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Solvent effects in electronically excited states using the continuum solvation model COSMO in combination with multireference configuration interaction with singles and doubles (MR-CISD)

Silmar Andrade do Monte[1], **Thomas Müller**[2], **Michal Dallos**[1], **Hans Lischka**[1], **Michael Diedenhofen**[3]
Andreas Klamt[3]

[1] Institute for Theoretical Chemistry and Structural Biology, University of Vienna, Währingerstrasse 17, 1090, Austria
[2] Central Institute for Applied Mathematics, Research Center Jülich, 52425, Jülich, Germany
[3] COSMOlogic GmbH & Co. KG, Burscheider Strasse 515, 51381 Leverkusen, Germany

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Abstract. An implementation of the COSMO continuum solvation model into the MCSCF and MR-CISD programs of the COLUMBUS program system is reported. Equilibrium solvation and non-equilibrium solvation models for the treatment of electronic excitations have been used. Solvatochromic effects have been computed for a representative set of n-π^* and π-π^* states of formaldehyde, acrolein and pyrazine using several solvents ranging from some with apolar character to water. Agreement with experimental shifts is good within the limits of a continuum model.

Keywords: Solvatochromic effects – Multireference CI – n-π^* and π-π^* states – Polar and apolar solvents

Introduction

Continuum models constitute an important approach to molecular solvation processes. For an overview on different classes of models see the recent reviews [1, 2, 3, 4]. Most of the investigations have concentrated on the electronic ground state in combination with self-consistent-field (SCF) or density functional (DFT) methods (see for example [5, 6, 7, 8]). Implementations within the Møller-Plesset perturbation theory to second order (MP2) [9] and complete active space perturbation theory to second order (CASPT2) [10] have been given as well. Non-equilibrium theories have been developed for the treatment of vertical electronic excitations [11, 12, 13, 14] and applied within the framework of multiconfiguration SCF (MCSCF) theory [15, 16, 17, 18, 19] and configuration interaction (CI) [20].

Quantum chemical calculations on excited states are usually much more demanding than those for the electronic ground state, since the wave function usually shows a significantly larger multireference character in the excited state. MCSCF calculations can take into account this multireference character but lack important dynamical electron correlation effects. Multireference configuration interaction with singles and doubles (MR-CISD) and related methods including size-extensivity corrections (such as quadruples corrections according to Davidson [21] extended to the MR case [22] (MR-CISD + Q), multireference averaged quadratic coupled cluster (MR-AQCC [23, 24]) or MR-AQCC for linear response theory (MR-AQCC-LRT [25]) are adequate methods for the accurate description of excited states.

It is the purpose of this work to report a first implementation of the Conductor-like Screening Model (COSMO) [6] into the MCSCF and MR-CISD sections of the COLUMBUS program system [26, 27, 28]. COSMO has been used very successfully for ground state calculations (see for instance its recent TURBOMOLE implementation [8]). A non-equilibrium solvation theory has been developed within COSMO [14] as well, which has been applied only to semiempirical methods so far. The COLUMBUS program is specialized for extended multireference calculations, which are required, for example, in many calculations on electronically excited states (see for example calculations on formaldehyde [29, 30, 31], acetylene [32] and malonaldehyde [33]). One major aim was to achieve a modular combination of both program systems with minimum interference of the different codes on each other. The possibilities of the COLUMBUS-COSMO combination are demonstrated for three examples (formaldehyde, acrolein, and pyrazine) with a multitude of excited states of n-π^* and π-π^* character. The π-π^* states are espe-

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Correspondence to: H. Lischka
e-mail: Hans.Lischka@univie.ac.at

cially difficult to compute; large and flexible reference spaces are needed. Both gas-phase and solvent results are discussed.

