On the Calculation of Infrared Intensities in Solution within the Polarizable Continuum Model

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We present a methodology for the theoretical evaluation of infrared intensities for molecules in solution in the polarizable continuum model (PCM) framework. In particular we focus on the calculation of terms related to the solvent polarization induced by the probing field (cavity field term) and on their dependence on the cavity geometry. Numerical tests for few model molecules have been done and compared with semiclassical models.

1. Introduction

This paper will treat the calculation of infrared (IR) intensities for molecules in solution. We will propose a theoretical approach with the aim of obtaining values for IR intensities directly comparable with experimental data. Other papers with analogous scopes with regard to linear and nonlinear optical properties for molecules in solution have recently been done: we quote for example the works of Wortmann et al.,[1] of Ågren et al.,[2] and of our group.[3,4]

Different formulations for the calculation of IR intensities in solution have been proposed in the past, both regarding pure liquids[5–7] and systems in solution.[8–12] The common point of all these approaches is the derivation of relations between absorption integrated intensities in liquid and in gas phase.

The mentioned classical formulations are generally based on Onsager's theory of dielectric polarization,[13] with the exception of Chako's work.[5] In the Onsager approach the molecule, which is simply approximated by a dipole, is inside a cavity (of spherical shape) created in the liquid, which is modeled as a continuum, infinite, homogeneous and isotropic dielectric medium. The effect of the medium on IR intensity is separated in two terms: the first one, represented by mean of a "reaction field", is connected with the response (polarization) of the dielectric medium to the molecule charge distribution. The second term (the cavity field) depends on the polarization of the dielectric induced by the externally applied electric field, once the cavity has been created.

We intend to show how the ab initio calculation of vibrational intensities for molecules in solution can be treated within the polarizable continuum model (PCM).[14] The approach we will present is not limited to the treatment of molecules in isotropic solutions but can be extended also to anisotropic dielectric media (for example liquid crystals) or composite media (molecules adsorbed on metal particles): that is due to the versatility of the PCM method already pointed out in ref 15.

In the PCM, the solvent is modeled as a continuum, infinite, homogeneous, and generally isotropic dielectric medium, characterized by a dielectric constant ϵ. The molecule is into a cavity modeled on its real shape and the electrostatic solute–solvent interaction (including also self-polarization effects) is calculated by introducing an apparent surface charge distribution (ASC) spread on the cavity surface. The differences between the PCM and Onsager's model is the use of a molecular-shaped cavity (instead of a spherical cavity) and the fact that the solvent–solute interaction is not simply reduced to the dipole term. In addition, in the PCM the solute is described by mean of its electronic wave function.

Solvent effects on IR intensities due to dielectric polarization (which as already said are treated in the classical theory by using the "reaction field") have already been treated in the PCM framework by assuming a complete response of the solvent (equilibrium model).[16] Other terms, similar to the "cavity field", have never been introduced in the PCM for the calculation of IR intensities. We will then focus on the formulation of such contributions.

In this paper we will not propose any comparison between calculated and experimental data: that is due to the fact that the study of other effects (in particular nonequilibrium effects), which could in principle have some importance, is under development in our group. We will then postpone this comparison to future communications.

2. Theory

The absorbance (Abs) relative to an absorption band can be expressed by mean of the well-known Lambert–Beer Law, as

$$\mathrm{Abs}(\tilde{\nu}) = a(\tilde{\nu})Cl \qquad (1)$$

where C is the molar concentration of the species under study, l is the length of the cell which contains the absorbing sample, and a is the so-called molar absorption coefficient (or extinction coefficient). As clearly underlined in eq 1, the absorption coefficient a and the absorbance depend on the wavenumber $\tilde{\nu}$ of the incident light. The total intensity of the transition is obtained by integrating a over the entire range of frequencies it spans (the band). This quantity can be expressed by means of the integrated absorption coefficient, A, as

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$$A = \ln 10 \int a(\tilde{\nu})\, d\tilde{\nu} \qquad (2)$$

If we neglect anharmonic effects, for the isolated molecule the integrated absorption A is related to the first derivative of the dipole moment $\boldsymbol{\mu}$ with respect to the mass-weighted normal coordinate Q associated to the vibrational mode i. The resulting expression is

$$A^{\mathrm{gas}} = \frac{\pi N_A}{3c^2}\left(\frac{\partial \boldsymbol{\mu}}{\partial Q_i}\right)^2 \qquad (3)$$

with N_A being Avogadro's number and c the velocity of light in a vacuum.

