Solvent Effects on Rotatory Strength Tensors. 1. Theory and Application of the Combined Coupled Cluster/Dielectric Continuum Model

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In this article we present the first theoretical study of solvent effects on the rotatory strength tensor. The system chosen is solvated formaldehyde for which only one tensor element is nonvanishing, and the solvent is modeled as a linear, homogeneous, and isotropic dielectric continuum. We present results using both an equilibrium and a nonequilibrium description of the solvent. Four illustrative solvents (ethyl ether, acetone, methanol, and water) are considered together with the corresponding results for formaldehyde in vacuum. We utilize the following ab initio methods: the coupled cluster model including singles and doubles (CCSD) and the coupled cluster second-order approximate singles and doubles (CC2). Furthermore, we compare the coupled cluster results with the corresponding uncorrelated self-consistent-field (SCF) results. In addition to the rotatory strength tensor we also present solvent effects on the low-lying electronic excitation energies and corresponding ordinary intensities using both the length and velocity gauges. We find that both correlation and solvent effects have a significant influence on the transition properties. The introduction of the solvent is, in some cases, found to result in a sign change of the rotatory strength tensor elements which clearly demonstrates the importance of a proper description of the solvent influence on this property.

I. Introduction

Electronic circular dichroism (CD) is defined as the difference in absorption coefficients of left and right circularly polarized radiation,[1] and the molecular response property governing the oriented CD is referred to the rotatory strength tensor.[1] Generally, the expression for the rotatory strength tensor may be derived by considering the interaction between matter and radiation using a fully retarded expression for the vector potential.[2] Assuming that the molecular dimensions are much smaller than the wavelength, the fully retarded expression for the rotatory strength may be expanded and includes, to first order, electric dipole, magnetic dipole, and electric quadrupole contributions. For samples of randomly oriented molecules the tensor must be orientationally averaged and, because the electric quadrupole contribution vanishes upon averaging,[2,3] the CD is then proportional to the scalar product of the electric and magnetic dipole transition moments.[1,4]

For an isotropic sample the individual molecules must be chiral in order to respond chiroptically. In contrast, for an oriented sample optical activity can be observed also for molecules belonging to the point group D_{2d} or one of its achiral subgroups.[5] This is due to the difference in the symmetry rules between oriented and randomly oriented situations.

Theoretical predictions of optical activity are a challenging task as both large basis sets and electronic structure methods which account for electron correlation should be used. The effects of dynamical correlation are particularly important and should be accounted for. A method which previously has been shown to predict molecular properties very accurately is the coupled cluster (CC) model.[6,7] In comparison to other correlated ab initio methods the CC model has some important advantages which motivates our choice of electronic structure model: (i) the CC method is size extensive, (ii) CC describes the dynamical correlation very accurately, and (iii) the CC method allows for a systematic increase in accuracy using a hierarchy of CC methods, CCS, CC2, CCSD, CC3,[8,9] and so forth (or SCF, MP2, CCSD, CCSD(T) if only ground state static properties are studied). We note that the CC method has been used to calculate natural chiroptical spectra for molecules in vacuum.[10,11]

Because most experiments related to optical activity are performed in condensed phases, it is imperative to develop a model capable of describing environmental effects on the rotatory strength. In this article we will focus on solvation effects. A common approach for describing a solvated system is to use classical simulations, either molecular dynamics (MD) or Monte Carlo (MC) methods.[12] Although these methods mostly perform well for bulk structural properties of electronic ground state molecules, they often fail when considering electronically excited states and properties related to electronic excited states, and hence, quantum mechanics must be employed. Historically, solvent effects on properties related to

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optical activity have been described by including local field factors (f^{ω}) into the expression for the specific property. The Lorentz local field factors[13] are of the type

$$f^{\omega} = (\epsilon(\omega) + 2)/3 = (n(\omega)^2 + 2)/3 \tag{1}$$

where $\epsilon(\omega)$ and $n(\omega)$ are the dielectric constant and the refractive index, respectively, of the solvent at the frequency ω of the external perturbation. However, the inclusion of such effective field factors only accounts for the difference in the external and microscopic (the field acting on the molecule in solution) fields and does *not* account for the direct solvent effects, related to the interactions between the solute and solvent, on the specific properties. By direct we mean the effect of changes in the electronic wave function due to the presence of the solvent. The solvent may also induce geometrical distortions in the molecules and thereby change the rotatory strengths. However, even for rigid molecules the solvent dependence on optical properties is found to vary significantly in different solvents,[14] and a method which describes the direct solvent effects on the rotatory strength is therefore crucial, in particular when theory is invoked to assign absolute configurations of chiral molecules.

A method capable of treating direct solvent effects is the supermolecular or semicontinuum approach. In this approach, the whole or a larger part of the central or solvated system is treated using quantum mechanics. We note that for nonlocal properties the supermolecular approach must be used in connection with the differential shell approach[15] which requires that basis set superposition errors (BSSE) must be considered.

However, systems containing more than a few small molecules cannot be treated with sufficient accuracy using the supermolecular approach mainly because of limitations in correlation and basis set effects. Methods which partly overcome these problems are of the mixed quantum/classical descriptions. Here, dielectric continuum models[16−28] are very useful, but they may suffer from problems related to the treatment of the cavity and the complete neglect of the solvent structure. The great advantages of the dielectric models are, however, that the coupling between the quantum and classical systems is relatively simple and, moreover, that these models are not too computationally demanding. Thus, solvent effects on molecules which may be accurately described in vacuum may in general also be described using dielectric continuum models. A dielectric continuum model capable of describing the solute with sufficient accuracy is the combined coupled cluster/dielectric continuum (CC/DC) model[29,30] which is used in this work. The main characteristics for this model are (i) the use of a spherical cavity, (ii) the multipole expansion of the solute charge distribution to any given order, and (iii) the inclusion of nonequilibrium effects.

We note that Stephens et al. have studied solvent effects on optical rotations using the polarizable continuum model[31,32] (PCM) to calculate the effective field factors,[33] and that direct solvent effects on properties related to optical activity have been considered by Mennucci et al.[34] using PCM together with density functional theory. Also, MD simulations, at different temperatures, of a chiral molecule in an achiral solvent have been reported by Fidler et al.[35,36] In their work it was demonstrated that the chiral solute molecule induces chiral solvent structures (even in the case of achiral solvent molecules) leading to observable effects on the CD spectrum. However, in the works mentioned above only the isotropic situation was considered, that is, only solvent effects on the contribution from the electric and magnetic dipole transition moments were investigated.

In this work we study the solvent effects on the lowest excitations of formaldehyde and the corresponding rotatory strength tensor consisting of both electric dipole−magnetic dipole and electric dipole−electric quadrupole contributions. Thus, this work represents the first study of solvent effects on the rotatory strength tensor appropriate for oriented molecules. Furthermore, no other methods for calculating the solvent effects on properties related to optical rotatory power using a correlated ab initio wave function have been presented. The choice of formaldehyde for this purpose may possibly seem somewhat odd since the C_{2v} ground state structure of formaldehyde is achiral, and the isotropic CD intensity vanishes identically for all excitations. However, C_{2v} is one of the achiral subgroups of D_{2d} implying that some of the elements of the rotatory strength tensor may be nonvanishing. By a judicious choice of molecular coordinate system only one distinct element of the tensor is nonzero, and the basis set, correlation, and solvent effects can therefore be studied for this single element without the added complication of the unitary transformations of the tensor elements caused by the rotation of the principal tensor axes which generally will follow changes in the computational scheme.

This article has the following structure. In section II we outline the theory for linear response functions within the CC/DC model. Furthermore, we describe the calculation of the linear and circular intensities, that is, the oscillator and rotatory strengths, respectively. Section III contains the computational details, and in section IV we present the results together with a discussion of the solvent effects. Finally, section V contains a summary.

