Theoretical Approach to the Calculation of Vibrational Raman Spectra in Solution within the Polarizable Continuum Model

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Received: March 22, 2001; In Final Form: July 2, 2001

A methodology for the theoretical evaluation of vibrational Raman scattering intensities for molecules in solution in the polarizable continuum model (PCM) framework is presented. Raman intensities are expressed in terms of derivatives of the dynamic effective polarizability with respect to nuclear coordinates. Local field effects are included by considering both the solvent polarization induced by the probing field (cavity field) and the solvent reaction field. The dependence of computed Raman intensities on the parameters of the calculation (basis set, exchange-correlation functional for DFT calculations, and cavity size) is discussed. A comparison between PCM and semiclassical values for simple molecules in various solvents is made.

1. Introduction

Infrared (IR) and Raman spectroscopies are nowadays widely used as standard tools for structural characterization. The application of these techniques to complex systems is greatly assisted by quantum-chemical calculations, which permit the evaluation of normal-mode frequencies and band intensities. Because IR and Raman spectra are often measured in condensed phase, the availability of theoretical methodologies for the account of environmental factors permits the prediction of vibrational spectra which are of help in elucidating the structure of solvated systems.

With regard to IR spectra, environmental factors may affect frequencies and intensities as well as the band shape. Various theoretical approaches have been proposed for the treatment of solvent effects on frequencies and intensities; an overview of such models can be found in a recent paper of our group.[1] Passing to Raman spectra, the medium effect on frequencies can be treated, as a first approximation, by using the same methodologies as in the case of IR spectra.

The calculation of Raman intensities for isolated molecules is usually done by exploiting Placzek's approach:[2] within the Born−Oppenheimer approximation, by assuming the electronic ground-state being nondegenerate and the exciting frequency being very much less than any electronic frequency of the molecule, Raman intensities can be expressed in terms of dynamic polarizability derivatives with respect to nuclear coordinates.

Theoretical modeling of solvent effects on Raman intensities has been a matter of study for many years.[3−6] The various formulations are based on the consideration that when the light interacts with a molecule in condensed phase the "local field" that is experienced by the molecule is different from the Maxwell field in the medium. The local field can be separated in two terms. The first one, the "reaction field", is connected with the response (polarization) of the medium to the molecule charge distribution. The second term (the "cavity field") depends on the polarization of the medium induced by the externally applied electric field, once the cavity, which hosts the molecule, has been created. Local field effects are also important in the study of other properties, such as linear and nonlinear optical properties[7−10] and infrared intensities.[11]

The need for a local field correction in Raman spectra was first suggested by Woodward and George,[12] who, however, made no attempt to present a quantitative expression for the magnitude of the effect. Starting from Onsager's theory of dielectric polarization,[13] Pivovarov derived an expression for the ratio between polarizability derivatives (and then Raman intensities) in solution and in vacuo.[4] On the other hand, Rea[3] assumed that the local field factor which had been derived for IR spectra[14−17] could also be applied to Raman spectroscopy. The assumption of Rea was questioned by Nestor and Lippincott,[18] who noted the fundamental differences between absorption and scattering processes. Still starting from the Onsager's theory, Mirone et al.[5,19] proposed a relation for the ratio between Raman intensities in solution and in vacuo. If it is applied to pure liquids, such expression reduces to the one proposed by Eckhardt and Wagner.[6] All of the mentioned models are based on a continuum description of the solvent and approximate the solute as a classical polarizable dipole placed in a spherical cavity.

Still exploiting a solvent continuum model, in more recent years, Wong et al.[20] formulated an ab initio self-consistent reaction field Onsager model (SCRF−Onsager), which uses a spherical cavity and a dipole-originated reaction field, for the calculation of static polarizability derivatives; such a model assumes that the solvent polarization is always equilibrated to the momentary solute charge distribution.

Static polarizability derivatives can be used to evaluate approximate Raman intensities (static Raman intensities); the SCRF−Onsager model has been used by Suhai and co-workers for the calculation of Raman spectra of biological molecules.[21]

In this paper, we will show how the ab initio calculation of Raman intensities for molecules in solution can be treated within

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10.1021/jp011079c CCC: $20.00

the polarizable continuum model (PCM).[22,23] 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 described by means of its electronic wave function and is housed in a molecular-shaped cavity; the electrostatic solute–solvent interaction (including also self-polarization effects) is calculated by introducing an apparent surface charge (ASC) distribution spread on the cavity surface. The differences between PCM and the SCRF–Onsager model are 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, because of the versatility of the PCM method, our approach 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).[24]

Similarly to what is done for isolated molecules, Raman intensities in solution can be related to geometric derivatives of the dynamic polarizability. For molecules in solution, the proper quantity to be used is an effective dynamic polarizability, which takes into account local field effects.