The starting point to derive the integrated absorption A^{gas} in eq 3 is the expression for the transition probability between two vibrational states 0 and 1 as induced by a radiation of frequency ω in the dipolar approximation

$$W^{\mathrm{gas}}_{1\leftarrow 0} = \frac{2\pi}{\hbar}\delta(E_1 - E_0 - \hbar\omega)|\langle 1|\boldsymbol{\mu}\cdot\mathbf{F}|0\rangle|^2 \qquad (4)$$

In eq 4, E_1 and E_0 are the energies of the vibrational state 1 and 0, respectively, $\boldsymbol{\mu}$ is the dipole moment and $\mathbf{F}$ is the electric field acting on the molecule.

Passing to molecules in solution, eq 4 is still valid but some refinements are needed. It is in fact necessary to replace $\mathbf{F}$ with the (Maxwell) electric field of the radiation in the medium, $\mathbf{F}^{\mathrm{M}}$,[17] and the dipole moment $\boldsymbol{\mu}$ with a quantity equivalent to the so-called external dielectric moment in the Onsager approach.[12,13,18] This quantity can be expressed as the sum of the dipole moment $\boldsymbol{\mu}$ of the molecule and the dipole moment $\tilde{\boldsymbol{\mu}}$ arising from the polarization induced by the molecule on the dielectric: the total interaction can then be written as $-(\boldsymbol{\mu} + \tilde{\boldsymbol{\mu}})\cdot\mathbf{F}^{M}$. As we will show later, the term related to $\tilde{\boldsymbol{\mu}}$ introduces the cavity field effect.

By substituting this formula into eq 4 we obtain the transition probability in solution between two vibrational states 0 and 1 as induced by a radiation of frequency ω

$$W^{\mathrm{sol}}_{1\leftarrow 0} = \frac{2\pi}{\hbar}\delta(E_1 - E_0 - \hbar\omega)|\langle 1|(\boldsymbol{\mu} + \tilde{\boldsymbol{\mu}})\cdot\mathbf{F}^{M}|0\rangle|^2 \qquad (5)$$

Similar to what has been previously shown for the isolated molecule, it is possible to derive from eq 5 the analogue of eq 3 for molecules in solution

$$A^{\mathrm{sol}}_{\mu+\tilde{\mu}} = \frac{\pi N_A}{3n_s c^2}\left(\frac{\partial(\boldsymbol{\mu} + \tilde{\boldsymbol{\mu}})}{\partial Q_i}\right)^2 \qquad (6)$$

The calculation of $A^{\mathrm{sol}}_{\mu+\tilde{\mu}}$ by means of eq 6 requires the knowledge of the $\partial\boldsymbol{\mu}/\partial Q$ and $\partial\tilde{\boldsymbol{\mu}}/\partial Q$ terms. In the following sections we will show how they can be computed for a PCM solute described at the ab initio level within the finite basis set approximation.

To end this section it is worth noticing the dependence of $A^{\mathrm{sol}}_{\mu+\tilde{\mu}}$ in eq 6 on the refractive index n_s of the solution under study. It follows from the relation between the intensity I of the radiation and the electric field $\mathbf{F}^{\mathrm{M}}$ in solution,[19] namely,

$$I = \frac{\epsilon_s c}{2\pi n_s}(\mathbf{F}^{\mathrm{M}})^2 \approx \frac{n_s c}{2\pi}(\mathbf{F}^{\mathrm{M}})^2 \qquad (7)$$

In eq 7 we have assumed the dielectric constant of the solution ϵ_s to be equal to square of the refractive index n_s^2: this corresponds to the assumption that the magnetic permittivity of the medium is roughly equal to 1.

2.1. The $\partial\boldsymbol{\mu}/\partial Q$ Term. The dipole moment $\boldsymbol{\mu}$ is written in terms of the density matrix $\mathbf{P}$ of the unperturbed solute calculated (in solution) at the HF or DFT level as

$$\mu_t = -tr[\mathbf{P}\mathbf{m}_t] + \mu_{N,t} \qquad (8)$$

where $\mathbf{m}_t$ collects the integrals of the tth Cartesian component of the dipole moment operator and $\mu_{N,t}$ indicates the nuclear contribution to the t component of $\boldsymbol{\mu}$.