II. Method

II.A. The Coupled Cluster Linear Response Function Formalism. To describe the response of the central part of the system, the solute molecule, we use coupled cluster response theory.[37] Thus, we consider a molecular system perturbed by a time-dependent periodic electromagnetic field. An appropriate quasienergy CC Lagrangian, $L_{\mathrm{CC}}(t)$, is constructed,[9] and as shown in detail in ref 37, we may obtain the response functions as derivatives of the time-averaged CC quasienergy $\{L(t)\}_T$, that is

$$\langle\langle \hat{X}, \hat{Y}\rangle\rangle_{\omega_y} = \frac{1}{2} C^{\pm\omega} \frac{d^2\{L_{\mathrm{CC}}(t)\}_T}{\mathrm{d}\epsilon_x(\omega_x)\,\mathrm{d}\epsilon_y(\omega_y)} \tag{2}$$

The derivative must be evaluated at zero field strengths and $\omega_x = -\omega_y$. The operator $C^{\pm\omega}$, defined as

$$C^{\pm\omega} f^{XY}(\omega_x,\omega_y) = f^{XY}(\omega_x,\omega_y) + (f^{XY}(-\omega_x, -\omega_y))^* \tag{3}$$

ensures correct symmetry of the response function, $f^{XY}(\omega_x,\omega_y)$, under complex conjugation. Substitution of the $\hat{X}$ and $\hat{Y}$ operators with special choices of operators allows for a determination of specific response properties (see section II.C.). For derivations and implementations of the vacuum CC response functions, see, for example, refs 8, 9, 37−41.

II.B. The Coupled Cluster/Dielectric Continuum Model. This section presents a brief introduction to the coupled cluster/dielectric continuum model with special attention to the capability of describing linear response properties of solvated molecules as described in detail in ref 30. In a later section (II.C.) we will relate the derived general expressions to the calculation of specific molecular properties, for example, the rotatory strength tensor.

In the DC model the molecular charge distribution $\rho(\vec{r}\,')$, which is assumed to be located inside the spherical cavity with radius a, gives rise to an electric field $\mathbf{E}(\vec{r})$ at the position $\vec{r}$

$$\mathbf{E}(\vec{r}) = -\nabla \int \mathrm{d}\vec{r}\,' \frac{\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} \tag{4}$$

This electric field induces polarization charges in the dielectric medium characterized by the polarization vector $\mathbf{P}(\vec{r})$ which, in turn, gives rise to an additional electric field at the solute molecule. Here, we assume that the polarization vector depends *linearly* on the electric field through the susceptibility, χ, as

$$\mathbf{P}(\vec{r}) = \chi \mathbf{E}(\vec{r}) \tag{5}$$

Generalization of eq 5 to include quadrupolar terms, due to the quadrupole moment of the solvent molecules, has recently been developed by Jeon and Kim.[42−44] However, for polar solvents such as water the first nonvanishing and dominating multipole moment is the dipolar term which justifies the linear approximation outlined above. When a multipole expansion of the solute charge distribution with the origin of the expansion at the center of the cavity is performed, the total energy is found to be[16,19]

$$E^{\mathrm{eq}} = E_{\mathrm{vac}} + \sum_{lm} g_l(\epsilon) \langle M_{lm}^{\dagger} \rangle \langle M_{lm} \rangle \tag{6}$$

where the symbol eq means equilibrium, that is, the charge distributions of the solute and the solvent are in equilibrium. This is a point to which we shall return later in this section when discussing the molecular response due to external time-dependent electromagnetic fields. In eq 6, the terms $\langle M_{lm} \rangle$ are the solute charge multipole moments which are expressed in terms of spherical polynomials.[16,19] The function, $g_l(\epsilon)$, is the reaction field factor which depends on the spherical cavity dimension (of radius a), the order of the multipole expansion (l), and the dielectric constant (ϵ)

$$g_l(\epsilon) = -\frac{a^{-(2l+1)}(l+1)(\epsilon - 1)}{2[l + \epsilon(l+1)]} \tag{7}$$

Concerning the quantum mechanical description of the solute molecule, the charge multipole density moments are expressed in terms of real Hermitian operators, $\hat{T}_{lm}$, which are found as linear combinations of the spherical polynomials used to define the solute charge multipole moments.

In order to derive the CC/DC model we follow refs 29 and 30 where a variational CC/DC Lagrangian is defined as

$$L_{\mathrm{CC/DC}} = L_{\mathrm{CC}}^{\mathrm{vac}} + \sum_{lm} g_l(\epsilon) \langle \Lambda | \hat{T}_{lm} | \mathrm{CC} \rangle^2 \tag{8}$$

Here, the term $L_{\mathrm{CC}}^{\mathrm{vac}}$ is the vacuum Lagrangian evaluated using the condensed phase wave function and the state $\langle \Lambda |$ is the so-called auxiliary coupled cluster state.[37] The application of the variational condition to this Lagrangian leads to the equations appropriate for optimizing the ground state for a molecule coupled to a dielectric continuum. These equations merely involve modification of the corresponding vacuum equations by the introduction of an effective one-electron solvent operator. As shown in detail in ref 30 this leads to a coupling between the $\mathbf{t}$ and $\bar{\mathbf{t}}$ equations used to define the coupled cluster and the auxiliary states, respectively, as opposed to the vacuum case where these equations are completely uncoupled. Therefore, an (macro)iterative procedure is employed to obtain a self-consistent solution of the coupled equations. On convergence, the Lagrangian in eq 8 gives the total ground state energy.

For the derivation of the linear CC/DC response function we augment[29,30] the vacuum quasienergy Lagrangian (as described in section II.A.) with the multipole expanded interaction term. Concerning the calculation of dynamically properties, the question of equilibrium versus nonequilibrium solvation must be considered, as in many cases the solvent is not in its equilibrium configuration. In the CC/DC model this problem is addressed by treating the total polarization vector as a sum of two contributions:[24,45] the optical (fast) and inertial (slow) polarization. Correspondingly, two dielectric constants must be considered: ϵ_{op} and ϵ_{st} corresponding to the optical and total polarizations, respectively. Assuming now that the optical polarization is always in equilibrium with the solute, although this is *not* the case for the inertial polarization, the appropriate energy expressions for the solute−solvent system may be derived.[30] Here, we merely mention that the appropriate nonequilibrium Lagrangian to be considered is

$$\begin{aligned} {}^{\mathrm{neq}}L_{\mathrm{CC/DC}}(t) = {} & L_{\mathrm{CC}}^{\mathrm{vac}}(t) + \sum_{lm} g_l(\epsilon_{\mathrm{op}}) \langle \tilde{\Lambda} | \hat{T}_{lm} | \widetilde{\mathrm{CC}} \rangle^2 + \\ & \sum_{lm} g_l(\epsilon_{\mathrm{st}},\epsilon_{\mathrm{op}}) [2 \langle \tilde{\Lambda} | \hat{T}_{lm} | \widetilde{\mathrm{CC}} \rangle - \langle \Lambda | \hat{T}_{lm} | \mathrm{CC} \rangle] \langle \Lambda | \hat{T}_{lm} | \mathrm{CC} \rangle \end{aligned} \tag{9}$$

where the function $g_l(\epsilon_{\mathrm{st}}, \epsilon_{\mathrm{op}})$ is defined as

$$g_l(\epsilon_{\mathrm{st}}, \epsilon_{\mathrm{op}}) = g_l(\epsilon_{\mathrm{st}}) - g_l(\epsilon_{\mathrm{op}}) \tag{10}$$

and where a tilde has been introduced in order to state the explicit time dependence of the states. In the equilibrium case the Lagrangian in eq 9 is reduced to ${}^{\mathrm{eq}}L_{\mathrm{CC/DC}}(t) = L_{CC}^{\mathrm{vac}}(t) + \sum_{lm} g_l(\epsilon) \langle \tilde{\Lambda} | \hat{T}_{lm} | \widetilde{\mathrm{CC}} \rangle^2$.