Review of the theory

The COSMO continuum model has been described in detail previously [6, 7, 8]. As in other, related, continuum models, the solute is located in a cavity constructed from overlapping spheres centered at the individual atoms of the solute [6]. The effect of the polarized continuum is represented by screening charges q_i located at surface segments i, (i = 1...m) created by discretization of the cavity surface into m segments. Only electrostatic terms are taken into account. The screening charges are obtained from the equation

$$\mathbf{q}(\varepsilon, \mathbf{P}) = -f(\varepsilon)\mathbf{A}^{-1}\Phi^X(\mathbf{P}), \tag{1}$$

where **A** is the symmetric matrix representing the Coulomb interactions between the screening charges, **q** is the vector of screening charges, $\Phi^X(\mathbf{P})$ is the vector of the electrostatic potential of the solute X in a given electronic state (characterized by the density **P**) and

$$f(\varepsilon) = \frac{\varepsilon - 1}{\varepsilon + 0.5}. \tag{2}$$

The factor $f(\varepsilon)$ corrects the result for a conductor ($\varepsilon = \infty$) to finite ε.

Following the concepts of Lippert [11] and McRae [12], the solvation effect on electronic excitation is treated as a non-equilibrium process where the total response of the solvent is split into a fast contribution described by the electronic relaxation and into a slow component related to the orientational relaxation of the solvent (see for example [13, 14]). The former contribution is characterized by the susceptibility

$$\chi_{\mathrm{el}} = n^2 - 1 \tag{3}$$

where n is the solvent refractive index, and the latter contribution by

$$\chi_{\mathrm{or}} = \varepsilon - n^2. \tag{4}$$

The total susceptibility χ_{tot} is given as

$$\chi_{\mathrm{tot}} = \chi_{\mathrm{el}} + \chi_{\mathrm{or}}. \tag{5}$$

For the electronic ground state (characterized by the density $\mathbf{P}_0$) the screening charges are split according to the ratios of the susceptibilities into an orientational part

$$\mathbf{q}_{\mathrm{or}}(\varepsilon, \mathbf{P}_0) = \frac{\chi_{\mathrm{or}}}{\chi_{\mathrm{tot}}}\mathbf{q}(\varepsilon, \mathbf{P}_0) \tag{6}$$

and into an electronic part

$$\mathbf{q}_{\mathrm{el}}(\varepsilon, \mathbf{P}_0) = \frac{\chi_{\mathrm{el}}}{\chi_{\mathrm{tot}}}\mathbf{q}(\varepsilon, \mathbf{P}_0). \tag{7}$$

In these equations, the origin of the screening charges has been characterized explicitly by giving the dielectric constant ε and the ground state density in parentheses.

For the fast vertical electronic transition the orientational part of the susceptibility is kept fixed to the ground-state value while only the electronic part is allowed to adjust instantaneously to the excitation. The total electrostatic potential Φ'_{ex} on the solute surface arises from the density $\mathbf{P}_{\mathrm{ex}}$ of the excited state and the frozen ground-state orientational screening charges $\mathbf{q}_{\mathrm{or}}(\varepsilon,\mathbf{P}_0)$, giving

$$\Phi'_{\mathrm{ex}} = \Phi^X(\mathbf{P}_{\mathrm{ex}}) + \mathbf{A}\mathbf{q}_{\mathrm{or}} \tag{8}$$

This potential is screened by the electronic polarizability alone; in other words by a dielectric medium of $\varepsilon = n^2$, yielding additional screening charges

$$\mathbf{q}'_{\mathrm{ex}} = -f(n^2)\mathbf{A}^{-1}\Phi'_{\mathrm{ex}} \tag{9}$$

As has been shown in [14], the total screening charges can be written in the following form:

$$\mathbf{q}_{\mathrm{ex}}^{\mathrm{tot}} = \mathbf{q}'_{\mathrm{ex}} + \mathbf{q}_{\mathrm{or}}(\varepsilon, \mathbf{P}_0) = \mathbf{q}(n^2, \Delta) + \mathbf{q}(\varepsilon, \mathbf{P}_0) \tag{10}$$

Δ is the difference density $\mathbf{P}_{\mathrm{ex}}$–$\mathbf{P}_0$. The values in parentheses indicate the value of the dielectric constant and the electronic density to be used in Eq. 1 for the determination of the screening charges.

