Theory of Dispersion Energy and Solvent Effects on Molecular Spectra

J. Mahanty
Department of Theoretical Physics, Research School of Physical Sciences
The Australian National University Canberra, A.C.T. 2600, Australia

and C. N. R. Rao *
Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India

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The theory of dispersion energy has been shown to directly give an explicit expression for the solvent shifts in the spectra of non-polar solute molecules.

Solvent effects on the spectra of molecules arise from various interactions between the solute and solvent molecules[1,2]. Dispersion effects are primarily responsible for the influence of non-polar solvents on the spectra of non-polar solutes and can in the simplest form be regarded as arising from London dipole interactions. Such effects on spectra are generally discussed in the literature[2] in terms of Onsager's reaction field. In this paper we analyze solvent effects on spectra from the viewpoint of the dispersion energy[3] of the solute molecule in the solvent medium and show that in this way an explicit relation for solvent-induced spectral shifts similar to that obtained from perturbation theory can be derived.

The Method

The dispersion energy of a molecule arises from the change in the energy of the electromagnetic field due to the presence of the molecule. If we consider a fluctuating dipole moment $\boldsymbol{p}(\omega)$ on the molecule located at $\boldsymbol{R}$, the electric field due to that can be written as

$$\boldsymbol{\varepsilon}(\boldsymbol{r}, \omega) = 4\pi\, \mathbf{G}(\boldsymbol{r}, \boldsymbol{R}; \omega)\, \boldsymbol{p}(\omega) \tag{1}$$

where $4\pi\,\mathbf{G}(\boldsymbol{r}, \boldsymbol{R}; \omega)$ is the diadic Green's function giving the electric field at $\boldsymbol{r}$ with a unit dipole source at $\boldsymbol{R}$. The dipole moment of the molecule can be considered as being due to the same field at $\boldsymbol{R}$, i. e.,

$$\begin{aligned} \boldsymbol{p}(\omega) &= \alpha(\omega)\, \boldsymbol{\varepsilon}(\boldsymbol{R}) \\ &= 4\pi\, \alpha(\omega)\, \mathbf{G}(\boldsymbol{R}, \boldsymbol{R}; \omega)\, \boldsymbol{p}(\omega)\,. \end{aligned} \tag{2}$$

The electrostatic diadic Green's function $\mathbf{G}(\boldsymbol{r}, \boldsymbol{r}'; \omega)$ will diverge if $r \to r' \to R$, but the finite size of the molecule at $\boldsymbol{R}$ removes this divergence by folding the Green's function with a form factor function representing the distribution of polarization over the size of the molecules[3]. In that case, Eq. (2) is replaced by

$$\boldsymbol{p}(\omega) = 4\pi\, \mathbf{G}(\boldsymbol{R}, \boldsymbol{R}; \omega)\, \boldsymbol{p}(\omega) \tag{3}$$

where

$$\mathbf{G}_n(\boldsymbol{r}, \boldsymbol{r}'; \omega) = \int \mathbf{G}(\boldsymbol{r}, \boldsymbol{r}''; \omega)\, \alpha_n(\boldsymbol{r}'' - \boldsymbol{r}'; \omega)\, \mathrm{d}^3 r'' \tag{4}$$

$\alpha_n(r)$ being the polarizability density of the molecule, assumed to be in the n-th quantum state.

The frequencies for which solutions of Eq. (3) will exist will give the perturbed frequencies of the electromagnetic field. They are roots of the (3×3) determinant

$$D_n(\omega) \equiv |\mathbf{I} - 4\pi\, \mathbf{G}_n(\boldsymbol{R}, \boldsymbol{R}; \omega)| = 0\,. \tag{5}$$

The change in the zero-point energy of the electromagnetic field due to the presence of the molecule, which is the dispersion energy of the molecule, is given by

$$\begin{aligned} E_n{}^{\mathrm{s}} &= -\frac{\hbar}{4\pi i} \oint \mathrm{d}\omega \ln |\mathbf{I} - 4\pi\, \mathbf{G}_n(\boldsymbol{R}, \boldsymbol{R}; \omega)| \\ &\cong -\frac{\hbar}{i} \oint \mathrm{d}\omega\, \mathrm{Tr}\, \mathbf{G}_n(\boldsymbol{R}, \boldsymbol{R}; \omega) \end{aligned} \tag{6}$$

where the contour for ω-integration encloses the positive real axis.