The linear response functions may now be derived by using the appropriate expression for the Lagrangian (equilibrium or nonequilibrium) combined with the method outlined in section II.A. Here, we will not consider the explicit expressions for the response functions but refer to previous work on the subject.[30]

A pole and residue analysis of the CC/DC linear response function yields expressions for excitation energies and transition properties. An approximate decoupling of the $\mathbf{t}$ and $\bar{\mathbf{t}}$ parameters in the eigenvalue equations makes the calculation of these quantities a straightforward generalization of the vacuum case. This procedure has been rationalized and employed previously.[30]

We note that the outlined method treats the optical polarization classically (employing the so-called mean field method) and thereby excludes molecular interactions due to dispersion. Direct reaction field (DRF) methods designed for the description of molecular interactions have been proposed.[46−50] These methods include directly the dispersion interactions and thereby correlate the quantum mechanical solute to the classical environment. However, the DRF approach has been questioned by Ángyán in the calculation of C_6 coefficients[51] and Thole and van Duijnen[50] pointed out as early as in 1982 that even for simple systems such as two hydrogen atoms the C_6 coefficient is in error by a factor of 2. On the basis of these observations we propose the outlined method which includes the effect of induction but excludes the dispersion contribution.

II.C. The Rotatory Strength Tensor and the Oscillator Strength. Electronic circular dichroism (CD) is defined as the difference in absorption coefficients of left and right circularly polarized radiation.[1] Assuming that the molecular dimensions are much smaller than the wavelength of the radiation, the CD for an electronic excitation from $0 \rightarrow n$ for a sample of oriented molecules is proportional to[2,3] $\mathbf{u}^{T} \cdot {}^{n}\mathbf{R} \cdot \mathbf{u}$, where $\mathbf{u}$ is the unit vector along the direction of propagation of the radiation and ${}^n\mathbf{R}$ is the rotatory strength tensor for this excitation. The ordinary scalar rotatory strength, which is appropriate for samples of randomly oriented molecules, may be obtained as the orientational average of the rotatory strength tensor[1,3]

$$ {}^nR = \frac{1}{3}\sum_{j=1}^{3} {}^nR_{jj} \qquad (11)$$

The rotatory strength tensor may be written as a sum of an electric dipole−electric quadrupole contribution (${}^n\mathbf{R}^Q$), which is related to the residues of the electric dipole−electric quadrupole polarizability, and an electric dipole−magnetic dipole contribution (${}^n\mathbf{R}^m$), which similarly is related to the residues of the electric dipole−magnetic dipole polarizability. The definition of both ${}^n\mathbf{R}^Q$ and ${}^n\mathbf{R}^m$ depends on the specific gauge. In the velocity gauge (v) and in a Cartesian coordinate basis we have[3,5]

$$ {}^nR^{Qv}_{jk} = -\frac{3}{4\omega_n}P_{jk}\sum_{l,m=1}^{3}\epsilon_{jlm}\langle 0|p_l|n\rangle\langle n|(\mathbf{pr}+\mathbf{rp})_{mk}|\,0\rangle \qquad (12)$$

$$ {}^nR^{mv}_{jk} = \frac{3}{4\omega_n}P_{jk}(\delta_{jk}\langle 0|\mathbf{p}|n\rangle\cdot\langle n|\mathbf{L}|0\rangle - \langle 0|p_k|n\rangle\langle n|L_j|0\rangle) \qquad (13)$$

whereas the corresponding expressions in the length (r) gauge become

$$ R^{nQr}_{jk} = -\frac{3\omega_n}{4}P_{jk}\sum_{l,m=1}^{3}\epsilon_{jlm}\langle 0|r_l|n\rangle\langle n|(\mathbf{rr})_{mk}|0\rangle \qquad (14)$$

$$ R^{nmr}_{jk} = -\frac{3i}{4}P_{jk}(\delta_{jk}\langle 0|\mathbf{r}|n\rangle\cdot\langle n|\mathbf{L}|0\rangle - \langle 0|r_k|n\rangle\langle n|L_j|0\rangle) \qquad (15)$$

where we have introduced the symmetrizer $P_{jk}M_{jk} = {}^1/_2(M_{jk} + M_{kj})$. In eqs 12−15 ω_n is the electronic excitation energy associated with the excited state n, 0 is the reference state (in this work the ground state), and ϵ_{jlm} is the Cartesian Levi−Civita tensor. The operators $\mathbf{r}$, $\mathbf{p}$, and $\mathbf{L}$ are the electronic position, momentum, and orbital angular momentum operators, respectively. All expressions for the rotatory strengths are given in au. Conversion to cgs units requires multiplication with $e^2\hbar a_0/m_ec$ (m_e is the mass of the electron, a_0 the Bohr radius),[11] whereas conversion to SI units may be done by multiplication with[11] $4\pi\epsilon_0\hbar^3/m_e^2$.

For the scalar rotatory strength appropriate for a sample of randomly oriented molecules we obtain, according to eq 11

$$ {}^nR^v = \frac{1}{3}\sum_{j=1}^{3} {}^nR^{\mathrm{v}}_{jj} = \frac{1}{2\omega_n}\langle 0|\mathbf{p}|n\rangle\cdot\langle n|\mathbf{L}|\,0\rangle \qquad (16)$$

$$ {}^nR^r = \frac{1}{3}\sum_{j=1}^{3} {}^nR^{\mathrm{r}}_{jj} = \frac{-i}{2}\langle 0|\mathbf{r}|n\rangle\cdot\langle n|\mathbf{L}|\,0\rangle \qquad (17)$$

where it is noted that the trace of the electric dipole−electric quadrupole contribution vanishes. Concerning the selection rules for the rotatory strength tensor for an oriented sample, it is noted in the Introduction that the molecule does not need to be chiral in order to show an anisotropic rotatory response, that is, molecules which belong to D_{2d} or one of its achiral subgroups may show an anisotropic rotatory response.

We note that the ordinary (isotropic) absorption coefficient is proportional to the dimensionless oscillator strength[1] (${}^nf_{v/r}$)

$$ {}^nf_v = \frac{2}{3\omega_n}\langle 0|\mathbf{p}|n\rangle\cdot\langle n|\mathbf{p}|0\rangle \qquad (18)$$

$$ {}^nf_r = \frac{2\omega_n}{3}\langle 0|\mathbf{r}|n\rangle\cdot\langle n|\mathbf{r}|0\rangle \qquad (19)$$

assuming the electric dipole approximation.

At this stage a comment concerning gauge and origin invariance is appropriate. The question of gauge invariance arises from the fact that the expressions for transition properties may be derived using formally equivalent perturbation Hamiltonians related by gauge transformations.[1,52−55] In exact theory the results obtained for the transition properties are gauge independent. However, approximations made in either the one particle (basis set) or many particle descriptions may result in gauge-dependent properties, implying that the r and v formulations in eqs 12−19 may yield different numerical results and computed magnetic properties may depend on the (arbitrary) choice of molecular coordinate origin.

Pedersen and Koch have shown[10,56,57] that for conventional CC theory gauge invariance is only achieved for an untruncated cluster operator and using a complete basis set, although the former requirement can be circumvented using a modification of the CC approach employing simultaneous optimization of orbitals and cluster amplitudes.[58] For variational theories, in contrast, completeness of the basis set suffices to ensure gauge invariance. However, in conjunction with variational methods, the requirement of the complete basis set for obtaining origin independence may be circumvented[56] by using London atomic orbitals[59,60] (LAOs) and the natural orbital connection,[61,62] whereas the use of LAOs does not ensure origin independence in CC theory. As demonstrated in ref 3, the velocity gauge rotatory strength tensor is inherently origin invariant, in calculations employing conventional (non-LAOs) basis sets, because of cancellation of the translational terms in the electric dipole−electric quadrupole contribution and the electric dipole−magnetic dipole contribution, whereas the length gauge tensor is origin dependent. The origin dependence of the electric dipole−electric quadrupole and electric dipole−magnetic dipole contributions stresses the fact that neither is directly observable: effectively, different choices of origin transfer contributions between the two constituents of the total rotatory strength tensor in analogy to the well-known case of, for example, paramagnetic and diamagnetic contributions to the NMR shielding tensor. Point group symmetry may in practice “locate” the origin to some specific area of space (e.g., a line or a plane passing through the molecule) such that electric quadrupole and magnetic dipole selection rules can be applied. We stress, however, that this procedure is strictly mathematical and *not* physically motivated.