The first derivative of $\boldsymbol{\mu}$ with respect to the normal coordinate Q_i is obtained by differentiating eq 8:

$$\frac{\partial \mu_t}{\partial Q_i} = -tr[\mathbf{P}^i\mathbf{m}_t + \mathbf{P}\mathbf{m}_t^i] + \mu^i_{N,t} \qquad (9)$$

In the previous equation $\mathbf{P}^i$ is the density matrix derivative with respect to Q_i and is currently calculated by mean of the CPHF formalism with the explicit inclusion of solvent-dependent terms, i.e., terms dependent upon the solvent dielectric response.[20] These terms are determined by assuming an equilibrium solvent response, so that their expression depends on the static dielectric constant ϵ of the solvent. The presence of the $\mathbf{m}_t^i$ term, i.e., of the dipole moment matrix derivative in eq 9, is due to the dependence of $\mathbf{m}_t$ on the basis functions, which in turn depend on the nuclear coordinates. Finally we stress that the mass-weighted normal coordinates too are obtained taking into account solvent effects.[20]

2.2. The $\partial\tilde{\boldsymbol{\mu}}/\partial Q$ term. When having the aim of obtaining an expression of the $\partial\tilde{\boldsymbol{\mu}}/\partial Q$ term, we need first of all an expression for $\tilde{\boldsymbol{\mu}}$, which we recall is the dipole moment arising from the molecule-induced dielectric polarization. In the PCM framework this polarization is represented by mean of an apparent charge distribution on the cavity surface. In the computational practice this continuous distribution is discretized by point charges $\mathbf{q}$, each associated with a small portion (tessera) of the cavity surface and defined through a set of linear equations.

In the following we will exploit two different implementations of the PCM method: the original method called D-PCM[21] and the recent IEF−PCM[15] revised version. In the D-PCM the set of charges $\mathbf{q}$ is obtained in terms of the normal component of the solute electric field to the cavity surface. Within the IEF−PCM, in the case of an isotropic dielectric medium, the charges are computed from the potential generated from the solute charge distribution as follows[15d]

$$\mathbf{q} = -\mathbf{Q}\mathbf{v} \qquad (10)$$

where $\mathbf{v}$ is a column vector containing the solute potential, and $\mathbf{Q}$ is a square matrix with dimension equal to the number of tesserae, whose elements depend on geometrical cavity parameters and on the dielectric constant.

The D-PCM and the IEF−PCM are formally and physically equivalent, and the use of either is a matter of computational convenience and straightforwardness in the theoretical formulation.[22] The expression of $\tilde{\boldsymbol{\mu}}$ as a function of the previously mentioned apparent charges is

$$\tilde{\boldsymbol{\mu}} = \sum_j q_j \mathbf{s}_j \qquad (11)$$

In eq 11 q_j is the point charge on the j tessera, whose position is given by the vector $\mathbf{s}_j$.

To derive an expression of $\tilde{\boldsymbol{\mu}}$ as a function of the external field-induced apparent charges let us write

$$-\tilde{\boldsymbol{\mu}}\cdot\mathbf{F}^{\mathrm{M}} = \sum_j q_j V^{\mathrm{M}}(\mathbf{s}_j) \tag{12}$$

where V^{M} is the electric potential associated to the $\mathbf{F}^M$ field

$$V^{\mathrm{M}}(\mathbf{s}_j) = -\mathbf{F}^{\mathrm{M}}\cdot\mathbf{s}_j \tag{13}$$

By exploiting eq 10 and using the symmetry of the **Q** matrix the previous expression, eq 12 can be rewritten as

$$-\tilde{\boldsymbol{\mu}}\cdot\mathbf{F}^{\mathrm{M}} = -\sum_{j,l}(\mathbf{Q})_{jl}V(\mathbf{s}_l)V^{\mathrm{M}}(\mathbf{s}_j) = \sum_l V(\mathbf{s}_l)q_l^{\mathrm{M}} \tag{14}$$

where q_l^M are the external field-induced polarization charges. These charges depend linearly on the $\mathbf{F}^{\mathrm{M}}$ field, so that eq 14 can be rewritten as follows

$$-\tilde{\boldsymbol{\mu}}\cdot\mathbf{F}^{\mathrm{M}} = \left(\sum_l V(\mathbf{s}_l)\,\frac{\partial q_l^{\mathrm{M}}}{\partial \mathbf{F}^{M}}\right)\cdot\mathbf{F}^{M} \tag{15}$$

The final expression of $\tilde{\boldsymbol{\mu}}$ we were looking for is then

$$\tilde{\boldsymbol{\mu}} = -\left(\sum_l V(\mathbf{s}_l)\,\frac{\partial q_l^{\mathrm{M}}}{\partial \mathbf{F}^{\mathrm{M}}}\right) \tag{16}$$

It is worth noticing that exactly the same relation (eq 15) could have been obtained in a totally equivalent way by considering the electric field **F** acting on the molecule as a sum of the external field (which originates the $\boldsymbol{\mu}\cdot\mathbf{F}^{\mathrm{M}}$ term in eq 4) and of the field generated from the response of the solvent to the external field when the volume representing the molecular cavity has been created in the bulk of the solvent.[4] The latter field generates an interaction term in eq 4 equal to the one previously shown in eq 15.