In the formulation proposed here, the solvent comes into the picture through $\mathbf{G}$. We shall restrict ourselves here to the non-retarded form of $\mathbf{G}$, since retardation effects are unimportant in this problem.

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* Two whom all correspondence should be addressed.

Results and Discussion

Let us consider a particular spectral band arising out of a dipole transition from the state $|n\rangle$ to the state $|m\rangle$ in a molecule. When the molecule is outside the solvent, the observed band will correspond to the energy difference between two levels, the energy of each level incorporating the dispersion self-energy term:

$$\omega_{nm} = \frac{1}{\hbar}\,[(E_n + E_n{}^{\mathrm{s}}) - (E_m + E_m{}^{\mathrm{s}})]\,. \tag{7}$$

Here E_n is the n-th energy level of the molecule when it is uncoupled to the radiation field.

When the molecule goes into solution, several possibilities arise. If it interacts strongly with the solvent molecules, E_n would change substantially because of possible structural changes in the molecule. But if the interaction is weak, as in the case of a non-polar solute in a non-polar solvent, only $E_n{}^{\mathrm{s}}$ and $E_m{}^{\mathrm{s}}$ in Eq. (7) will be modified, so that the change in the frequency will be

$$(\varDelta\omega)_{nm} = \frac{1}{\hbar} - [\{E_n{}^{\mathrm{s}} - E_m{}^{\mathrm{s}}\}_{\mathrm{solvent}} - \{E_n{}^{\mathrm{s}} - E_m{}^{\mathrm{s}}\}_{\mathrm{vacuum}}]\,. \tag{8}$$

In terms of Eqs. (4) and (6), Eq. (8) may be written as

$$(\varDelta\omega)_{nm} = -\frac{1}{i}\oint \mathrm{d}w \int \mathrm{d}^3r'\,\mathrm{Tr}\,[\mathbf{G}_{\mathrm{solvent}}(\boldsymbol{R},\boldsymbol{r}';\omega) - \mathbf{G}_{\mathrm{vacuum}}(\boldsymbol{R},\boldsymbol{r}';\omega)] \cdot [\boldsymbol{\alpha}_n(\boldsymbol{r}'-\boldsymbol{R};\omega) - \boldsymbol{\alpha}_m(\boldsymbol{r}'-\boldsymbol{R};\omega)]\,. \tag{9}$$

Reasonable estimates of the above expression can be made as follows. The polarizability density of a molecule in a given state has a range comparable with the wave function in that state[3]. We shall make the assumption that it can be written as

$$a_n(\boldsymbol{r},\omega) \equiv a_n(\omega)\,F_n(\boldsymbol{r}) \tag{10}$$

where

$$a_n(\omega) = -\frac{2}{\hbar}\sum_l |\langle n|\mu|l\rangle|^2\,\omega_{nl}/(\omega^2-\omega_{nl}^2) = \sum f_{nl}/(\omega_{nl}^2-\omega^2)\,. \tag{11}$$

Here μ is the magnitude of the dipole moment of the molecule and $F_n(\boldsymbol{r})$ is a normalized density function having a range comparable with the size of the molecule. Not to dilute the essentials of the argument, we assume that there is one dominant absorption frequency corresponding to the dipole transition between the states $|n\rangle$ and $|m\rangle$. We would then get

$$a_n(\boldsymbol{r}) - a_m(\boldsymbol{r}) \cong -\frac{2}{\hbar}\,\frac{|\langle n|\mu|m\rangle|^2}{\omega^2-\omega_{nm}^2}\,[\omega_{nm}F_n(\boldsymbol{r}) - \omega_{mn}F_m(\boldsymbol{r})]\,.$$

The difference between $F_n(\boldsymbol{r})$ and $F_m(\boldsymbol{r})$ is not significant for our purpose and we replace them by a single density function $F(\boldsymbol{r})$, so that the above expression becomes

$$a_n(\boldsymbol{r}) - a_m(\boldsymbol{r}) \cong -\frac{4}{\hbar}\,\frac{|\langle n|\mu|m\rangle|^2}{\omega^2-\omega_{nm}^2}\,\omega_{nm}F(\boldsymbol{r})\,. \tag{12}$$