III. Computational Details

The CC/DC linear response model[29,30,63] has been implemented in the Dalton program package[64] at the coupled cluster singles and doubles (CCSD) and the coupled cluster second-order approximate singles and doubles (CC2)[8,65] levels of theory. The method for calculation of the rotatory strength tensor has been implemented in a local version of Dalton.[64] The SCF rotatory strength tensors (or equivalently rotatory strength tensors within the random phase approximation[3]) have been implemented in Dalton using the linear response nonequilibrium (multiconfigurational) self-consistent-reaction-field (MCSCRF) method.[24,45] The rotatory strength tensor elements are calculated from residues of the electric dipole−electric quadrupole and

TABLE 1: The SCF, CC2, and CCSD Results for the Five Lowest Vertical Electronic Excitation Energies (in eV) for CH_2O in Vacuum ($\epsilon_{st} = \epsilon_{op} = 1$) and Solution[a]

			SCF/DC			CC2/DC			CCSD/DC		
ϵ_{st}	ϵ_{op}	symmetry	E_{ex}	^nf_r	^nf_v	E_{ex}	^nf_r	^nf_v	E_{ex}	^nf_r	^nf_v
1.000	1.000	$1\ ^1A_2(n_y \rightarrow \pi^*)$	4.37			4.08			4.01		
		$1\ ^1B_2(n_y \rightarrow 3s)$	8.57	0.025	0.025	6.39	0.022	0.019	7.05	0.018	0.017
		$2\ ^1B_2(n_y \rightarrow 3p_z)$	9.43	0.050	0.049	7.47	0.036	0.036	7.99	0.044	0.045
		$2\ ^1A_1(n_y \rightarrow 3p_y)$	9.61	0.036	0.035	7.38	0.060	0.057	8.06	0.058	0.057
		$2\ ^1A_2(n_y \rightarrow 3p_x)$	10.20			8.06			8.62		
4.335	1.818	$1\ ^1A_2(n_y \rightarrow \pi^*)$	4.46			4.13			4.06		
		$1\ ^1B_2(n_y \rightarrow 3s)$	8.57	0.004	0.004	6.60	0.007	0.007	7.16	0.003	0.003
		$2\ ^1B_2(n_y \rightarrow 3p_z)$	9.61	0.101	0.098	7.53	0.071	0.071	8.13	0.080	0.085
		$2\ ^1A_1(n_y \rightarrow 3p_y)$	9.88	0.015	0.014	7.68	0.082	0.082	8.31	0.086	0.086
		$2\ ^1A_2(n_y \rightarrow 3p_x)$	10.21			8.18			8.71		
20.70	1.841	$1\ ^1A_2(n_y \rightarrow \pi^*)$	4.49			4.16			4.08		
		$1\ ^1B_2(n_y \rightarrow 3s)$	8.50	0.001	0.001	6.63	0.002	0.001	7.14	0.000	0.000
		$2\ ^1B_2(n_y \rightarrow 3p_z)$	9.73	0.111	0.107	7.62	0.080	0.080	8.25	0.087	0.092
		$2\ ^1A_1(n_y \rightarrow 3p_y)$	9.95	0.009	0.008	7.77	0.086	0.085	8.38	0.092	0.091
		$2\ ^1A_2(n_y \rightarrow 3p_x)$	10.20			8.21			8.73		
32.63	1.758	$1\ ^1A_2(n_y \rightarrow \pi^*)$	4.50			4.16			4.09		
		$1\ ^1B_2(n_y \rightarrow 3s)$	8.49	0.001	0.001	6.63	0.001	0.001	7.13	0.000	0.000
		$2\ ^1B_2(n_y \rightarrow 3p_z)$	9.75	0.111	0.107	7.64	0.080	0.079	8.27	0.087	0.090
		$2\ ^1A_1(n_y \rightarrow 3p_y)$	9.96	0.008	0.008	7.79	0.085	0.083	8.39	0.092	0.092
		$2\ ^1A_2(n_y \rightarrow 3p_x)$	10.20			8.22			8.74		
78.54	1.778	$1\ ^1A_2(n_y \rightarrow \pi^*)$	4.50			4.17			4.09		
		$1\ ^1B_2(n_y \rightarrow 3s)$	8.48	0.000	0.001	6.63	0.000	0.000	7.13	0.000	0.000
		$2\ ^1B_2(n_y \rightarrow 3p_z)$	9.76	0.112	0.108	7.65	0.081	0.080	8.28	0.087	0.091
		$2\ ^1A_1(n_y \rightarrow 3p_y)$	9.97	0.008	0.007	7.79	0.086	0.084	8.40	0.093	0.092
		$2\ ^1A_2(n_y \rightarrow 3p_x)$	10.20			8.22			8.74		

[a] Also shown are the corresponding oscillator strengths (dimensionless) using the length gauge (^nf_r) and velocity gauge (^nf_v). The basis set is the aug-cc-pVDZ basis set.

electric dipole−magnetic dipole polarizability. Finally, the dimensionless oscillator strengths, $^nf_{r(m)}$, are calculated from residues of the frequency-dependent electric dipole−dipole polarizability in the length and velocity gauges, respectively.

The structure of CH_2O is optimized at the density functional theory (DFT) B3LYP/cc-pVTZ level using the Gaussian 98 program package.[66] The intramolecular geometry is $R(CH) = 1.100$ Å, $R(CO) = 1.211$ Å, $\angle(OCH) = 121.9°$, and $\angle(HCH) = 116.2°$ which compares well with the experimental geometry of ref 67 ($R(CH) = 1.12 \pm 0.01$ Å, $R(CO) = 1.21 \pm 0.01$ Å, and $\angle(HCH) = 118° \pm 2°$). The formaldehyde molecule is placed in the yz plane with the oxygen atom pointing toward negative z-values, and it has a 2-fold axis aligned in the z-direction (C_{2v} symmetry). The carbon atom has the following coordinates (x,y,z): (0,0,0.011721) Å.

In the equilibrium and nonequilibrium CC/DC calculations the radius of the cavity is 5.123 au. This cavity radius is equal to the distance from the center-of-mass to the hydrogen atoms plus the van der Waals radius of hydrogen. The multipole expansion is truncated at $L_{max} = 10$.

The following solvents are studied: ethyl ether ($\epsilon_{st} = 4.335$, $\epsilon_{op} = 1.818$), acetone ($\epsilon_{st} = 20.7$, $\epsilon_{op} = 1.841$), methanol ($\epsilon_{st} = 32.63$, $\epsilon_{op} = 1.758$), and water ($\epsilon_{st} = 78.54$, $\epsilon_{op} = 1.778$). The case where $\epsilon_{st} = \epsilon_{op} = 1$ corresponds to the vacuum situation. For the equilibrium situation we have $\epsilon = \epsilon_{st} = \epsilon_{op}$.

In the nonequilibrium calculations we neglect the explicit frequency dependence of the optical polarization, that is, we do not adjust the optical polarization to the frequency of the perturbation. This approximation is widely used and accepted and is usually found to be very good. Furthermore, this has been validated for formaldehyde microsolvated by water using a discrete representation of the solvent molecules.[68]

In order to explore the convergence of the multipole expansion we have, according to eq 6, calculated the contribution to the solvation energy for each l. For the most polar solvent, for example, water, we find that the dominating contribution is due to the $l = 1$ (dipole) term, whereas the contribution due to the $l = 10$ term is totally negligible. The convergence is also quite fast, that is, the contributions due to the $l = 2$ to $l = 6$ terms are roughly of the same magnitude but ≃60 times smaller than the dipole contribution. The contributions due to the $l = 7$ to $l = 9$ terms are ≃1000 times smaller than the dipole contribution.