Program implementation

The combination of the COSMO routines and the MCSCF and MR-CISD codes of COLUMBUS was performed under consideration of maximum modularity. The link between both program packages is given by Eq. 1. The electrostatic potential $\Phi^X(\mathbf{P})$, which is computed quantum chemically (MCSCF or MR-CISD) at all surface points, is used to compute the surface charges. These surface charges are included in the one-electron part of the Hamiltonian and used within the standard iterative algorithms for the solution of the MCSCF or MR-CISD problem. The screening charges are updated within these iteration cycles so that finally a self-consistent solution in terms of these screening charges is achieved. Analogous procedures have been described previously, for example, in refs. [6, 7, 8, 13, 34, 35].

For the ground state (or any other state treated in equilibrium with the continuum) the following steps are executed within the MCSCF and MR-CISD programs, respectively:

1. Initialization steps:
   a. Reading of the COSMO input file and assignment of arrays required by the COSMO routines
   b. Determination of the coordinates of the cavity segments and evaluation of the interaction matrix **A**
2. Within the quantum chemical iteration scheme (for details see below):
   a. Evaluation of the electrostatic potential $\Phi^X(\mathbf{P}_0)$ at the segment coordinates
   b. Evaluation of the screening charges according to Eq. 1
   c. Insertion of the screening charges into the solute Hamiltonian as external one-electron potential, recomputation of the one-electron atomic orbital integrals, and transformation into the molecular orbital (MO) basis for further usage in the MCSCF or MR-CISD iteration scheme

d. Computation of the dielectric energy $E^0_{\text{diel}} = \frac{1}{2}\sum_i q_i \Phi_i^X$

e. Computation of $E_{\text{tot}} = E_{\text{exp}} - E^0_{\text{diel}}$ (see for example [9])

f. Cycle restarts at step a) until convergence

3. Concluding step: double cavity outlying charge correction as described in [36] for the small residual outlying charge, in other words the small deviation from Gauss' law, as it occurs with the COSMO boundary conditions.

The energy E_{exp} is the expectation value of the Hamiltonian operator for the solute including the screening charges as external potential using the current wave function.

For the MCSCF method (for a description of the single-state method see [37] and for the state-averaged formalism see [31]) steps 2a–2e are inserted right after a new set of MOs has been determined within the MCSCF optimization procedure. In the case of a state-averaged MCSCF calculation the averaged density matrix is used for the computation of the electrostatic potential.

For the MR-CISD method the situation is more complicated. The Davidson subspace diagonalization method [38] is used for the computation of the eigenvectors and eigenvalues of the Hamiltonian matrix. For more information on implementation and efficiency aspects within the COLUMBUS program system see [39]. In Davidson iteration number i a subspace expansion vector $\mathbf{v}_i$ is generated and the subspace Hamiltonian matrix $\mathbf{H}_{ij}^{\text{subsp}} = \mathbf{v}_i^t \mathbf{H}^{\text{CSF}} \mathbf{v}_j, j = 1 \ldots i$ is augmented by row i. $\mathbf{H}^{\text{CSF}}$ is the Hamiltonian matrix in the basis of configuration state functions (CSFs). Inserting steps 2a–2e into each Davidson iteration cycle would mean that the one-electron integrals change every time and that the whole subspace matrix $\mathbf{H}_{ij}^{\text{subsp}}$ would have to be corrected accordingly. Even though this would not be costly in terms of numerical operations, it would be quite expensive in terms of input/output operations since the subspace vectors usually have to be stored on disk. Therefore, we decided to use a slightly different scheme, which was also easier to implement. Steps 2a–2e are computed at the beginning using a starting guess for the CI wave function. Then a certain (small) number of subspace iterations are performed keeping the screening charges constant. When the maximum subspace dimension is reached, steps 2a–2e are performed again, and the subspace matrix $\mathbf{H}_{ij}^{\text{subsp}}$ is recomputed completely in the basis of the current approximations to the CI vector. Then a new set of Davidson iterations with fixed screening charges is performed. This scheme is repeated until convergence of the CI scheme and of the dielectric energy E_{diel} is achieved. Usually, the maximum subspace dimension is *nroot* + 2, where *nroot* is the number of roots to be calculated. Size-extensivity effects are computed a posteriori using a generalized Davidson approximation (denoted as MR-CISD+Q) [21, 22]). The size-extensivity correction is added to the final energy E_{tot} defined in step 2e after the outlying charge correction has been performed.