Equation (9) then becomes

$$(\varDelta\omega)_{nm} \cong \frac{4}{i\hbar}\,|\langle n|\mu|m\rangle|^2\,\omega_{nm}\oint\frac{\mathrm{d}\omega}{\omega^2-\omega_{nm}^2} \cdot \int \mathrm{d}^3r'\,\mathrm{Tr}\,[\mathbf{G}_{\mathrm{solvent}}(\boldsymbol{R},\boldsymbol{r}';\omega) - \mathbf{G}_{\mathrm{vacuum}}(\boldsymbol{R},\boldsymbol{r}';\omega)]\,F(\boldsymbol{r}'-\boldsymbol{R})\,. \tag{13}$$

It must be emphasized here that the approximations made in Eqs. (10), (12) and (13) are not strictly necessary – in principle, computations can be done exactly. But they help in bringing out the essential features of the problem without mathematical complications.

We shall consider the application of Eq. (13) to two situations.

(i) *Small solute molecule with negligible excluded volume in the solvent:* In this case, it is quite appropriate to treat the solvent as a dielectric continuum, with a dielectric constant $\varepsilon(\omega)$. The only difference between $\mathbf{G}_{\mathrm{solvent}}$ and $\mathbf{G}_{\mathrm{vacuum}}$ would be a factor $1/\varepsilon(\omega)$ for the former, so that we will have, after some algebra,

$$\int \mathrm{d}^3r'\,\mathrm{Tr}[\mathbf{G}_{\mathrm{solvent}}(\boldsymbol{R},\boldsymbol{r}';\omega) - \mathbf{G}_{\mathrm{vacuum}}(\boldsymbol{R},\boldsymbol{r}';\omega)]\,F(\boldsymbol{r}'-\boldsymbol{R}) = \left[\frac{1}{\varepsilon(\omega)}-1\right]\frac{F(0)}{4\pi} \cong \frac{1}{4\pi}\left[\frac{1}{\varepsilon(\omega)}-1\right]\frac{1}{a_{\mathrm{M}}{}^3}\,, \tag{14}$$

where a_{M} is of the order of the size of the molecule. The factor $1/a_{\mathrm{M}}{}^3$ arises through the normalization of $F(\boldsymbol{r})$. We thus get the result

$$(\varDelta\omega)_{nm} \cong \frac{1}{\hbar\,a_{\mathrm{M}}{}^3}\,|\langle n|\mu|m\rangle|^2\,\omega_{nm} \cdot \frac{1}{\pi i}\oint\frac{\mathrm{d}\omega}{\omega^2-\omega_{nm}^2}\left[\frac{1}{\varepsilon(\omega)}-1\right]. \tag{15}$$

If the solvent does not have strong absorption frequencies, a reasonable estimate of $(\Delta\omega)_{nm}$ would be obtained by taking the contribution from the pole at ω_{nm},

$$(\Delta\omega)_{nm} = \left(\frac{-1}{\hbar\, a_M{}^3}\right) |\langle n|\mu|m\rangle|^2 \cdot \frac{1}{2}\left[\frac{\varepsilon(\omega_{nm})-1}{\varepsilon(\omega_{nm})}\right]. \tag{16}$$

We see that the red-shift is dependent on the factor

$$\left[\frac{\varepsilon(\omega)-1}{\varepsilon(\omega)}\right]_{w\to w_{nm}}.$$

A factor similar to this using the static dielectric constant, $\varepsilon(0)$, was suggested by Sheppard[4] from a totally different point of view, involving an estimate of the change of the potential energy of a charged particle in the medium. It is coincidental that the same sort of factor arises in an estimate of the change in the dispersion energy. When $[1/\varepsilon(\omega)]$ has sharp poles, ω-integration has to be done more exactly.

(ii) *Excluded volume in the solvent:* Physically, a more realistic situation would be one where the dissolved molecule remains inside a region from which the solvent molecules have been expelled. This, in fact, is the model most commonly used in this problem[5, 6].

