \quad (2)$$

where n labels electronic states and i enumerates vibrational levels within the n th electronic state. This gives

$$\bar{\mu}_{mjni} = \int \psi_m^{*el}(x, q) \psi_{mj}^{*vibr}(q) \bar{\mu}(x, q) \psi_n^{el}(x, q) \psi_{ni}^{vibr}(q) dx dq. \quad (3)$$

The molecular dipole moment operator can be separated in the electronic and vibrational contributions as well

$$\bar{\mu}(x, q) = \bar{\mu}^{el}(x, q) + \bar{\mu}^{vibr}(q). \quad (4)$$

Assuming that the electronic component of the DM operator $\bar{\mu}^{el}(x, q)$ acts on the vibrational wave function $\psi_{ni}^{vibr}(q)$ only weakly, and similarly, the vibrational component of the DM operator $\bar{\mu}^{vibr}(q)$ acts on the electronic wave function $\psi_n^{el}(x, q)$ weakly, we obtain

$$\begin{aligned} \bar{\mu}_{mji} = & \int \psi_{mj}^{*vibr}(q) \psi_{ni}^{vibr}(q) dq \cdot \int \psi_m^{*el}(x, q) \bar{\mu}^{el}(x, q) \psi_n^{el}(x, q) dx + \\ & + \int \psi_{mj}^{*vibr}(q) \bar{\mu}^{vibr}(q) \psi_{ni}^{vibr}(q) dq \cdot \int \psi_m^{*el}(x, q) \psi_n^{el}(x, q) dx. \end{aligned} \quad (5)$$

Since $\psi_m^{el}(x, q)$ and $\psi_n^{el}(x, q)$ are eigenstates of the electronic Hamiltonian in the BO approximation, they are orthogonal, and the second line is zero. Thus, TDM is determined by the product of the matrix element of the electronic DM for fixed vibrational coordinates

$$\bar{\mu}_{mn}^{el}(q) = \int \psi_m^{*el}(x, q) \bar{\mu}^{el}(x, q) \psi_n^{el}(x, q) dx, \quad (6)$$

and vibrational overlap integral that defines the Franck-Condon factor. The electronic contribution to TDM determines the integral intensity of the electronic transition. The Franck-Condon factor governs the relative distribution of intensity, overall shape and structure of the electron-vibrational band.

Next, consider the change in the intensity of the electron-vibrational transition that occurs when the molecule is transferred from gas phase to a condensed environment. With “0” denoting gas phase functions, Eq. (6) is re-written as

$$\bar{\mu}_{mn}^{0el}(q) = \int \psi_m^{0el*}(x, q) \bar{\mu}^{0el}(x, q) \psi_n^{0el}(x, q) dx. \quad (7)$$

Molecular properties change in condensed phase. For instance, the ground and excited state dipole moments become¹

$$\bar{\mu}_g = \frac{\bar{\mu}_g^0}{1 - \alpha_g(f' + f'')}, \quad \bar{\mu}_e = \frac{\bar{\mu}_e^0}{1 - \alpha_e(f' + f'')}, \quad (8)$$

where f' , f'' are functions of the internal field of the liquid reflecting orientation and induction solute-solvent interactions:

$$f' = \frac{3}{2a^3} \frac{n^2 + 2}{2n^2 + 1} \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right), \quad f'' = \frac{3}{2a^3} \frac{n^2 - 1}{2n^2 + 1}, \quad (9)$$

where n and ε are the refractive index and dielectric permittivity of the medium, and a is the Onsager radius of the solute molecule. Note that in the simplest case, $\varepsilon = n^2$, and $f' = 0$. For instance, this is true for crystals at moderate measurement frequencies and temperatures. For

liquids, however, molecular motions such as dipole reorientation can have a dominant contribution to the static permittivity, and only the high frequency value of permittivity follows this simple relationship.

The solvent induced changes in the dipole moments can be very significant. Assuming that $\alpha \approx a^3$ and taking into account that $n^2 = \epsilon$ in the long-wavelength limit, gives a 50% change in the dipole moment of a solute dissolved in CCl_4 with $n = 1.446$.