The non-equilibrium formalism for excited-state solvation described above has been implemented at the CI level only. The preceding MCSCF calculation is carried out at a state-averaged level and is only meant to provide optimized MOs for the MR-CISD calculation. MOs computed from gas phase MCSCF or MCSCF-COSMO calculations can be used for the MR-CISD calculation. The influence of different MO choices will be discussed later for specific examples. The modifications for the introduction of the non-equilibrium formalism into the just-described equilibrium continuum solvation scheme are straightforward. According to Eq. 10 the screening charges $\mathbf{q}(n^2,\Delta)$ are computed from the electrostatic potential given by the difference density Δ. The total screening charges $\mathbf{q}_{\text{ex}}^{\text{tot}}$ are computed from Eq. 10 using the ground state charges corrected for outlying charges. The dielectric energy is computed as

$$E^{\text{ex}}_{\text{diel}} = E^0_{\text{diel,corr}} + E^{\text{ex}}_{\text{diel}}(\Delta), \tag{11}$$

where $E^0_{\text{diel,corr}}$ is the dielectric energy of the ground state corrected for outlying charge and

$$E^{\text{ex}}_{\text{diel}} = \frac{1}{2}\sum_i q_i\left(n^2,\Delta\right)\Phi_i^X(\Delta). \tag{12}$$

The total energy is

$$E^{\text{ex}}_{\text{CI,tot}} = E^{\text{ex}}_{\text{CI}} - E^{\text{ex}}_{\text{diel}}$$

Otherwise, the Davidson iteration scheme is exactly the same as for the ground state. After convergence of the Davidson procedure the outlying charge correction is performed using the electrostatic potential $\Phi^X(\Delta)$ at the outer cavity.

In addition to the dielectric energy, the solvent-screened energy ΔE_{solv} is defined for a given state as the difference between the total energies in solution and in gas phase:

$$\Delta E_{\text{solv}} = E_{\text{CI,tot}}(\text{solution}) - E_{\text{CI}}(\text{gas}) \tag{13}$$

The use of symmetry is of great importance for the computational efficiency of the CI calculation. Therefore, a simple, but very effective symmetry treatment has been incorporated into the COSMO scheme. In calculations that don't use symmetry the algorithm for the selection of surface points is such that symmetry-nonequivalent points are chosen for the description of the entire surface. Therefore, this set of points could not be used directly. In order to solve this problem, only the symmetry unique surface points contained in a predefined section of the coordinate space are constructed, and the remaining ones are created via symmetry operations. Only Abelian point groups are considered. This set of screening points can be used directly in the computation of one-electron integrals over symmetry-adapted basis functions. Because of the reduction to symmetry-unique coordinate points, the set of surface points constructed with and without symmetry constraints does not agree exactly and the computed dielectric energies will not agree exactly either. However, differences are small (about 1% of the dielectric energy for the default choice of surface points) and can be quite safely neglected. More sophisticated methods for direct construction of a symmetrized set of surface points have been described in [40] and [41].

Computational details

Geometry optimizations based on the DFT/B3LYP method [42, 43, 44] have been performed for the electronic ground states in gas-phase as well as in solution for the molecules investigated. For the calculations in solution the COSMO approach [6, 7, 8] has been used. For formaldehyde, the TZVP basis set [45, 46] was selected, while for the other molecules the respective TZP was chosen [45, 46]. All DFT calculations have been performed by means of the TURBOMOLE program [8, 47].