In a Raman scattering process (we neglect for the moment medium effects), the dynamic aspects of the process are to be described in terms of two time scales, one connected to the vibrational motions of the nuclei and the other to the oscillation of the incoming electric field (which gives origin to oscillations in the solute electronic density). In the presence of a solvent medium, both of the mentioned time scales originate nonequilibrium effects in the solvent response, being much faster than the time scale of the solvent inertial response.

The frequencies associated to nuclear vibrations lie in the infrared range, whereas those of the probing field (and then of the electronic density oscillation) usually lie in the visible range. Therefore, the modeling of the solvent response should be suitably tailored to the aspect of the Raman process to describe. In particular, in the case of the field-induced oscillation, we will consider a dynamic (nonequilibrium) response of the solvent, which will be described in terms of the optical dielectric constant ϵ_{opt}. With regard to vibrational motions, we will assume the solvent to be always equilibrated to the molecular charge distribution of the unperturbed momentary nuclear configuration. This means that we will not consider nonequilibrium effects on molecular vibrations. We note however that these effects seem to be important in the evaluation of infrared absorption intensities of molecules in solution;[1] we will postpone the study of similar effects on Raman spectra to further communications.

Notice that also the alteration of light collection geometry in the experimental apparatus, because of the refraction at the liquid–cell–air interfaces, affects Raman intensities.[3,12,18] We will not treat this effect, which is obviously dependent on the particular experimental apparatus used.

In the following sections, we will show how Raman intensities for molecules in solution can be computed from suitable effective dynamic polarizability derivatives and how such quantities can be defined within the PCM framework. We will then apply the procedure to the evaluation of solvent effects on Raman intensities of few simple molecules. To the best of our knowledge, the results we will present are the first example of calculation of dynamic Raman intensities in solution.

2. Theory

The radiant intensity $I^{\mathrm{sc}}(\mathbf{k})$ of the vibrational Raman scattering along the direction of the wave vector $\mathbf{k}$ is, for isolated molecules

$$I^{\mathrm{sc}}(\mathbf{k}) = Ik^4\left|\sum_{r\neq 0}\frac{\langle m|\boldsymbol{\mu}\cdot\mathbf{e}|r\rangle\langle r|\boldsymbol{\mu}\cdot\mathbf{e}'|0\rangle}{\hbar(\omega_{r0}-\omega)} + \frac{\langle m|\boldsymbol{\mu}\cdot\mathbf{e}'|r\rangle\langle r|\boldsymbol{\mu}\cdot\mathbf{e}|0\rangle}{\hbar(\omega_{r0}+\omega)}\right|^2 \tag{1}$$

where I is the intensity of the incident radiation, $\boldsymbol{\mu}$ is the dipole moment operator, and $\mathbf{e}$ and $\mathbf{e}'$ are the unit vectors of the scattered and incident radiation electric field. $\hbar\omega_{r0}$ is the energy difference between the vibronic states r and 0 (the ground state), and ω is the frequency of the incident radiation. Equation 1 implicitly assumes that only the ground state is populated and for this reason it can describe only the Stokes scattering.

In the Born–Oppenheimer approximation, each state $|r\rangle$ can be factorized into an electronic and a nuclear part. In particular, we will assume that the final state $|m\rangle$ is the product of the ground electronic state and an excited vibrational state.

Following a well-know procedure (see, for example, refs 2 and 25–29), for the nonresonant Raman scattering of a randomly oriented ensemble within the double harmonic approximation, it is possible to obtain an expression of $I^{\mathrm{sc}}(\mathbf{k})$ as a function of derivatives of the frequency-dependent electronic polarizability with respect to normal modes Q_{i}:

$$I^{\mathrm{sc}}(\mathbf{k}) = \frac{h}{4\pi\omega_{10}}Ik^4\frac{S}{45} \tag{2}$$

where $\hbar\omega_{10}$ is the energy difference between the first and the ground vibrational states. If the scattered radiation is collected perpendicularly to the linearly polarized incident radiation, the scattering factor S is defined as

$$S = 45\alpha'^2 + 7\gamma'^2 \tag{3}$$

In eq 3, α' is the derivative of the isotropic part of the polarizability with respect to Q_{i}:

$$\alpha' = \frac{1}{3}\frac{\partial}{\partial Q_{\mathrm{i}}}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{4}$$

and γ'^2 has the following expression:

$$\gamma'^2 = \frac{1}{2}\left\{\left(\frac{\partial\alpha_{xx}}{\partial Q_{\mathrm{i}}} - \frac{\partial\alpha_{yy}}{\partial Q_{\mathrm{i}}}\right)^2 + \left(\frac{\partial\alpha_{yy}}{\partial Q_{\mathrm{i}}} - \frac{\partial\alpha_{zz}}{\partial Q_{\mathrm{i}}}\right)^2 + \left(\frac{\partial\alpha_{zz}}{\partial Q_{\mathrm{i}}} - \frac{\partial\alpha_{xx}}{\partial Q_{\mathrm{i}}}\right)^2 + 6\left[\left(\frac{\partial\alpha_{xy}}{\partial Q_{\mathrm{i}}}\right)^2 + \left(\frac{\partial\alpha_{yz}}{\partial Q_{\mathrm{i}}}\right)^2 + \left(\frac{\partial\alpha_{zx}}{\partial Q_{\mathrm{i}}}\right)^2\right]\right\} \tag{5}$$

The α_{ij} terms are the elements of the polarizability tensor evaluated at frequency $\omega = kc$.