Generally, a molecule in a condensed phase is described by a new Hamiltonian with its own energies and wave functions. We will determine these wave functions using perturbation theory. The new potentials for the ground (V_g) and excited (V_e) electronic states are²

$$V_g = V_{G,g} - \frac{1}{2} \bar{\mu}^{el} \bar{R}_{g(or-ind)} - \alpha^{el} f_D \quad (10)$$

$$V_e = V_{G,e} - \frac{1}{2} \bar{\mu}^{el} \bar{R}_{g(or)} - \frac{1}{2} \bar{\mu}^{el} \bar{R}_{e(ind)}^{FC} - \alpha^{el} f_D. \quad (11)$$

Here, $V_{G,g}$ and $V_{G,e}$ are the unperturbed ground and excited state potentials describing the molecule in gas phase. $\bar{\mu}^{el}$ and α^{el} is the electronic dipole moment and polarizability operators.

The reactive fields \bar{R} describe the solute-solvent interaction and are defined³ together with f_D by

$$\bar{R}_{g(or-ind)} = (f' + f'') \bar{\mu}_g, \quad (12)$$

$$\bar{R}_{g(or)} = f' \bar{\mu}_g, \quad (13)$$

$$\bar{R}_{e(ind)}^{FC} = f'' \bar{\mu}_e^{FC}, \quad (14)$$

$$f_D = \frac{3}{2a^3} \cdot \frac{I \cdot I_p}{(I + I_p)} \cdot \frac{n^2 - 1}{n^2 + 2}, \quad (15)$$

where functions f' , f'' are defined by Eq. (9), and I , I_p are the ionization potentials of the solute and solvent molecules. The subscripts “*or*” and “*ind*” denote orientation and induction solute-solvent interactions. The superscript “*FC*” indicates the Franck-Condon approximation, assuming that the nuclear degrees of freedom do not have time to respond to the electronic excitation. Note that Eq. (11) for the perturbed excited state potential contains the ground state component of the orientation reactive field $\bar{R}_{g(or)}$, because the orientation of the molecule cannot respond on the time-scale of the electronic excitation. Similarly, the induction component $\bar{R}_{e(ind)}^{FC}$

depends on the dipole moment for the excited electronic state in the ground state molecular geometry, $\bar{\mu}_e^{FC}$.

In order to find the matrix element defined by Eq. (7) we use the first order of the perturbation theory. To the first order, the electronic wave function is

$$\psi_i^{el}(x, q) = \psi_i^{0el}(x, q) + \sum_{k \neq i} \frac{V_{ki}}{E_k^0 - E_i^0} \psi_k^{0el}(x, q), \quad (16)$$

where

$$V_{ki} = \int \psi_k^{0el*}(x, q) V_j \psi_i^{0el}(x, q) dx, \quad (17)$$

and the perturbation operators V_j are defined by Eq. (10), (11). Now, the ground-to-excited state TDM becomes

$$\bar{\mu}_{eg}^{el}(q) = \frac{1}{m} \left\{ \begin{aligned} & \bar{\mu}_{eg}^{0el}(q) + \frac{\bar{\mu}_g^0(f' + f'')}{2m} \sum_{k \neq g} \frac{\bar{\mu}_{gk}^0 \bar{\mu}_{ke}^0}{E_k^0 - E_g^0} + \frac{\bar{\mu}_g^0 f' + \bar{\mu}_e^{0FC} f''}{2m} \sum_{k \neq e} \frac{\bar{\mu}_{gk}^0 \bar{\mu}_{ke}^0}{E_k^0 - E_e^0} + \\ & + f_D \left[\sum \frac{\alpha_{ke} \bar{\mu}_{kg}^0}{E_k^0 - E_g^0} + \sum \frac{\alpha_{kg} \bar{\mu}_{ke}^0}{E_k^0 - E_e^0} \right] \end{aligned} \right\}. \quad (18)$$

The matrix elements are taken with respect to the unperturbed wave functions ψ_i^{0el} and ψ_j^{0el} describing the molecule in gas phase. The parameter $m = 1 - \alpha(f' + f'')$ describes the solvent induced change in the gas phase value of the corresponding dipole moment, as in Eqs. (8)