If the excluded volume is a sphere with the solute molecule at its centre, the relevant $\mathbf{G}_{\text{solvent}}$ will have two parts. One arises from the direct interaction term in which the solvent does not play any role. This will cancel with $\mathbf{G}_{\text{vacuum}}$. The other is due to induced polarization, and this, with the unit dipole located at the centre, has the well-known form[5]

$$\mathbf{G}_{\text{polarization}}(\boldsymbol{r}, \omega) = \frac{2}{a_S{}^3}\,\frac{\varepsilon(\omega)-1}{2\,\varepsilon(\omega)+1}\,\mathbf{I} \tag{17}$$

where a_S is the radius of the sphere representing the excluded volume, and $r < a_S$.

Hence, the equivalent of Eq. (14) becomes

$$\int d^3r'\, \mathrm{Tr}\,[\mathbf{G}_{\text{solvent}}(\boldsymbol{R}, \boldsymbol{r}'; \omega) - \mathbf{G}_{\text{vac}}(\boldsymbol{R}, \boldsymbol{r}'; \omega)]\, F(\boldsymbol{r}'-\boldsymbol{R}) \cong \frac{6}{a_S{}^3}\,\frac{\varepsilon(\omega)-1}{2\,\varepsilon(\omega)+1}. \tag{18}$$

This approximate result is valid if $a_S > a_M$. We thus get the result

$$(\Delta\omega)_{nm} \cong -\frac{4}{i\hbar}\,|\langle n|\mu|m\rangle|^2\, \omega_{nm} \oint \frac{d\omega}{\omega^2-\omega_{nm}^2} \cdot \frac{6}{a_S{}^3}\left[\frac{\varepsilon(\omega)-1}{2\,\varepsilon(\omega)+1}\right] \cong -\frac{12}{a_S{}^3}\,|\langle n|\mu|m\rangle|^2 \left[\frac{\varepsilon(\omega_{nm})-1}{2\,\varepsilon(\omega_{nm})+1}\right]. \tag{19}$$

The last expression is obtained if we take only the pole term at ω_{nm}.

This result is identical with that obtained by the reaction field method alluded to in Refs. 5 and 6, with the difference that $\varepsilon(\omega)$ is evaluated at the transition frequency, and can obviously be written as the square of the refractive index at that frequency, $n^2(\omega_{nm})$. Dependence of the dispersion shift on the refractive index term, $(n^2-1)/(2\,n^2+1)$ of the solvent is indicated from perturbation treatments as well[7, 8].

If the excluded volume has other shapes, the frequency shift can be calculated by evaluating the appropriate Green's functions. A relation similar to (19) would also be valid to describe the effect of polar solvents on the spectra of non-polar solutes. The dependence of $(\Delta\omega)_{n,m}$ on the $\varepsilon(\omega_{nm})$ or $n^2(\omega_{nm})$ in Eq. (19) can, for all practical purposes, be replaced by $\varepsilon(0)$ or $n_D{}^2$. This would simplify correlation of experimentally observed solvent shifts of the spectra of non-polar molecules in non-polar solvents. In the literature[2, 9], it has been shown that the solvent red-shifts of the electronic spectral bands of non-polar molecules such as aromatic hydrocarbons in non-polar solvents are linearly related to the refractive index term $(n^2-1)/(2\,n^2+1)$. Solvent shifts of infrared frequencies have similarly been correlated with the $(\varepsilon-1)$ $(2\,\varepsilon+1)$ or $(n^2-1)/(2\,n^2+1)$ term[10].

Concluding Remarks

The approach used here is rather direct, and illustrates the main physical fact that the shift in frequency due to solvent effects would be firstly proportional to the oscillator strength of the transition, and secondly it would depend on the dielectric constant of the medium. The important factor here is $[\varepsilon(\omega_{nm})-1] \propto 4\,\pi\,\varrho\, a_S(\omega_{nm})$ where ϱ is the density of the solvent molecules and $\alpha_S(\omega)$ is their polarizability. A similar result is implicit in earlier perturbation theoretic approaches to this problem[8], but the advantages of the continuum model amenable to a Green's function method followed here is obvious.

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