Similarly to what is already said in the previous section, it is convenient to write $\tilde{\boldsymbol{\mu}}$ in terms of the density matrix **P** as

$$\tilde{\mu}_t = -tr[\mathbf{P}\tilde{\mathbf{m}}_t] + \tilde{\mu}_{N,t} \tag{17}$$

where $\tilde{\mu}_{N,t}$ indicates the nuclear contribution to the t component of $\tilde{\boldsymbol{\mu}}$. By defining $V_N(\mathbf{r})$ as the potential generated by the nuclei at the position **r**, we obtain

$$\tilde{\mu}_{N,t} = -\left(\sum_l V_N(\mathbf{s}_l)\,\frac{\partial q_l^{\mathrm{M}}}{\partial \mathrm{F}_t^{\mathrm{M}}}\right) \tag{18}$$

The $\tilde{\mathbf{m}}_t$ matrix in eq 17 is defined starting from the $V_{\kappa\lambda}$ potential integrals evaluated at the point $\mathbf{s}_l$ as

$$\tilde{m}_{t,\kappa\lambda} = -\left(\sum_l V_{\kappa\lambda}(\mathbf{s}_l)\,\frac{\partial q_l^{\mathrm{M}}}{\partial \mathrm{F}_t^{\mathrm{M}}}\right) \tag{19}$$

Once $\tilde{\mu}_t$ has been obtained we can finally write a relation for the first derivative of $\tilde{\boldsymbol{\mu}}$ with respect to the nuclear coordinates. By differentiating eq 17 with respect to the normal coordinate Q_i we obtain by analogy with eq 9

$$\frac{\partial\tilde{\mu}_t}{\partial Q_i} = -tr[\mathbf{P}^i\tilde{\mathbf{m}}_t + \mathbf{P}\tilde{\mathbf{m}}_t^i] + \tilde{\mu}_{N,t}^i \tag{20}$$

In this case, $\tilde{\mathbf{m}}_t^i$, the derivative of the $\tilde{\mathbf{m}}_t$ matrix with respect to Q_i, can be written as a sum of two contributions: the first one ($\tilde{\mathbf{m}}_{t,\mathrm{fix}}^i$) arises from the dependence of the basis functions (and then of the $V_{\kappa\lambda}$ potentials) on the nuclei positions and the other ($\tilde{\mathbf{m}}_{t,\mathrm{geom}}^i$) is due to the dependence of the cavity geometry (i.e., of the charge positions q_l^{M}) on the nuclear geometry.[3] The expression of the first term, $\tilde{\mathbf{m}}_{t,\mathrm{fix}}^i$, is

$$(\tilde{m}_{t,\kappa\lambda}^i)_{\mathrm{fix}} = -\sum_l\left(\frac{\partial V_{\kappa\lambda}(\mathbf{s}_l)}{\partial Q_i}\right)\frac{\partial q_l^{\mathrm{M}}}{\partial F_t^{\mathrm{M}}} \tag{21}$$

On the other hand, the expression of the $\tilde{\mathbf{m}}_{t,\mathrm{geom}}^i$ terms is

$$(\tilde{m}_{t,\kappa\lambda}^i)_{\mathrm{geom}} = -\sum_l V_{\kappa\lambda}(\mathbf{s}_l)\left[\frac{\partial}{\partial Q_i}\left(\frac{\partial q_l^{\mathrm{M}}}{\partial F_t^{\mathrm{M}}}\right)\right] \tag{22}$$

We will come back to this term in a following section.