We deploy Dunning's[69] aug-cc-pVDZ and aug-cc-pVTZ basis sets. We note that the inclusion of a double augmentation in the basis set normally is required in order to describe the rather diffuse excited states. We have investigated the effect of using the d-aug-cc-pVTZ basis set in the calculations. In vacuum and using the CCSD method, the only significant difference, as compared to the aug-cc-pVTZ results, is that the 2^1A_2 state is lowered by approximately 0.2 eV upon double augmentation. The deviations in the other electronic excitation energies as obtained using either the aug-cc-pVTZ or the d-aug-cc-pVTZ basis sets are approximately within 0.1 eV. However, using a double augmentation in the basis set in conjunction with the dielectric continuum model may lead to serious artifacts, because the rather diffuse states may tunnel into the dielectric medium and thereby cause unrealistic solvent effects. This should in particular be seen in the light of the neglect of short range repulsion effects in most dielectric continuum models. Therefore, based on the relatively small deviations between the vacuum aug-cc-pVTZ and d-aug-cc-pVTZ results, we do not include a double augmentation in the basis set but consider only the aug-cc-pVDZ and aug-cc-pVTZ basis sets.

All the condensed phase calculations neglect the difference in the external and microscopic electromagnetic fields, that is, we assume local field factors equal to unity and concentrate on the direct solvent effects on the specific properties.

IV. Results and Discussion

IV.A. Excitation Energies and Oscillator Strengths. In Tables 1 and 2 we report the five lowest vertical electronic

TABLE 2: The SCF, CC2, and CCSD Results for the Five Lowest Vertical Electronic Excitation Energies (in eV) for CH_2O in Vacuum ($\epsilon_{st} = \epsilon_{op} = 1$) and Solution[a]

			SCF/DC			CC2/DC			CCSD/DC		
ϵ_{st}	ϵ_{op}	symmetry	E_{ex}	^nf_r	^nf_v	E_{ex}	^nf_r	^nf_v	E_{ex}	^nf_r	^nf_v
1.000	1.000	$1\,^1A_2(n_y \rightarrow \pi^*)$	4.38			4.05			4.00		
		$1\,^1B_2(n_y \rightarrow 3s)$	8.59	0.023	0.023	6.56	0.022	0.020	7.24	0.018	0.018
		$2\,^1B_2(n_y \rightarrow 3p_z)$	9.40	0.047	0.047	7.57	0.033	0.031	8.13	0.040	0.042
		$2\,^1A_1(n_y \rightarrow 3p_y)$	9.59	0.025	0.025	7.52	0.055	0.054	8.22	0.054	0.055
		$2\,^1A_2(n_y \rightarrow 3p_x)$	10.04			8.05			8.66		
4.335	1.818	$1\,^1A_2(n_y \rightarrow \pi^*)$	4.47			4.11			4.05		
		$1\,^1B_2(n_y \rightarrow 3s)$	8.55	0.002	0.003	6.75	0.005	0.006	7.32	0.002	0.002
		$2\,^1B_2(n_y \rightarrow 3p_z)$	9.58	0.100	0.099	7.63	0.070	0.071	8.27	0.079	0.086
		$2\,^1A_1(n_y \rightarrow 3p_y)$	9.81	0.006	0.006	7.77	0.075	0.077	8.42	0.081	0.085
		$2\,^1A_2(n_y \rightarrow 3p_x)$	10.03			8.14			8.72		
20.70	1.841	$1\,^1A_2(n_y \rightarrow \pi^*)$	4.51			4.13			4.07		
		$1\,^1B_2(n_y \rightarrow 3s)$	8.46	0.000	0.000	6.75	0.000	0.000	7.27	0.000	0.000
		$2\,^1B_2(n_y \rightarrow 3p_z)$	9.69	0.107	0.106	7.71	0.077	0.078	8.38	0.083	0.090
		$2\,^1A_1(n_y \rightarrow 3p_y)$	9.85	0.001	0.001	7.83	0.077	0.078	8.45	0.085	0.089
		$2\,^1A_2(n_y \rightarrow 3p_x)$	10.00			8.16			8.73		
32.63	1.758	$1\,^1A_2(n_y \rightarrow \pi^*)$	4.51			4.14			4.08		
		$1\,^1B_2(n_y \rightarrow 3s)$	8.45	0.000	0.000	6.74	0.000	0.000	7.27	0.000	0.000
		$2\,^1B_2(n_y \rightarrow 3p_z)$	9.70	0.106	0.106	7.73	0.077	0.077	8.40	0.082	0.088
		$2\,^1A_1(n_y \rightarrow 3p_y)$	9.86	0.001	0.001	7.84	0.076	0.077	8.45	0.084	0.088
		$2\,^1A_2(n_y \rightarrow 3p_x)$	9.99			8.17			8.73		
78.54	1.778	$1\,^1A_2(n_y \rightarrow \pi^*)$	4.52			4.14			4.08		
		$1\,^1B_2(n_y \rightarrow 3s)$	8.43	0.000	0.000	6.74	0.000	0.000	7.26	0.000	0.000
		$2\,^1B_2(n_y \rightarrow 3p_z)$	9.71	0.107	0.106	7.74	0.077	0.078	8.41	0.082	0.088
		$2\,^1A_1(n_y \rightarrow 3p_y)$	9.86	0.001	0.001	7.84	0.076	0.078	8.45	0.085	0.089
		$2\,^1A_2(n_y \rightarrow 3p_x)$	9.98			8.17			8.73		

[a] Also shown are the corresponding oscillator strengths (dimensionless) using the length gauge (^nf_r) and velocity gauge (^nf_v). The basis set is the aug-cc-pVTZ basis set.

excitation energies as calculated using SCF, CC2, and CCSD for CH_2O in vacuum or solution. Also, we give the corresponding oscillator strengths using the length gauge (^nf_r) and velocity gauge (^nf_v). In Table 1 the basis set used for the calculations is the aug-cc-pVDZ basis, whereas the aug-cc-pVTZ basis set is used for the results in Table 2. From these tables we find that the SCF method overestimates the electronic excitation energies as compared to methods which include correlation effects. For the 1^1A_2 excitation the hierarchy SCF, CC2, CCSD (and CC3 for vacuum) lowers the electronic excitation energy as more dynamical correlation is included in the wave function. However, for the other excitations studied in this work the CCSD results are between the SCF and CC2 results leading to the conclusion that the SCF model overestimates the excitation energies whereas the CC2 model underestimates the corresponding excitation energies. However, the overestimation obtained in the SCF results is usually much more pronounced than the underestimation of the CC2 results, that is, the SCF results are up to 1.6 eV higher than the corresponding CCSD results. We also observe that the $^1B_2$ and $^1A_1$ transitions are the ones most sensitive to basis set effects. However, the basis set effects are relatively small, ranging from around 0.2% for the 1^1A_2 transition to around 2.7% for the 1^1B_2 transition using the CC method.

Also, the reported vacuum values for the electronic excitation energies compare well with the CCSD results of ref 70 using larger basis sets. In order to estimate the effects of triples excitations (on the vacuum results) we have used the CC3 method[9] together with the aug-cc-pVTZ basis set and obtain for the five lowest excitations (with the same assignment as for the SCF, CC2, and CCSD results) 3.95, 7.19, 8.09, 8.19, and 8.64 eV. Thus, the effect of triples excitations is found to lower the excitation energies, but the effect is much smaller than in going from CC2 to CCSD. The lowering of the excitation energies due to the effects of triples excitations has also been observed in ref 70.