To treat molecules in solution, we have to reconsider the approximation on which eq 1 is based. This equation can be obtained by using a second-order perturbation theory in the dipolar approximation, which assumes the perturbation to be written as $-\boldsymbol{\mu}\cdot\mathbf{F}$, where $\mathbf{F}$ is the radiation electric field. Passing to molecules in solution, the radiation field $\mathbf{F}$ has to be replaced with the Maxwell electric field of the radiation in the medium, $\mathbf{F}^{\mathrm{M}}$, and the dipole moment $\boldsymbol{\mu}$ with a quantity equivalent to the so-called external dielectric moment in the Onsager approach.[5,13] The perturbation can thus be expressed as $-(\boldsymbol{\mu} + \tilde{\boldsymbol{\mu}})\cdot\mathbf{F}^{\mathrm{M}}$ where $\boldsymbol{\mu}$ is the molecular dipole moment and $\tilde{\boldsymbol{\mu}}$ is the dipole moment arising from the polarization induced by the molecule on the dielectric. A similar procedure has been exploited by our group for the evaluation of infrared absorption intensities in solution.[11]

The analogue of eq 1 for the intensity of the vibrational Raman scattering in solution, $I^{\mathrm{sc}}_{\mathrm{sol}}(\mathbf{k})$, is then

$$I^{\mathrm{sc}}_{\mathrm{sol}}(\mathbf{k}) = Ik^4 \left| \sum_{r\neq 0} \frac{\langle m|(\boldsymbol{\mu}+\tilde{\boldsymbol{\mu}})\cdot\mathbf{e}^{\mathrm{M}}|r\rangle\langle r|(\boldsymbol{\mu}+\tilde{\boldsymbol{\mu}})\cdot\mathbf{e}'^{\mathrm{M}}|0\rangle}{\hbar(\omega_{r0}-\omega)} + \frac{\langle m|(\boldsymbol{\mu}+\tilde{\boldsymbol{\mu}})\cdot\mathbf{e}'^{\mathrm{M}}|r\rangle\langle r|(\boldsymbol{\mu}+\tilde{\boldsymbol{\mu}})\cdot\mathbf{e}^{\mathrm{M}}|0\rangle}{\hbar(\omega_{r0}+\omega)} \right|^2 \quad (6)$$

Starting from eq 6, we obtain the scattering factor in solution, S_{sol}:

$$S_{\mathrm{sol}} = 45\alpha'^2_{\mathrm{sol}} + 7\gamma'^2_{\mathrm{sol}} \quad (7)$$

where

$$\alpha'_{\mathrm{sol}} = \frac{1}{3}\frac{\partial}{\partial Q_{\mathrm{i}}}(\alpha^*_{xx} + \alpha^*_{yy} + \alpha^*_{zz}) \quad (8)$$

$$\gamma'^2_{\mathrm{sol}} = \frac{1}{2}\left\{\left(\frac{\partial\alpha^*_{xx}}{\partial Q_{\mathrm{i}}} - \frac{\partial\alpha^*_{yy}}{\partial Q_{\mathrm{i}}}\right)^2 + \left(\frac{\partial\alpha^*_{yy}}{\partial Q_{\mathrm{i}}} - \frac{\partial\alpha^*_{zz}}{\partial Q_{\mathrm{i}}}\right)^2 + \left(\frac{\partial\alpha^*_{zz}}{\partial Q_{\mathrm{i}}} - \frac{\partial\alpha^*_{xx}}{\partial Q_{\mathrm{i}}}\right)^2 + 6\left[\left(\frac{\partial\alpha^*_{xy}}{\partial Q_{\mathrm{i}}}\right)^2 + \left(\frac{\partial\alpha^*_{yz}}{\partial Q_{\mathrm{i}}}\right)^2 + \left(\frac{\partial\alpha^*_{zx}}{\partial Q_{\mathrm{i}}}\right)^2\right]\right\} \quad (9)$$

The α^* quantity that appears in eqs 8 and 9 is the dynamic generalization of the polarizability defined in eq 32 of ref 10. α^* can be expressed as

$$\alpha^*_{\alpha\beta}(-\omega;\omega) = -tr[(\mathbf{m}_\alpha + \tilde{\mathbf{m}}_\alpha(\omega))\mathbf{P}^\beta(\omega)] \quad (10)$$

where $\mathbf{m}_\alpha$ collects the integrals of the αth Cartesian component of the dipole moment operator. α^* is calculated at the HF or DFT level through $\mathbf{P}^\beta(\omega)$, i.e., the density matrix derivative with respect to the β field coordinate.