To end this section, we remark that also the nuclear term in eq 20, $\tilde{\mu}_{N,t}^i$ can be similarly decomposed in two contributions. Their expressions are

$$(\tilde{\mu}_{N,t}^i)_{\mathrm{fix}} = -\sum_l\left(\frac{\partial V_N(\mathbf{s}_l)}{\partial Q_i}\right)\frac{\partial q_l^{\mathrm{M}}}{\partial F_t^{\mathrm{M}}} \tag{23}$$

$$(\tilde{\mu}_{N,t}^i)_{\mathrm{geom}} = -\sum_l V_N(\mathbf{s}_l)\left[\frac{\partial}{\partial Q_i}\left(\frac{\partial q_l^{\mathrm{M}}}{\partial F_t^{\mathrm{M}}}\right)\right] \tag{24}$$

2.3. Evaluation of the $\partial q_l^{\mathrm{M}}/\partial \mathbf{F}_t^{\mathrm{M}}$ Terms. The starting point to derive an expression for the $\partial q_l^{\mathrm{M}}/\partial F_t^{\mathrm{M}}$ terms (eqs 21−24) is a relation between the $\mathbf{F}^{\mathrm{M}}$ field-induced charges q_l^{M} and $\mathbf{F}^{\mathrm{M}}$ itself. Regarding this point two choices are possible: the first one is to exploit an IEF-like equation, which would connect the charges to the field through the potential. The second approach consists of using relations analogous to those used in the D-PCM method, which would directly relate the charges to the field. In the following we will present only a treatment based on the D-PCM method, which in this case is computationally convenient especially for the evaluation of the geometry-dependent terms in eqs 22 and 24. Regardless, numerical tests confirmed the substantial equivalence in the results obtained by means of both of the approaches.

The relation between the q_l^{M} charges and the $\mathbf{F}^{\mathrm{M}}$ field is

$$\mathbf{q}^{\mathrm{M}} = -\mathbf{D}^{-1}\mathbf{f}_n^{\mathrm{M}} \tag{25}$$

where $\mathbf{f}_n^{\mathrm{M}}$ is a vector collecting the normal components of the radiation electric field $\mathbf{F}^{\mathrm{M}}$ to the cavity surface and $\mathbf{D}^{-1}$ is a matrix (different from the **Q** matrix in eq 10) whose elements depend on the geometrical parameters of the cavity and on the dielectric constant of the medium.[21] Strictly speaking, the dielectric constant to be used should, in principle, be the one at the field frequency. Anyway, sufficiently far from frequencies that correspond to absorption bands of the solvent, it is a good approximation to use the permittivity value as measured in the field of optical frequencies (sodium D-line) ϵ_{opt}. It is in fact reasonable to assume that for values of the frequency comparable to the ones of the vibrational motions, the contribution to the dielectric constant due to the reorientation of the solvent molecules is negligible and that the electronic contribution is fairly well approximated by what is measured at optical frequencies. On the other hand, this assumption prevents us from treating pure liquids, because in that case the absorption bands of the "solvent" would coincide with those of the "solute" so that the approximation of the dielectric constant with ϵ_{opt} would not be justified.

Coming back to the evaluation of the $\partial q_l^{\text{M}}/\partial F_t^{\text{M}}$ term, the relation to use can be obtained by applying eq 25 and differentiating it with respect to F_t^{M}

$$\frac{\partial \mathbf{q}^{\text{M}}}{\partial \text{F}_t^{\text{M}}} = -\mathbf{D}^{-1}\mathbf{n}_t \qquad (26)$$

In eq 26, $\mathbf{n}_t$ indicates the vector collecting the t components of the normal versors to the cavity surface.

2.4. Evaluation of the Geometry-Dependent Terms: $\tilde{\mathbf{m}}^i_{t,\text{geom}}$, $\tilde{\boldsymbol{\mu}}^i_{t,\text{geom}}$. The evaluation of the $\tilde{\mathbf{m}}^i_{t,\text{fix}}$ and $\tilde{\mu}^i_{t,\text{fix}}$ terms (the ones independent from the geometry) has already been treated in previous works concerning the calculation of static vibrational polarizabilities and first hyperpolarizabilities for molecules in solution.[3] The geometry-dependent terms, instead, have never been treated. We will report in the following a way of analytically evaluating them.

The problem of calculating the $\tilde{\mathbf{m}}^i_{t,\text{geom}}$ and $\tilde{\mu}^i_{t,\text{geom}}$ terms concerns the evaluation of the derivatives $[\partial/\partial Q_i(\partial q_l^{\text{M}}/\partial \text{F}_t^{\text{M}})]$ (see eqs 22 and 24). To obtain a relation for the $[\partial/\partial Q_i(\partial q_l^{\text{M}}/\partial \text{F}_t^{\text{M}})]$ terms, let us derive eq 26 with respect to Q_i. The resulting formula is

$$\frac{\partial}{\partial Q_i}\left(\frac{\partial \mathbf{q}^{\text{M}}}{\partial \text{F}_t^{\text{M}}}\right) = -\left(\frac{\partial}{\partial Q_i}\mathbf{D}^{-1}\right)\mathbf{n}_t - \mathbf{D}^{-1}\left(\frac{\partial}{\partial Q_i}\mathbf{n}_t\right) \qquad (27)$$