Using these geometries, MR-CISD [47], MR-CISD + Q [21, 22], MR-AQCC [23, 24] and MR-AQCC-LRT [25] calculations have been performed on ground and excited states of the molecules studied in this paper. The first computational step consisted of a state-averaged MCSCF calculation [31] where the same weights were given to all states considered. The active space used for each molecule will be described below. The MCSCF orbitals are used in subsequent MR-CISD and MR-AQCC calculations. The final expansion space for the MR-CISD and MR-AQCC calculations was constructed from the reference configuration state functions (CSFs) and all single and double excitations thereof into all virtual orbitals. Unless stated differently, only reference configurations having the same symmetry as the state to be computed were selected and the interacting space restriction was applied [49]. In some cases all reference symmetries were chosen and the interacting space restriction was removed. These calculations will be marked by the specification *′-f* added to the name of the reference space. In all post-MCSCF calculations the core orbitals were kept frozen. If not mentioned differently, only gas phase optimized MCSCF orbitals were used in the MR-CISD calculations. The COLUMBUS program system [26, 27, 28] was used for all MR-CISD, MR-CISD + Q and MR-AQCC-LRT calculations. The atomic orbital (AO) integrals were computed using the DALTON program system [50]. In the systems considered in this paper, no Rydberg states are relevant for the n–π^* and π-π^* transitions, and hence such states have been neglected.

Formaldehyde

The complete active space CAS(6,4) used for the CASSCF calculations in formaldehyde consisted of six electrons and the $\sigma(5a_1)$, $\pi(1b_1)$, $n(2b_2)$ and $\pi^*(2b_1)$ orbitals. The $^1A_1$ ground state and the first excited state, $^1A_2$ (n–π^*), were computed. The 1–4a_1 and $1b_2$ orbitals were kept doubly occupied. In the MR-CISD and MR-CISD + Q calculations the same CAS(6,4) reference space was used as in the CASSCF calculations. Only the 1–2a_1 core orbitals were frozen. The Atomic Natural Orbitals (ANOs) of Widmark et al. [51] with the [3*s*,2*p*,1*d*] contraction for C and O and the [2*s*] contraction for H was used. The solvents used were hexane ($\varepsilon = 1.92$, $n = 1.37$), chloroform ($\varepsilon = 4.9$, $n = 1.45$), acetonitrile ($\varepsilon = 35.69$, $n = 1.34$) and water ($\varepsilon = 78.39$, $n = 1.33$).

Acrolein

The MCSCF calculations were performed using a scheme of restricted active orbitals (RAS), CAS and auxiliary (AUX) orbitals. The RAS consisted of the 9–13a′ (n(13a′) and σ(9–12a′) and 1a″ (π_1) orbitals, the CAS of the 2a″-6a″ (2a″, 3a″ and 4a″ are denominated as π_2, π_3^* and π_4^* orbitals, respectively) orbitals and the AUX of the 14–17a′ orbitals. Originally, the RAS space is doubly occupied and the AUX space is empty. Subsequently, single excitations were allowed from RAS into CAS and AUX and from CAS into AUX. The purpose of this selection was to include σ as well as π orbitals into the active space while keeping the size of the CSF expansion space manageable. The four lowest states: S_0 ($1^1A'$), S_1 ($1^1A''(n\text{-}\pi_3^*)$), S_2 ($2^1A''(n\text{-}\pi_4^*)$) and S_3 ($2^1A'(\pi\text{-}\pi^*)$) were computed.

Based on these MCSCF orbitals, several reference spaces have been studied in gas-phase calculations, especially for the π-π^* state in order to obtain an improved description of this state. The first choice involves a CAS(5,6) where the five orbitals consist of the oxygen lone pair orbital (13a′) and the four π orbitals (1–4a″). All other orbitals are either reference doubly occupied (RAS orbitals of the MCSCF calculation) or virtual (AUX and virtual orbitals of the MCSCF calculation). This reference space is denominated *ref1*. The second choice (*ref2*) is a CAS(4,4) in the four π orbitals 1–4a″. For the following reference spaces orbitals of type RAS and AUX were included, leading to the following choices: *ref*: RAS (12–13a′)/CAS(4,4)/AUX(14a′,5–6a″) and *ref4* RAS(10–13a′)/CAS(4,4)/AUX(14–17a′,5a″). Again, only single excitations from RAS into CAS and AUX and from CAS into AUX were allowed. The 6–31G* basis set [52] was used in most cases. Additionally, calculations with the 6–311G** and 6–311 + G** [53] basis sets containing diffuse functions and polarization functions on hydrogen, respectively, have been performed for the CAS (5,6) reference space. For the CAS (5,6) reference space calculations allowing all reference symmetries and removing the interacting space restriction have been carried out as well (*ref1-f*).