The $\tilde{\mathbf{m}}_\alpha(\omega)$ matrix represents the operator associated to the dipole moment $\tilde{\boldsymbol{\mu}}$, previously discussed. Within the PCM, it is possible to express $\tilde{\mathbf{m}}_\alpha(\omega)$ in terms of an apparent charge distribution spread on the cavity surface.[11] In practice, this continuous distribution is discretized by point charges q^{M}_l, each associated with a small portion (tessera) of the cavity surface and placed at $\mathbf{s}_l$. The expression of $\tilde{\mathbf{m}}_\alpha(\omega)$ as a function of these charges is

$$\tilde{\mathrm{m}}_{\alpha,\kappa\lambda}(\omega) = -\left(\sum_l V_{\kappa\lambda}(\mathbf{s}_l)\frac{\partial q^{\mathrm{M}}_l}{\partial F^{\mathrm{M}}_\alpha}\right) \quad (11)$$

$V_{\kappa\lambda}(\mathbf{s}_l)$ are the potential integrals evaluated at $\mathbf{s}_l$, and the q^{M}_l charges represent the component of the solvent polarization that is induced by the external field $\mathbf{F}^{\mathrm{M}}$ oscillating at the frequency ω. We note that α^* is computed by considering both the solvent response to the molecular charge distribution (the reaction field) and the cavity field, i.e., the solvent response to the external electric field once the cavity has been created.

$\mathbf{P}^\beta(\omega)$ is the first-order density matrix derivative with respect to the βth component of the external electric field $\mathbf{F}^{\mathrm{M}}$. Limiting ourselves to a one-determinant wave function with orbital expansion over a finite basis set, $\mathbf{P}^\beta(\omega)$ can be calculated by solving the time-dependent Hartree−Fock (TDHF) or time-dependent Kohn−Sham (TDKS) equation:

$$\mathbf{F}'\mathbf{C} - i\frac{\partial}{\partial t}\mathbf{SC} = \mathbf{SC}\epsilon \quad (12)$$

TABLE 1: Static ϵ_0 and Optical ϵ_{opt} (λ = 589.3 nm) Dielectric Constants of the Solvents Used

	ϵ_0	ϵ_{opt}
carbon tetrachloride (T = 298 K)	2.228	2.129
carbon disulfide (T = 298 K)	2.64	2.64
acetonitrile (T = 293 K)	36.64	1.806

with the proper orthonormality condition. In eq 12, $\mathbf{S}$ represents the overlap matrix, $\mathbf{C}$ represents the matrix collecting the MO coefficients, and ϵ represents the orbital energies. The $\mathbf{F}'$ Fock matrix has the following expression:

$$\mathbf{F}' = \mathbf{h} + \mathbf{j} + \mathbf{G}(\mathbf{P}) + \mathbf{X}(\mathbf{P}) + \sum_\alpha[\mathbf{m}_\alpha + \tilde{\mathbf{m}}_\alpha(\omega)]F^{\mathrm{M}}_\alpha(\mathrm{e}^{i\omega t} + \mathrm{e}^{-i\omega t}) \quad (13)$$

and accounts for solvent-induced contributions through the $\mathbf{j}$, $\mathbf{X}(\mathbf{P})$, and $\tilde{\mathbf{m}}_\alpha(\omega)$ matrices. $\mathbf{j}$ and $\mathbf{X}(\mathbf{P})$ are related to the reaction field: their expressions can be found in ref 22b. The presence of terms dependent on $\tilde{\mathbf{m}}_\alpha(\omega)$ in eq 13 follows from the assumption that the perturbation is $-(\boldsymbol{\mu}+\tilde{\boldsymbol{\mu}})\cdot\mathbf{F}^{\mathrm{M}}$ and, as noticed in ref 11, is connected to the cavity field. As a consequence $\mathbf{P}^\beta(\omega)$ takes into account both the reaction and cavity fields. $\mathbf{P}^\beta(\omega)$ is obtained from the TDHF eq 12 by expanding all the matrices involved (in particular the $\mathbf{P}$ matrix) in powers of the field components.[30]

The extension of the methodology to the DFT level is done by substituting the bielectronic $\mathbf{G}(\mathbf{P})$ term with the sum of the Coulomb and exchange-correlation terms.