The elements of $(\partial/\partial Q_i)\mathbf{D}^{-1}$ can be calculated from the relation

$$\frac{\partial}{\partial Q_i}\mathbf{D}^{-1} = -\mathbf{D}^{-1}\left(\frac{\partial}{\partial Q_i}\mathbf{D}\right)\mathbf{D}^{-1} \qquad (28)$$

The evaluation of $(\partial/\partial Q_i)\mathbf{D}$ requires the calculation of the derivatives of cavity geometrical parameters (such as, for example, areas and positions of the tesserae). For the explicit expressions of such derivatives and of the column vector $(\partial/\partial Q_i)\mathbf{n}_t$, we address the reader to ref 23.

3. Numerical Results and Discussion

We will report in this section data on IR intensities for various model molecules (HCHO, CH_3CHO, CH_3CH_2CHO, $(CH_3)_3CCHO$, and HC≡CCHO) in water ($\epsilon = 78.39$, $\epsilon_{\text{opt}} = 1.776$, at 298 K). All of the calculations were performed using the density functional theory (with the B3LYP hybrid functional) and the 6-31G* basis set. The use of this quite limited basis set is justified, as the scope of the present paper is the analysis of relative quantities obtained as ratios of values computed at the same level of approximation and not the evaluation of absolute values of intensities. To evaluate the quality of our results, additional calculations exploiting the 6-31+G* basis set were done.

The calculation of the $\partial\boldsymbol{\mu}/\partial Q$ terms was implemented in a development version of the GAUSSIAN package,[24] which performs also analytical second derivatives with respect to nuclear coordinates within the IEF−PCM framework. Molecular-shaped cavities were used. The cavities were defined in terms of interlocking spheres centered on the solute nuclei. The CH_3, CH_2 and CH groups were included in a single sphere. The radii of the spheres exploited in the calculations are listed in Table 1. Such values were multiplied by a cavity size factor α equal to 1.2. To evaluate the dependence of the results on the cavity size, additional calculation were performed by using $\alpha = 1.1$ and $\alpha = 1.3$. The geometrical parameters of the molecules were optimized both in vacuo and in solution.

TABLE 1: Sphere Radii Used to Build the Molecular Cavity (Å)

	CH_3	CH_2	CH	C	≡C	O	H
R	2.0	2.0	1.9	1.7	1.9	1.5	1.2

TABLE 2: Carbonyl Stretching Frequency Values for Various Solutes in Gas Phase and in Water (cm^{-1})

	gas	aq
HCHO	1850	1823
CH_3CHO	1843	1809
CH_3CH_2CHO	1838	1803
$(CH_3)_3CCHO$	1831	1799
HC≡CCHO	1776	1744

TABLE 3: Semiclassical Expressions for *f*

Hirota[8]	$f_{\text{H}} = \dfrac{(n^2+2)(2\epsilon+1)}{3(n^2+2\epsilon)}$
Buckingham[11]	$f_{\text{B}} = \dfrac{9\epsilon_{\text{opt}}}{(\epsilon_{\text{opt}}+2)(2\epsilon_{\text{opt}}+1)}\left[\dfrac{(n^2+2)(2\epsilon+1)}{3(n^2+2\epsilon)}\right]$
Mallard-Straley,[9] Person[10]	$f_{\text{MSP}} = \dfrac{1}{\sqrt{\epsilon_{\text{opt}}}}\left[\dfrac{n^2+2}{(n^2/\epsilon_{\text{opt}})+2}\right]$

We will present calculated IR intensities for the carbonyl stretching mode of the series of aldehydes mentioned above. We report in Table 2 the calculated frequencies of this vibrational mode both in vacuo and in water. As already noticed, there exist in the literature semiclassical relations between the absorption intensity in solution, A^{sol}, and in vacuo, A^{gas}. Such expressions, used to rationalize solvent effects on IR intensities (see for example refs 25 and 26) are of the type

$$\frac{A^{\text{sol}}}{A^{\text{gas}}} = f \qquad (29)$$

In eq 29, f is a numerical factor for the expression of which various relations have been proposed. Some of the most used defining statements for such factor are reported in Table 3. In such expressions, ϵ and ϵ_{opt} are the already defined static dielectric constants of the solvent and dielectric constants of the solvent at the sodium D-line: n is the refractive index of the pure solute (i.e., of the aldehyde under study). We would like to remark that rigorously speaking we should consider, rather than ϵ and ϵ_{opt}, the dielectric constant of the solution: because we will refer to infinitely dilute solutions, we can safely approximate them with the dielectric constants of the pure solvent.