Concerning the CC2 results, we note that in vacuum this model predicts a different ordering of the 2^1B_2 and 2^1A_1 excitations than the SCF and CCSD calculations. Furthermore, the 1^1A_2 excitation is increased whereas the other excitations are lowered as compared to CCSD. However, the shift in excitation energy, that is, $\delta E_{ex} = E_{ex}^{solvent} - E_{ex}^{vacuum}$ for the lowest excitation compares relatively well with the CCSD results. For example, using water as a solvent we obtain for the blue-shifts using the aug-cc-pVDZ basis set: $\delta E_{ex}^{CC2} = 710$ cm^{-1} and $\delta E_{ex}^{CCSD} = 670$ cm^{-1}, whereas we obtain $\delta E_{ex}^{CC2} = 694$ cm^{-1} and $\delta E_{ex}^{CCSD} = 678$ cm^{-1} using the aug-cc-pVTZ basis set. For the SCF method we obtain a blue-shift of $\simeq$1002 cm^{-1} and 1080 cm^{-1} using the aug-cc-pVDZ or aug-cc-pVTZ basis sets, respectively. Hence, using an uncorrelated description leads to a serious overestimation of the blue-shift.

The experimental result for the vertical 1^1A_2 transition is 4.07 eV,[71] whereas the adiabatic excitation energy is 3.50 eV.[72,73] The significant difference in these two excitation energies is due to the large geometry changes which occur in formaldehyde after excitation. Thus, all the reported excitation energies including correlation effects are underestimated (for the aug-cc-pVTZ basis set in the range of 0.02−0.12 eV) as compared to experiment. (For further discussion of the vacuum spectrum, including higher excited states and experimental results, we refer to ref 70.) Also, the reported SCF results are overestimated ($\simeq$0.3 eV) as compared to experiment. Concerning the blue-shift of the 1^1A_2 excitation we note that this issue has been discussed extensively in the literature (see ref 74 and references therein) and that a blue-shift ~1900 cm^{-1} is expected from the blue-shift of acetone.[75] In this work we obtain a blue-shift around 680 cm^{-1} (depending on the model and basis set used) which is close to the result of Mennucci et al.[76] (595 cm^{-1} for equilibrium solvation and 944 cm^{-1} for nonequilibrium solvation) obtained using the PCM together with multiconfigurational self-consistent-field (MCSCF) theory and to the calculation by

TABLE 3: The SCF, CC2, and CCSD Results for the Rotatory Tensors for CH_2O as Calculated Using the Length (*r*) and Velocity (*v*) Gauges[a]

				SCF/DC			CC2/DC			CCSD/DC		
ϵ_{st}	ϵ_{op}	symmetry		$^nR^Q_{XY}$	$^nR^m_{XY}$	$^nR_{XY}$	$^nR^Q_{XY}$	$^nR^m_{XY}$	$^nR_{XY}$	$^nR^Q_{XY}$	$^nR^m_{XY}$	$^nR_{XY}$
1.000	1.000	$1\,^1B_2(n_y \rightarrow 3s)$	*r*	−31.32	32.38	1.06	−26.25	26.38	0.14	−24.45	27.88	3.44
			v	−30.98	32.23	1.26	−24.55	24.59	0.03	−24.05	27.00	2.94
		$2\,^1B_2(n_y \rightarrow 3p_z)$	*r*	−0.84	−65.68	−66.52	8.03	−66.51	−58.48	4.73	−67.43	−62.70
			v	−1.69	−65.27	−66.96	7.58	−66.01	−58.43	4.32	−68.68	−64.36
		$2\,^1A_1(n_y \rightarrow 3p_y)$	*r*	26.82		26.82	27.31		27.31	26.44		26.44
			v	27.52		27.52	26.24		26.24	26.98		26.98
4.335	1.818	$1\,^1B_2(n_y \rightarrow 3s)$	*r*	−11.73	17.64	5.91	−15.83	22.96	7.13	−9.58	15.30	5.73
			v	−11.76	18.22	6.46	−15.59	22.64	7.06	−9.85	15.63	5.78
		$2\,^1B_2(n_y \rightarrow 3p_z)$	*r*	−24.09	−49.85	−73.94	−2.85	−62.95	−65.79	−11.11	−53.26	−64.37
			v	−25.11	−49.17	−74.28	−4.09	−63.19	−67.29	−13.09	−54.87	−67.96
		$2\,^1A_1(n_y \rightarrow 3p_y)$	*r*	16.08		16.08	25.49		25.49	24.60		24.60
			v	16.50		16.50	27.28		27.28	27.72		27.72
20.70	1.841	$1\,^1B_2(n_y \rightarrow 3s)$	*r*	−4.35	7.00	2.65	−7.24	11.72	4.53	−1.94	3.35	1.41
			v	−4.78	8.00	3.22	−7.04	11.58	4.54	−2.07	3.59	1.52
		$2\,^1B_2(n_y \rightarrow 3p_z)$	*r*	−31.34	−34.30	−65.64	−10.02	−48.21	−58.23	−17.28	−36.62	−53.90
			v	−30.43	−33.78	−64.21	−11.32	−48.06	−59.38	−19.49	−37.50	−56.99
		$2\,^1A_1(n_y \rightarrow 3p_y)$	*r*	11.51		11.51	22.10		22.10	21.07		21.07
			v	11.79		11.79	24.33		24.33	24.57		24.57
32.63	1.758	$1\,^1B_2(n_y \rightarrow 3s)$	*r*	−3.55	5.76	2.21	−6.15	10.11	3.96	−1.09	1.89	0.80
			v	−4.05	6.80	2.71	−5.91	9.86	3.95	−1.19	2.08	0.89
		$2\,^1B_2(n_y \rightarrow 3p_z)$	*r*	−31.62	−31.77	−63.39	−10.70	−45.94	−56.63	−17.69	−34.39	−52.08
			v	−30.72	−32.27	−62.99	−11.91	−45.64	−57.55	−19.81	−35.11	−54.92
		$2\,^1A_1(n_y \rightarrow 3p_y)$	*r*	11.00		11.00	21.48		21.48	20.42		20.42
			v	11.26		11.26	23.64		23.64	23.86		23.86
78.54	1.778	$1\,^1B_2(n_y \rightarrow 3s)$	*r*	−2.90	4.71	1.81	−5.26	8.73	3.47	−0.37	0.64	0.27
			v	−3.42	5.81	2.39	−5.06	8.53	3.47	−0.48	0.85	0.37
		$2\,^1B_2(n_y \rightarrow 3p_z)$	*r*	−31.26	−30.44	−61.70	−11.45	−44.00	−55.45	−18.24	−32.44	−50.68
			v	−32.15	−29.96	−62.11	−12.66	−43.71	−56.37	−20.39	−33.11	−53.50
		$2\,^1A_1(n_y \rightarrow 3p_y)$	*r*	10.48		10.48	21.09		21.09	20.02		20.02
			v	10.72		10.72	23.34		23.34	23.53		23.53

[a] The only nonvanishing element is the *XY* component. The term $^nR^Q_{XY}$ is the electric dipole−electric quadrupole component, the term $^nR^m_{XY}$ is the electric dipole−magnetic dipole component, and the term $^nR_{XY}$ is the total tensor element. Results are in 10^{-40} cgs. The basis set is the aug-cc-pVDZ basis set.

Mikkelsen et al.[45] (589 cm^{-1}) using MCSCF together with a nonequilibrium description of the solvent. However, even though the agreement with experiment in this case is not excellent, we may improve the results significantly by introducing one or two water molecules explicitly into the coupled cluster calculation.[68] This is easily done as the excitation energies of water are far from the very localized 1^1A_2 excitation in formaldehyde.

For the more intense excitations, we note that the deviations between the *v* and *r* formulations are less than 9% using either basis set, which is significantly better agreement than that obtained for ethylene in ref 11. Also we note that the 1^1B_2 transition becomes less intense in solution whereas the 2^1B_2 and 2^1A_1 excitations become more intense. However, for the SCF method the oscillator strength for the 2^1A_1 excitation actually decreases as function of the solvent dielectric constant.