For the calculation of Raman activity in solution (eq 7), the derivatives of the α^* polarizability are needed (see eqs 8 and 9). In this paper, these quantities will be computed numerically by calculating the dynamic polarizability at a set of molecular geometries which are obtained by making small Cartesian displacements of all of the atoms from the equilibrium geometry. Notice that the derivatives of the dynamic α^* polarizability cannot be computed by using the same procedure exploited in the calculation of derivatives of the static polarizabilities, i.e., by means of numerical differentiation of the dipole derivatives with respect to the applied electric field.

3. Numerical Results and Discussion

In the following, we will show some examples of the application of the method with the aim of investigating the dependence of the results on the parameters of the calculation (basis set, functional for DFT calculations, and size of the molecular cavity). In addition, we will compare our results in various solvents for some test molecules (CCl_4, $CHCl_3$, CH_3CN, and H_2O) with what can be obtained by using the Mirone[5,19] semiclassical approach. The static and optical dielectric constants for the solvents are listed in Table 1. The IEF version of PCM[31,32] was used for all of the calculations in solution. The calculations both in vacuo and in solution were performed by using a development version of the Gaussian package.[33]

All Raman scattering factors we will report are obtained in the harmonic approximation by numerically differentiating dynamic polarizabilities. The data reported in the tables were calculated by making for all of the atoms Cartesian displacements of 0.0010 Å from the equilibrium geometry. To check the validity of the results, we have repeated the calculations by varying the displacements in the range 0.0007−0.0015 Å. Raman intensities are not affected from such changes.

Raman scattering factors we will report are calculated by assuming the wavelength of the incident radiation to be 589.3 nm.

3.1. Dependence of Calculated Raman Scattering Factors in Solution on the Parameters of the Calculation. In this

TABLE 2: Radii (in Å) of the Spheres Used to Build the Cavities

	H	Cl	≡C	N	CH_3	C	O
R	1.2	2.0	1.7	1.5	2.0	1.7	1.5

TABLE 3: Effect of the Choice of the Basis Set on Absolute Raman Scattering Factors *S* (Å^4/amu) for H_2O in Various Solvents[a]

	vacuum	carbon tetrachloride	carbon disulfide	acetonitrile
6-31+G(d)	86.5	179.9 (2.08)	208.9 (2.42)	144.6 (1.67)
6-31+G(2d,p)	77.0	166.7 (2.16)	195.6 (2.54)	134.6 (1.75)
6-31+G(2d,2p)	80.5	176.9 (2.20)	212.2 (2.64)	143.2 (1.78)
6-31+G(3d,3p)	86.6	199.7 (2.31)	237.9 (2.75)	161.9 (1.87)
6-311++G(2d,2p)	90.5	190.2 (2.10)	222.2 (2.45)	150.7 (1.67)
Sadlej pVTZ	113.2	257.9 (2.28)	306.1 (2.70)	206.5 (1.82)

[a] In parentheses, $S_{\rm sol}^{\rm sc}/S_{\rm vac}^{\rm sc}$ is reported. The functional used is B3LYP, and the α cavity size factor is 1.2. The data are related to the O−H symmetric stretch.

section, we will discuss the dependence of calculated Raman scattering factors on the parameters of the calculation. We will use H_2O as test molecule, and we will describe it at the DFT level (by using the widely employed B3LYP exchange-correlation hybrid functional). For the calculations in solution, the H_2O molecule is buried into a cavity of molecular shape and built by interlocking spheres. The radii of the spheres are obtained by multiplying the values listed in Table 2 by the $\alpha = 1.2$ cavity size factor. The geometry of the solute is optimized in each solvent.

First let us investigate the dependence of the results on the choice of the basis set. With regard to this problem, a comprehensive study has been done by Halls and Schlegel[34] for the calculation of static Raman intensities (i.e., intensities calculated by means of the derivatives of the static polarizability) for molecules in gas phase. Among the basis sets used in the cited paper, we have chosen the 6-31+G(d), 6-31+G(2d,p), 6-31+G(2d,2p), and 6-31+G(3d,3p). This choice permits to put in evidence the effects on the calculation because of the addition of polarization functions. In addition, still following Halls and Schlegel, we have used the medium sized Sadlej's pVTZ, which is fitted to reproduce molecular polarizabilities[35] and which performs similarly to the aug-cc-pVTZ basis in reproducing experimental Raman intensities in gas phase, but it is less demanding from the computational point of view. A further test was also done with the 6-311++G(2d,2p) basis set, which has been proposed in refs 36 and 37 for the calculation of vibrational frequencies of water.

We report in Table 3 the Raman scattering factors of the symmetric O−H stretching mode evaluated by using the different basis sets (functional: B3LYP). The differences between the absolute values obtained for the first five sets in Table 3 are within 20%. On the contrary, the absolute results obtained by using the Sadlej's set are noticeably greater.