It is necessary to specify that the expression for f originally proposed by Buckingham[11] contains a term that is dependent on the derivative of the molecular polarizability with respect to the normal coordinate. Unlike dielectric constants and refractive indexes, this quantity is not immediately available (theoretical calculations or Raman measurements are needed to estimate it). For this reason we will use in the following the simplified formula shown in Table 3. It is worth noticing the analogy between the Mallard-Straley, Person (MSP) equation[9,10] for solutions and the Polo−Wilson[6] for pure liquids, which reads

$$f = \frac{1}{n}\left(\frac{n^2+2}{3}\right)^2 \qquad (30)$$

The MSP equation reduces to the Polo−Wilson by considering $\sqrt{\epsilon_{\text{opt}}} = n$.

TABLE 4: PCM ($f_{\mu+\tilde{\mu}}$) and Semiclassical *f* Values (see Table 3 for the definition)

	f_H	f_B	f_{MSP}	$f_{\mu+\tilde{\mu}}$
HCHO	1.667	1.442	1.210	1.434
CH_3CHO	1.567	1.355	1.188	1.586
CH_3CH_2CHO	1.640	1.418	1.205	1.609
$(CH_3)_3CCHO$	1.673	1.447	1.212	1.791
$HC{\equiv}CCHO$				1.729

TABLE 5: $f_{\mu+\tilde{\mu}}$ as a Function of the Basis Set and of the Cavity Size Factor α

	6-31G* α = 1.2	6-31+G* α = 1.2	6-31G* α = 1.1	6-31G* α = 1.3
HCHO	1.434	1.502	1.553	1.345
CH_3CHO	1.586	1.655	1.744	1.453
CH_3CH_2CHO	1.609	1.711	1.809	1.475
$(CH_3)_3CCHO$	1.791	1.948	2.008	1.647
$HC{\equiv}CCHO$	1.729	1.861	1.936	1.585

We report in Table 4 the calculated results for the *f* factor. For the sake of comparison we also report what we obtain by exploiting the above-mentioned semiclassical approaches (see Table 3). The $f_{\mu+\tilde{\mu}}$ factor in Table 4 is defined from $A^{sol}_{\mu+\tilde{\mu}}$ (as obtained by using eq 6) and A^{gas} (defined by mean of eq 3), as

$$f_{\mu+\tilde{\mu}} = \frac{A^{sol}_{\mu+\tilde{\mu}}}{A^{gas}} \tag{31}$$

where $f_{\mu+\tilde{\mu}}$ takes into account both the effects on the IR intensity arising from the dielectric polarization (as caused by the molecule) and the so-called "cavity effects" (connected to $\partial\tilde{\boldsymbol{\mu}}/\partial Q$).

The data reported in Table 4 deserve some comments. First, it is evident that our calculated results are generally different from what was obtained by means of semiclassical relations. The difference not only concerns values for the same compound, but there is also a discrepancy in the observed trend in passing from one species to another. It is clear, for example, that the minimum value of *f* calculated by means of semiclassical approaches is the value for CH_3CHO. The minimum value for *f* in our formulation is instead shown by HCHO. We can also see that the greatest difference between our and semiclassical data is shown by the results calculated by exploiting the MSP equation: these data are in fact the lowest in the series. In our opinion this is reasonable; in fact, the dependence on ϵ, which is explicitly considered in our approach as well as in Hirota's and Buckingham's equations, is not present in f_{MSP} (we recall that in our formulation this dependence is explicit in the calculation of the $\partial\boldsymbol{\mu}/\partial Q$ terms).

In Table 5 we report the calculated results for the $f_{\mu+\tilde{\mu}}$ factor as obtained by using the larger 6-31+G* basis set and different values of the α cavity size factor. The differences in the results are less than 10% as a function of both the basis set and the cavity size.

It is useful to evaluate the contribution to the solvent effect on IR intensities due only to the "cavity" term, which, as already said before, is connected to the derivative $\partial\tilde{\boldsymbol{\mu}}/\partial Q$. To extract such contribution we will define $f_{\tilde{\mu}}$ as

$$f_{\tilde{\mu}} = \frac{A^{sol}_{\mu+\tilde{\mu}}}{A^{sol}_{\mu}} \tag{32}$$

In eq 32 A^{sol}_{μ} is obtained from eq 6 by neglecting the $\partial\tilde{\boldsymbol{\mu}}/\partial Q$ term.