Applied to the lowest energy excitation, the above expression is dominated by the terms with the smallest energy differences $E_k^0 - E_e^0$ and $E_k^0 - E_g^0$. I.e. $k = g$ in $E_k^0 - E_e^0$ and $k = e$ in $E_k^0 - E_g^0$. Then, Eq. (18) simplifies to

$$\bar{\mu}_{eg}^{el}(q) = \frac{\bar{\mu}_{eg}^{0el}(q)}{m} \left[1 + \frac{f' \bar{\mu}_g^0 (\bar{\mu}_e^0 - \bar{\mu}_g^0)}{2mh\nu_{eg}} + \frac{f_D (\alpha_e - \alpha_g)}{h\nu_{eg}} \right], \quad (19)$$

where ν_{eg} is the frequency of the electronic excitation and h is Planck's constant. Eq. (19) describes to the first order the change in TDM that occurs when the molecule moves from gas phase to a condensed environment. Comparing to Eq. (18) note that the f'' term disappears. At the same time, the f' term is asymmetric with respect to the ground and excited state dipole moments, because the orientation component of the reactive field, Eq. (13), entering the perturbed excited state potential contains the ground state dipole moment due to the Franck-

Condon approximation, as discussed above. It follows that the largest change in the integrated absorption intensity can be expected for polar molecules in polar solvents. The change of the molecular polarizability that takes place upon electronic excitation plays an appreciable role and becomes the dominant lowest order term for non-polar solutes.

The change in the absorption intensity of a molecule is a linear function of the applied electric field in both solution and gas phase. This can be shown theoretically by considering the square of the TDM, which determines the absorption intensity. Expanding the DMs encountered in Eq. (19) in the electric field \vec{E}

$$\vec{\mu}_{eg}^{0el}(E) = \vec{\mu}_{eg}^{0el}(0) + \alpha_{eg}\vec{E}, \quad \vec{\mu}_g^0(E) = \vec{\mu}_g^0(0) + \alpha_g\vec{E}, \quad \vec{\mu}_e^0(E) = \vec{\mu}_e^0(0) + \alpha_e\vec{E}, \quad (20)$$

one can show to the lowest order in \vec{E} that the square of the TDM is also a linear function of \vec{E} ,

$$\begin{aligned} |\vec{\mu}_{eg}^{el}|^2(E) &= |\vec{\mu}_{eg}^{0el}|^2(0) \left[1 + \frac{f' \vec{\mu}_g^0(0)(\vec{\mu}_e^0(0) - \vec{\mu}_g^0(0))}{mh\nu_{eg}} + \frac{f_D(\alpha_e - \alpha_g)}{h\nu_{eg}} \right]^2 \\ &+ \vec{E} \cdot 2\vec{\mu}_{eg}^{0el}(0)\alpha_{eg} \left[1 + \frac{f' \vec{\mu}_g^0(0)(\vec{\mu}_e^0(0) - \vec{\mu}_g^0(0))}{mh\nu_{eg}} + \frac{f_D(\alpha_e - \alpha_g)}{h\nu_{eg}} \right] \\ &+ \vec{E} \cdot 2|\vec{\mu}_{eg}^{0el}|^2(0) \left[1 + \frac{f' \vec{\mu}_g^0(0)(\vec{\mu}_e^0(0) - \vec{\mu}_g^0(0))}{mh\nu_{eg}} + \frac{f_D(\alpha_e - \alpha_g)}{h\nu_{eg}} \right] \\ &\quad \times \frac{f'}{mh\nu_{eg}} \left[\alpha_g(\vec{\mu}_e^0(0) - \vec{\mu}_g^0(0)) + \vec{\mu}_g^0(0)(\alpha_e - \alpha_g) \right] \end{aligned} \quad (21)$$

The second term in the above equation involves the change in the molecular TDM induced by the electric field in gas phase $\alpha_{eg}\vec{E}$. In gas phase $f' = f_D = 0$, the third term in the last two lines of Eq. (21) disappear altogether, and $2\alpha_{eg}\vec{\mu}_{eg}^{0el}(0) \cdot \vec{E}$ determines the overall effect of the electric field. In the presence of the solvent the effect of the electric field is greatly amplified by the terms containing f' and f_D .

References

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