To focus on solvent effect on molecular properties, it is convenient to switch the attention from absolute to relative values. In the case of Raman intensities, it is convenient to consider the $S_{\rm sol}^{\rm sc}/S_{\rm vac}^{\rm sc}$ ratio, whose values are reported in Table 3. In this case, the differences are within 10%, and the ratios calculated with the Sadlej's set are similar to the others. Thus, the differences between absolute $S_{\rm sol}^{\rm sc}$ obtained with the Sadlej's set and the others are not due to a large dependency of the solvent effects on the basis but can be addressed, similarly to in vacuo values, to an intrinsic dependence of this quantity on the basis set.

TABLE 4: Effect of the Choice of the Functional on Absolute Raman Scattering Factors *S* (Å^4/amu) for H_2O in Various Solvents[a]

	vacuum	carbon tetrachloride	carbon disulfide	acetonitrile
B3LYP	86.5	179.9 (2.08)	208.9 (2.42)	144.6 (1.67)
PBE0	82.3	170.5 (2.07)	198.2 (2.41)	136.8 (1.66)
PBE	86.5	182.6 (2.11)	212.8 (2.46)	147.9 (1.71)

[a] In parentheses, $S_{\rm sol}^{\rm sc}/S_{\rm vac}^{\rm sc}$ is reported. The basis set used is 6-31+G(d), and the α cavity size factor is 1.2. The data are related to the O−H symmetric stretch.

TABLE 5: Effect of the Cavity Size on Absolute Raman Scattering Factors *S* (Å^4/amu) for H_2O in Various Solvents[a]

	carbon tetrachloride	carbon disulfide	acetonitrile
$\alpha = 1.2$	179.9	208.9	144.6
$\alpha = 1.1$	179.8	208.7	141.6
$\alpha = 1.3$	181.0	210.0	152.4
ref 44	181.0		

[a] Calculated B3LYP/6-31+G(d) values. The data are related to the O−H symmetric stretch.

Passing to investigate the dependence of the results on the choice of the exchange-correlation functional for the DFT calculation, it is well-known that hybrid functionals give good estimates for dynamic polarizabilities in gas phase[38] and a good description of molecular vibrations:[1,39,40] as a consequence Raman intensities should be accurately predicted. Among the different hybrid functionals, following Van Caillie and Amos,[41] besides the B3LYP, we have chosen the PBE0 functional specifically tailored for the calculation of molecular polarizabilities.[42] As a further test, we have used the generalized gradient approximation (GGA) functional PBE,[43] from which the PBE0 is derived. The data reported in Table 4 [basis set: 6-31+G(d)] show small differences both in the absolute scattering factors and in the $S_{\rm sol}^{\rm sc}/S_{\rm vac}^{\rm sc}$ ratios. The observed trends in passing from a solvent to another are unaffected.

Let us investigate now the parameters specific for the calculations in solution. Actually, the molecular cavity size is the only adjustable parameter in the PCM description of the solvent. Therefore, it is of interest to estimate how it affects calculated intensities. In Table 5, we report Raman scattering factors obtained by varying the α cavity size factor from 1.1 to 1.3. Small variations (less than 10%) can be noted. We have also performed a test by using the cavity proposed by Luque et al. for the calculation of solvation energies in carbon tetrachloride,[44] which is built similarly to the PCM one but by using a radius of 1.45 Å for the oxygen sphere, a radius of 0.9 Å for the hydrogen sphere, and a α cavity size factor of 1.8. As it can be seen from Table 5, the value is very similar to the standard PCM one.

From the analysis proposed above, it can be noted that the parameter which mostly affects calculated data is the choice of the basis set. Because Raman intensities are calculated from the derivatives of the polarizability with respect to nuclear coordinates, it is of interest to compare the dependence of polarizabilities on the basis set with that of Raman intensities. We report in Table 6 calculated isotropic dynamic polarizabilities with the previously used basis sets. The differences in the absolute values are similar to the ones found for Raman intensities. Lower discrepancies (around 3%) in the ratio between values in solution and in vacuo are present (compare Table 6 with Table 3).

TABLE 6: Effect of the Choice of the Basis Set on Isotropic Dynamic ($\lambda = 589.3$ nm) Polarizabilities (Å^3) for H_2O in Various Solvents (Functional: B3LYP; $\alpha = 1.2$)[a]

	vacuum	carbon tetrachloride	carbon disulfide	acetonitrile
6-31+G(d)	1.050	1.308 (1.246)	1.368 (1.303)	1.249 (1.190)
6-31+G(2d,p)	1.189	1.508 (1.268)	1.583 (1.331)	1.434 (1.206)
6-31+G(2d,2p)	1.205	1.531 (1.271)	1.618 (1.343)	1.455 (1.207)
6-31+G(3d,3p)	1.388	1.784 (1.285)	1.878 (1.353)	1.695 (1.221)
6-311++G(2d,2p)	1.268	1.604 (1.265)	1.683 (1.327)	1.518 (1.197)
Sadlej pVTZ	1.526	1.945 (1.275)	2.044 (1.339)	1.845 (1.209)

[a] In parentheses, the ratio between the polarizability in solution and in vacuo is reported.