TABLE 6: Classical (f_{Ons}) and PCM ($f_{\tilde{\mu}}$) Cavity Field Factors (see text)

	f_{Ons}	$f_{\tilde{\mu}}$
HCHO	1.370	1.287
CH_3CHO		1.257
CH_3CH_2CHO		1.250
$(CH_3)_3CCHO$		1.285
$HC{\equiv}CCHO$		1.235

TABLE 7: $f_{\tilde{\mu}}$ as a Function of the Cavity Size Factor α

	α = 1.1	α = 1.2	α = 1.3
HCHO	1.281	1.287	1.305
CH_3CHO	1.243	1.257	1.271
CH_3CH_2CHO	1.235	1.250	1.264
$(CH_3)_3CCHO$	1.269	1.285	1.290
$HC{\equiv}CCHO$	1.221	1.235	1.251

TABLE 8: Calculated IR Intensities (km/mol)[a]

	$A_{\mu+\tilde{\mu}}$	$(A_{\mu+\tilde{\mu}})_{fix}$
HCHO	142	145
CH_3CHO	249	248
CH_3CH_2CHO	241	242
$(CH_3)_3CCHO$	292	295
$HC{\equiv}CCHO$	306	301

[a] $A_{\mu+\tilde{\mu}}$ includes geometrical terms, $(A_{\mu+\tilde{\mu}})_{fix}$ neglects them. For the definition, see text

TABLE 9: $A_{\mu+\tilde{\mu}}$ (km/mol) as a Function of the Cavity Size Factor α

	α = 1.1	α = 1.2	α = 1.3
HCHO	154	142	133
CH_3CHO	276	249	230
CH_3CH_2CHO	270	241	220
$(CH_3)_3CCHO$	325	292	266
$HC{\equiv}CCHO$	343	306	281

This quantity can be reasonably compared with the classical parameter f_{Ons} deriving from Onsager's theory of dielectric polarization, which states for a spherical cavity that

$$f_{Ons} = \left(\frac{3\epsilon_{opt}}{2\epsilon_{opt} + 1}\right)^2 \tag{33}$$

The data reported in Table 6 show that f_{Ons} is a fairly good approximation of our result when the molecular cavity we are using is almost spherical (i.e., in the case of HCHO and $(CH_3)_3CCHO$). In the other cases the difference is larger. The maximum deviation occurs for $HC{\equiv}CCHO$, whose molecular cavity, more or less of a cylindrical shape, is badly approximated by a sphere.

The results reported in Table 7 show that only small differences (of the order of 1%) arise as a result of the change in the cavity size.

To end this section it is worth evaluating the weight of the $\tilde{\mathbf{m}}^{i}_{t,\mathrm{geom}}$, $\tilde{\mu}^{i}_{t,\mathrm{geom}}$ terms, which, as already said in the theoretical section, depend on the variation of the cavity geometry as a result of molecular vibration. We report in Table 8 the intensity values obtained by including these terms, $A^{sol}_{\mu+\tilde{\mu}}$, and by neglecting them, $(A^{sol}_{\mu+\tilde{\mu}})_{fix}$. As it is clearly shown, the account of geometrical terms is not crucial in the calculations. For this reason, as already pointed out by Cammi et al. as regards the calculation of effective vibrational polarizabilities,[3] they can be neglected: this will require less computational effort. The behavior of the $A^{sol}_{\mu+\tilde{\mu}}$ values as a function of the cavity size is finally reported in Table 9.

4. Conclusions

We have given and justified algorithms for the calculation of IR intensities for solutes in infinite dilute solutions, on the basis of physical models more detailed than the ones previously used. These algorithms have been implemented in a molecular calculation package of great diffusion and versatility.

The present work is a part of a larger research program under development in our group addressed to put in evidence merits and limitations of the continuum model in the description of molecular properties in solution. To coherently develop this program, the models to be used for the properties have to be accurately elaborated, with the aim of eliminating, as much as possible, any inaccuracy not strictly related to the model. With this scope we will list below some limitations of the present implementation that we will overtake in the future.

(1) The model has been developed within the harmonic approximation. The PCM approach is suitable for describing electric and mechanical anharmonic effects on IR intensities, but our experience is thus far limited to old versions of the PCM.[16]

(2) The model assumes an equilibrium response of the solvent to vibrations. The description of dynamic effects is under study and will be the subject of future communications.[27]

(3) The model does not account for solvent fluctuation effects, which could, in principle, influence the band shape. Our intention is to resume approaches partially developed in the past.[28]

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