IV.B. The Rotatory Strength Tensor Elements. In Tables 3 and 4 we present the SCF, CC2, and CCSD rotatory strength tensors for CH_2O as calculated using the length and velocity gauges, noting that point group symmetry dictates that the only unique nonvanishing tensor element is the *XY* component. The basis set used for the calculations shown in Table 3 is the aug-cc-pVDZ basis set, whereas the corresponding results obtained using the aug-cc-pVTZ basis set are given in Table 4. Generally, transitions which are electric dipole forbidden cannot contribute to the rotatory strengths. Consequently, the $^1A_2$ excitations have rotatory strengths which are identically zero and are therefore not shown in the Tables. Also, in the coordinate system chosen for these calculations, the $^1A_1$ excitations are magnetic dipole forbidden and the corresponding electric dipole−magnetic dipole contribution to the rotatory strength is hence identically zero, whereas the electric dipole−electric quadrupole contribution is nonvanishing.

Concerning the vacuum calculations we find for the 1^1B_2 excitation a relatively small rotatory strength. However, this actually results from cancellation of two significant contributions with opposite signs. Also, the rotatory strength for the 2^1B_2 excitation is, in the CC calculations, dominated by the electric dipole−magnetic dipole contribution, whereas the 2^1A_1 rotatory strength consists, as discussed above, only of the electric dipole−electric quadrupole contribution. For the SCF description of the rotatory strength for the 2^1B_2 excitation, we find in vacuum the electric dipole−magnetic dipole contribution to be dominating whereas the situation is reversed in polar solvents.

For the 2^1B_2 and 2^1A_1 transitions we observe a decrease in the (numerical) values of the rotatory strengths, corresponding to a weakening of the CD intensities, when going from the aug-cc-pVDZ to the aug-cc-pVTZ basis sets. Generally, this is not the case for the 1^1B_2 excitation, but this transition shows, however, only very small basis set effects.

Generally, we find that basis set effects for the CD intensities are much more significant than for the electronic excitation energies. Also, the basis set effects are increased as a function of the solvent dielectric constants. For example, for the CC results of the 2^1B_2 excitation a basis set effect of around 7.5% (relative to the aug-cc-pVTZ results) is found in the vacuum case, whereas the corresponding basis set effect for formaldehyde in aqueous solution is found to be around 44%. Also, we find that introducing a solvent leads to overestimated CD intensities for all the examined excitations using the aug-cc-pVDZ basis sets. The basis set effects may also result in a sign

TABLE 4: The SCF, CC2, and CCSD Results for the Rotatory Tensors for CH_2O as Calculated Using the Length (*r*) and Velocity (*v*) Gauges[a]

				SCF/DC			CC2/DC			CCSD/DC		
ϵ_{st}	ϵ_{op}	symmetry		${}^nR^Q_{XY}$	${}^nR^m_{XY}$	${}^nR_{XY}$	${}^nR^Q_{XY}$	${}^nR^m_{XY}$	${}^nR_{XY}$	${}^nR^Q_{XY}$	${}^nR^m_{XY}$	${}^nR_{XY}$
1.000	1.000	$1\ {}^1B_2(n_y \rightarrow 3s)$	*r*	−29.52	31.02	1.60	−25.73	25.68	−0.05	−24.13	27.62	3.49
			v	−29.42	31.00	1.48	−24.36	24.57	0.20	−24.20	27.38	3.18
		$2\ {}^1B_2(n_y \rightarrow 3p_z)$	*r*	−2.07	−60.73	−62.74	6.54	−60.58	−54.04	3.06	−62.15	−59.09
			v	−2.01	−60.82	−62.89	6.57	−59.44	−52.87	3.49	−63.34	−59.86
		$2\ {}^1A_1(n_y \rightarrow 3p_y)$	*r*	21.54		21.54	24.21		24.21	23.88		23.88
			v	21.75		21.75	23.30		23.30	24.23		24.23
4.335	1.818	$1\ {}^1B_2(n_y \rightarrow 3s)$	*r*	−8.83	13.63	4.80	−13.42	20.02	6.61	−7.54	12.41	4.88
			v	−8.92	13.86	4.94	−13.66	20.34	6.69	−8.02	12.91	4.89
		$2\ {}^1B_2(n_y \rightarrow 3p_z)$	*r*	−27.21	−37.27	−64.48	−6.54	−51.27	−57.81	−14.85	−41.09	−55.93
			v	−26.85	−37.16	−64.01	−6.48	−51.81	−58.29	−15.54	−42.84	−58.38
		$2\ {}^1A_1(n_y \rightarrow 3p_y)$	*r*	8.78		8.78	19.84		19.84	19.01		19.01
			v	8.98		8.98	20.96		20.96	20.98		20.98
20.70	1.841	$1\ {}^1B_2(n_y \rightarrow 3s)$	*r*	−1.86	3.04	1.18	−4.46	7.41	2.95	−0.08	0.14	0.06
			v	−2.05	3.39	1.34	−4.58	7.61	3.03	−0.11	0.19	0.08
		$2\ {}^1B_2(n_y \rightarrow 3p_z)$	*r*	−32.81	−16.49	−49.30	−13.94	−31.44	−45.38	−20.54	−19.65	−40.19
			v	−32.32	−16.44	−48.76	−13.81	−31.69	−45.49	−21.44	−20.42	−41.86
		$2\ {}^1A_1(n_y \rightarrow 3p_y)$	*r*	3.49		3.49	15.24		15.24	14.12		14.12
			v	3.62		3.62	16.52		16.52	16.15		16.15
32.63	1.758	$1\ {}^1B_2(n_y \rightarrow 3s)$	*r*	−1.15	1.89	0.74	−3.41	5.73	2.32	0.70	−1.24	−0.54
			v	−1.35	2.24	0.89	−3.49	5.86	2.37	0.73	−1.27	−0.54
		$2\ {}^1B_2(n_y \rightarrow 3p_z)$	*r*	−32.92	−13.91	−46.83	−14.54	−28.67	−43.21	−20.80	−16.95	−37.75
			v	−32.42	−13.86	−46.28	−14.32	−28.81	−43.13	−21.62	−17.57	−39.19
		$2\ {}^1A_1(n_y \rightarrow 3p_y)$	*r*	2.92		2.92	14.53		14.53	13.40		13.40
			v	3.03		3.03	15.75		15.75	15.34		15.34
78.54	1.778	$1\ {}^1B_2(n_y \rightarrow 3s)$	*r*	−0.55	0.90	0.35	−2.54	4.29	1.75	1.36	−2.43	−1.07
			v	−0.76	1.27	0.51	−2.62	4.43	1.82	1.43	−2.49	−1.06
		$2\ {}^1B_2(n_y \rightarrow 3p_z)$	*r*	−33.32	−11.40	−44.72	−15.24	−26.17	−41.41	−21.24	−14.43	−35.66
			v	−32.79	−11.37	−44.16	−15.02	−26.31	−41.33	−22.07	−14.96	−37.03
		$2\ {}^1A_1(n_y \rightarrow 3p_y)$	*r*	2.34		2.34	14.01		14.01	12.84		12.84
			v	2.44		2.44	15.27		15.27	14.81		14.81

[a] The only nonvanishing element is the *XY* component. The term ${}^nR^Q_{XY}$ is the electric dipole−electric quadrupole component, the term ${}^nR^m_{XY}$ is the electric dipole−magnetic dipole component, and the term ${}^nR_{XY}$ is the total tensor element. Results are in 10^{-40} cgs. The basis set is the aug-cc-pVTZ basis set.

change in the rotatory strength. This is first observed when using CCSD and methanol ($\epsilon_{st} = 32.63$, $\epsilon_{op} = 1.758$) as solvent. However, the cases where the basis set effects result in a sign change show rather weak CD intensities.