TABLE 7: B3LYP/6-31+G(d) Calculated Raman Scattering Factors *S* (Å^4/amu) of Various Solutes (CCl_4, $CHCl_3$, CH_3CN, and H_2O) in Vacuo and in Different Solvents[a]

	CCl_4	$CHCl_3$	CH_3CN	H_2O
$\bar{\nu}$ (cm^{-1})	459[b]	667[b]	2249[b]	3280[c]
vacuum	25.5	13.9	81.7	86.5
carbon tetrachloride	58.3	33.2	184.8	179.9
carbon disulfide	64.2	38.0	224.1	208.9
acetonitrile	54.3	27.3	176.8	144.6

[a] $\bar{\nu}$ is the experimental vibrational frequency (for the pure liquid) of the normal mode under examination. [b] Reference 19. [c] Reference 51.

3.2. Comparison between PCM and Semiclassical Raman Intensities. In Table 7, we report calculated Raman scattering factors in various solvent for selected vibrational modes of CCl_4, $CHCl_3$, CH_3CN, and H_2O (the radii of the spheres used to generate the molecular cavity are reported in Table 2). For pure liquids, the vibrational frequencies of the "solvent" coincide with those of the "solute", and thus the behavior of the dielectric constant of the solvent at the solute vibrational frequency is typical of the resonant regions. In our model, this problem is neglected because the solvent response to the solute vibration is calculated by means of the static dielectric constant of the liquid.

As already said in the Introduction, various semiclassical theories for the evaluation of solvent effects on Raman intensities have been formulated. A common point of such theories is the derivation of an expression for the ratio:

$$f = \frac{S_{\mathrm{sol}}^{\mathrm{sc}}}{S_{\mathrm{vac}}^{\mathrm{sc}}} \tag{14}$$

Among these theories, the approach of Mirone has been the most used.[45,46] In the formulation of Mirone, the solute is simply described as a polarizable dipole placed in a spherical cavity inside a dielectric medium which models the solvent. Within this approach, the f_M factor is given by the following formula:

$$f_M = \left[\frac{3\epsilon_{\mathrm{opt}}}{(2\epsilon_{\mathrm{opt}} + 1)\left(1 - \frac{2\epsilon_{\mathrm{opt}} - 2}{2\epsilon_{\mathrm{opt}} + 1}\frac{\alpha}{r^3}\right)}\right]^4 \tag{15}$$

where α is the molecular polarizability, r is the cavity radius, and ϵ_{opt} is the optical dielectric constant of the solution. As a further assumption, the ratio α/r^3 is approximated by using the Lorenz-Lorentz formula:

$$\frac{\alpha}{r^3} = \frac{n^2 - 1}{n^2 + 2} \tag{16}$$

TABLE 8: B3LYP/6-31+G(d) f_{PCM} and f_M (see text) of Various Solutes (CCl_4, $CHCl_3$, CH_3CN, and H_2O) in Various Solvents

	CCl_4		$CHCl_3$		CH_3CN		H_2O	
	f_{PCM}	f_M	f_{PCM}	f_M	f_{PCM}	f_M	f_{PCM}	f_M
carbon tetrachloride	2.51	3.67	2.55	3.62	2.26	3.24	2.08	3.15
carbon disulfide	2.77	5.02	2.92	4.60	2.74	4.04	2.42	3.98
acetonitrile	2.34	2.88	2.10	2.85	2.16	2.61	1.67	2.57

TABLE 9: f_M and f_M^{corr} (see text) for H_2O in Various Solvents[a]

	f_{PCM}	f_M	f_M^{corr}
carbon tetrachloride	2.08	3.15	2.81
carbon disulfide	2.42	3.98	3.47
acetonitrile	1.67	2.57	2.34

[a] For the sake of comparison, also, f_{PCM} is shown.

TABLE 10: f_{PCM} for the Various Bands of H_2O in Different Solvents[a]

	f_{PCM}			f_M
	δ	ν_s	ν_{as}	all
carbon tetrachloride	1.53	2.08	1.89	3.15
carbon disulfide	1.65	2.42	2.15	3.98
acetonitrile	1.39	1.67	1.57	2.57

[a] For the sake of comparison, also, f_M is shown. δ is the HOH bending mode, ν_s is the symmetric O−H stretching mode, and ν_{as} is the asymmetric one.

where n is the refractive index of the pure liquid solute. Equation 15 then becomes

$$f_M = \left[\frac{n^2 + 2}{\frac{n^2}{\epsilon_{\mathrm{opt}}} + 2}\right]^4 \tag{17}$$

We report in Table 8 the f_M values obtained through eq 17 and the corresponding PCM values ($f_{\mathrm{PCM}} = S_{\mathrm{sol}}^{\mathrm{sc}}/S_{\mathrm{vac}}^{\mathrm{sc}}$) for selected modes of CCl_4, $CHCl_3$, CH_3CN, and H_2O. The values of f_{PCM} are quite different from those of f_M: in particular, the range of variation of our results (1.67−2.92) is smaller than the one of f_M (2.57−5.02). It is possible to ascribe such discrepancies to the different level of description of the solute and of the cavity between our model and the semiclassical one. In particular, in the case of CCl_4, the assumption of a spherical cavity is reasonable (our cavity is not so different from a sphere) and then the discrepancies are probably due to the approximation of the solute to a polarizable dipole. In the other cases, both the polarizable dipole approximation and the spherical cavity one may lead to differences in the results.

To check the extent of the Lorenz−Lorentz approximation (16), we report in Table 9 the data for f_M^{corr} that we obtain for H_2O in various solvents by replacing the α/r^3 ratio in eq 15 with the calculated data obtained by using the in vacuo molecular polarizability of H_2O and the radius of the sphere whose volume is equivalent to the PCM cavity. The differences between f_M and f_M^{corr} are of the order of 10−15%, and the overtaking of the Lorenz−Lorentz approximation makes the semiclassical values decrease, i.e., go in the direction of the PCM ones.

To end this section, we note that the f_M factor defined in eq 17 only depends on the dielectric properties of a given solute and a given solvent and is the same for all of the bands of the spectrum. Thus, the relative intensities calculated by using this model do not depend on the choice of the medium and are those

TABLE 11: Scattering Factors for the Various Bands of H_2O in Different Media Relative to the Symmetric Stretching Mode Ones[a]

	δ	ν_s	ν_{as}
vacuum	0.037	1.00	0.495
carbon tetrachloride	0.027	1.00	0.450
carbon disulfide	0.025	1.00	0.440
acetonitrile	0.031	1.00	0.464

[a] δ is the *HOH* bending mode, ν_s is the symmetric O−H stretching mode and ν_{as} is the asymmetric one.

calculated in vacuo. On the contrary, in our model, a different f_{PCM} factor is obtained for each band (see Table 10), and thus, relative scattering factors change in passing from a medium to another (see Table 11).

4. Conclusions

In this paper, we have presented a methodology for the calculation of vibrational Raman scattering intensities for solutes in infinite diluted solutions. Our method overtakes some of the assumptions on which commonly used semiclassical approaches are based, such as the polarizable dipole approximation and the use of a spherical cavity. In addition, we also consider local field effects and we properly calculate Raman intensities as derivatives of the dynamic polarizability. However, some limitations of the model have to be stressed. In particular, the model has been developed within the harmonic approximation: this prevents us for example from describing Fermi resonances and then from reproducing spectra in details. In addition, we have taken into account the solvent dynamic response to probing field-induced oscillations in the molecular electronic density, but we have neglected nonequilibrium effects due to an incomplete solvent response to solute vibrations. These effects, which can be important in the case of IR intensities,[1] are under study and will be the subject of future communications. An additional problem which can occur regards the modeling of Raman spectra for systems exhibiting strong solute−solvent specific interactions (e.g., hydrogen bond): in this case, the group of Suhai has shown that a simple SCRF−Onsager model fails in reproducing Raman intensities, whereas the inclusion of few explicit solvent molecules improves the results.[21] A similar strategy has already been used within PCM for the treatment of vibrational frequencies,[39] NMR shieldings,[47] and reaction mechanisms,[48] for which it has given good results.

The numerical procedure we have used in the calculations is quite costly. A possible way of reducing the computational effort is to exploit the symmetry of the solute;[49] studies in this direction are in progress. The bottleneck in the computations is the numerical differentiation with respect to nuclear coordinates, which has to be done because of the lack (also in vacuo) of implementations of quadratic time-dependent response theories at the DFT level, which are needed to obtain the derivatives of the dynamic polarizability.

An actual time saving could be achieved if only a part of the spectrum is of interest. In this case, displacements along the normal coordinates of only a few bands are needed.

As final remark, we note that our model does not consider any dependence of bands on transition dipole−transition dipole intermolecular coupling, which is thought to give rise to the so-called noncoincidence effect, i.e., the separation between the anisotropic and isotropic components of a Raman band in liquids.[50]

Acknowledgment. C.C. and S.C. acknowledge MURST (Ministero dell'Università e della Ricerca Scientifica e Tecnologica: "Progetto Giovani Ricercatori 2000") for financial support. R.C. acknowledges the Italian CNR (Consiglio Nazionale delle Ricerche: Progetto Finalizzato "Materiali Speciali per Tecnologie Avanzate II") and MURST (Ministero dell'Università e della Ricerca Scientifica e Tecnologica: "Cofinanziamento 99") for financial support.

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