The results obtained using the aug-cc-pVTZ basis set show that solvent effects on the rotatory strengths are significant. The CD intensity for the 1^1B_2 excitation is relatively weak as a function of the solvent dielectric constant. However, the contributions from the electric dipole−magnetic dipole and the electric dipole−electric quadrupole terms exhibit considerable solvent effects. Thus, in the vacuum case, the rotatory strength is a sum of two significant contributions (but with opposite signs), whereas introducing a solvent the rotatory strength is actually a sum of two small contributions. We find that the solvent effects on the electric dipole−magnetic dipole and electric dipole−electric quadrupole behave monotonically as a function of the dielectric constant. However, because the solvent effects on these two contributions are physically different the *sum*, that is, the rotatory strength, does not need to behave in the same way. This is also what is observed in Table 4 for the 1^1B_2 excitation, that is, introducing a solvent with small dielectric constants (nonpolar environment) leads to an increase in the rotatory strength whereas a decrease is found when introducing a polar solvent.

For the vacuum results we observe that the 2^1B_2 excitation, in the chosen molecular coordinate system, is dominated by the electric dipole−magnetic dipole contribution. As seen from Table 4 this actually changes for both SCF and CCSD as a function of the dielectric constants. For formaldehyde in aqueous solution the 2^1B_2 excitation is dominated by the electric dipole−electric quadrupole contribution. Thus, as for the 1^1B_2 excitation, the molecular physical mechanism governing the CD is changed upon introduction of a solvent in CCSD.

In the case of formaldehyde the polar solvents have induced a sign change in the CCSD and CC2 rotatory strength associated with the 1^1B_2 excitation. This rotatory strength is, however, also the (numerically) smallest one and no sign changes are observed for the much more intense 2^1B_2 and 2^1A_1 excitations although a sign change (for CC2 and CCSD) in the electric dipole−electric quadrupole contribution to the rotatory strength of the 2^1B_2 excitation is observed.

As seen from Table 4 correlation effects are of great importance and are certainly coupled to the introduction of a solvent. Actually, in order to get the intensities qualitatively correct, CCSD must be used. In vacuum the CD at the CCSD level of theory is generally more intense than the corresponding CC2 results (at least in the *v* gauge), and a sign change occurs for the 1^1B_2 excitation. The introduction of a solvent leads to the change that the CC2 results now overestimates the rotatory strength intensities as compared to CCSD. For the 2^1B_2 excitation SCF overestimates the rotatory strength in both vacuum and solvent, whereas the rotatory strength for the 2^1A_1 excitation is underestimated.

IV.C. Discussion of Equilibrium versus Nonequilibrium Solvation. In order to address the question of equilibrium versus nonequilibrium solvation we have shown in Table 5 the SCF, CC2, and CCSD results of the five lowest vertical electronic excitation energies for formaldehyde in water using an equilibrium description of the solvent ($\epsilon_{st} = \epsilon_{op} = 78.54$). Also shown are the corresponding oscillator strengths using the length and velocity gauges. The basis set used in the calculations is the aug-cc-pVTZ basis. Comparison of Tables 2 and 5 leads to

TABLE 5: The SCF, CC2, and CCSD Results for the Five Lowest Vertical Electronic Excitation Energies (in eV) for CH_2O in Water Using an Equilibrium Description of the Solvent ($\epsilon_{st} = \epsilon_{op} = 78.54$)[a]

			SCF/DC			CC2/DC			CCSD/MM		
ϵ_{st}	ϵ_{op}	symmetry	E_{ex}	^nf_r	^nf_v	E_{ex}	^nf_r	^nf_v	E_{ex}	^nf_r	^nf_v
78.54	78.54	$1\ ^1A_2(n_y \rightarrow \pi^*)$	4.51			4.12			4.07		
		$1\ ^1B_2(n_y \rightarrow 3s)$	8.40	0.000	0.000	6.69	0.002	0.002	7.21	0.000	0.000
		$2\ ^1B_2(n_y \rightarrow 3p_z)$	9.58	0.141	0.141	7.60	0.101	0.116	8.26	0.109	0.131
		$2\ ^1A_1(n_y \rightarrow 3p_y)$	9.84	0.000	0.000	7.75	0.107	0.124	8.36	0.123	0.141
		$2\ ^1A_2(n_y \rightarrow 3p_x)$	9.98			8.15			8.72		

[a] Also shown are the corresponding oscillator strengths (dimensionless) using the length gauge (^nf_r) and velocity gauge (^nf_v). The basis set is the aug-cc-pVTZ basis set.

TABLE 6: The SCF, CC2, and CCSD Results for the Rotatory Tensors as Calculated Using the Length (r) and Velocity (v) Gauges for CH_2O in Water Using an Equilibrium Description ($\epsilon_{st} = \epsilon_{op} = 78.54$)[a]

				SCF/DC			CC2/DC			CCSD/DC		
ϵ_{st}	ϵ_{op}	symmetry		$^nR^Q_{XY}$	$^nR^m_{XY}$	$^nR_{XY}$	$^nR^Q_{XY}$	$^nR^m_{XY}$	$^nR_{XY}$	$^nR^Q_{XY}$	$^nR^m_{XY}$	$^nR_{XY}$
78.54	78.54	$1\ ^1B_2(n_y \rightarrow 3s)$	r	−3.52	5.56	2.04	−7.41	11.83	4.42	−1.61	2.75	1.14
			v	−3.73	5.93	2.20	−9.00	14.00	5.00	−2.42	3.97	1.55
		$2\ ^1B_2(n_y \rightarrow 3p_z)$	r	−41.73	−16.46	−58.19	−18.05	−35.99	−54.04	−26.54	−21.42	−47.96
			v	−41.15	−16.42	−57.57	−20.25	−38.67	−58.92	−30.61	−23.51	−54.12
		$2\ ^1A_1(n_y \rightarrow 3p_y)$	r	2.66		2.66	19.72		19.72	18.16		18.16
			v	2.76		2.76	24.04		24.04	23.00		23.00

[a] Results are in 10^{-40} cgs. The basis set is the aug-cc-pVTZ basis set.

the conclusion that the equilibrium solvation scheme underestimates the electronic excitation energies. This has also been observed in ref 30 using the CC/DC model and in refs. 24 and 45 using the multiconfigurational self-consistent-reaction-field method. Also, the oscillator strengths are overestimated as compared to the nonequilibrium solvation situation.

Concerning the rotatory strengths in Table 6, we observe that neglecting nonequilibrium solvation effects leads to a sign change in the CCSD rotatory strength for the 1^1B_2 excitation. Furthermore, the CD intensities are overestimated as compared to the nonequilibrium solvation. We note, however, that the SCF and CCSD rotatory strengths associated with the 2^1B_2 excitation are dominated by the electric dipole−electric quadrupole term as it should be according to the nonequilibrium solvation description.

V. Summary

In this article we have presented the first study of solvent effects on the rotatory strength tensor, and we have performed calculations employing correlated ab initio methods using solvated formaldehyde. The solvent has been modeled as a linear, homogeneous, and isotropic dielectric continuum. We note that describing the solvent as a dielectric continuum introduces solvent effects in an averaged way because the discrete nature of the solvent molecules is neglected. However, the dielectric continuum approach allows us to determine solvent effects on molecular properties using ab initio electronic structure theory which clearly represents an improvement as compared to the Lorentz local field factor approach, which traditionally has been used to model solvation effects on properties related to optical activity.

The rotatory strength tensor elements have been calculated using coupled cluster theory, which accounts for the dynamical correlation effects, and we have studied the importance of including none (SCF) and less (CC2) versus more (CCSD) correlation effects into the calculations. We have shown that, in addition to correlation and basis set effects, solvent effects have a significant influence on the rotatory strengths, and the introduction of the solvent is, in some cases, found to result in a sign change in the rotatory strength tensor elements. In particular, we have shown that the introduction of nonequilibrium effects is important when calculating rotatory strength tensor elements for molecules in solution. This clearly illustrates the importance of a proper description of the solvent influence on this specific property and that it is not advisable just to consider the effect of the Lorentz local field factors.

An obvious extension of this work is to include the effect of the discreteness of the solvent molecules directly in the calculations. This issue may be addressed by using the linear response methodology as implemented in the combined coupled cluster/molecular mechanics method[77] which is an ongoing research project.

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