For solvent calculations the *ref1* reference space and the 6–31G* and 6–311 + G** basis sets have been used.

The solvents hexane, acetonitrile and water have been considered.

Pyrazine

For pyrazine a CAS(8,10) has been used for the MCSCF as well as the MR-CISD calculations, where the eight orbitals correspond to the symmetric ($n_+(6a_g)$) and antisymmetric ($n_-(5b_{1u})$) combinations of the nitrogen lonepairs plus the six π orbitals ($\pi_1(1b_{3u})$, $\pi_2(1b_{2g})$, $\pi_3(1b_{1g})$, $\pi_4^*(2b_{3u})$, $\pi_5^*(1a_u)$ and $\pi_6^*(2b_{2g})$). The molecule is located in the *yz* plane. The three lowest states have been averaged in the MCSCF calculation. This reference space is called *ref1*. A second reference space (*ref2*) was considered for the MR-CISD calculations, where the n orbitals are treated as RAS and the π orbitals as CAS. Only single excitations from RAS into CAS were allowed for the construction of the reference wave function. In this case a reference space without interactive space restriction and with all reference symmetries allowed (*ref2-f*) has also been employed. The 6–31G* basis set was chosen for the *ref1*, *ref2* and *ref2-f*, while the 6–311G** basis set was used for *ref2*.

Results and discussion

Formaldehyde

In the supplementary material the optimized ground state geometries of formaldehyde computed at the B3LYP/TZVP level are given. The calculated gas-phase geometry is in good agreement with the experimental geometry [54]. As we can see from these results, the C–O distance increases with the polarity of the solvent with the difference between the values in acetonitrile and water being almost negligible. The C–H bond distance decreases with increasing solvent polarity, with slightly smaller variations compared to the C–O bond distance.

In Table 1 and Table 2 the vertical n-π* excitation energies of formaldehyde are given using gas-phase optimized and solvent optimized geometries, respectively. The calculated vertical excitation energy in gas-phase is higher by about 0.36 eV than the experimental value. Similar results have been obtained by Mennucci et al. [20] in their MR-CI/6–31G** calculations. To get better agreement one would have to use larger reference spaces and size-extensivity corrections beyond the Davidson correction, as has been done in previous MR-AQCC-LRT calculations [30]. From a comparison of the calculated gas-phase excitation energy with the excitation energy in hexane one finds a non-negligible shift of ≈0.1 eV. As already pointed out by Klamt [14] such differences have to be taken into account when comparing calculated gas-phase excitations with experimental data in non-polar solvents.

Table 1. Total energies E_{total} and vertical excitation energies ΔE for formaldehyde using the gas-phase optimized geometry

States	E_{total} [a.u.][a]		ΔE [eV]	
	MR-CISD	MR-CISD + Q	MR-CISD	MR-CISD + Q
Gas-phase				
1^1A_1	0.197154	0.220281	–	–
1^1A_2(n-π*)	0.042199	0.067703	4.22	4.15 (3.79)[b]
Hexane				
1^1A_1	0.199640	0.222754	–	–
1^1A_2(n-π*)	0.040949	0.066680	4.32	4.25
Chloroform				
1^1A_1	0.202230	0.225395	–	–
1^1A_2(n-π*)	0.040312	0.066421	4.41	4.33
Acetonitrile				
1^1A_1	0.204260	0.227510	–	–
1^1A_2(n-π*)	0.040202	0.066733	4.46	4.37
Water				
1^1A_1	0.204464	0.227725	–	–
1^1A_2(n-π*)	0.040209	0.066785	4.47	4.38

[a] numbers given as – (E_{total} + 114)
[b] exp. value [80]

Table 2. Vertical excitation energies of formaldehyde using solvent-optimized geometries

States	E_{total} [a.u][a]		ΔE [eV]	
	MR-CISD	MR-CISD + Q	MR-CISD	MR-CISD + Q
Hexane				
1^1A_1	0.199690	0.222799	–	–
1^1A_2(n-π*)	0.041612	0.067231	4.30	4.23
Chloroform				
1^1A_1	0.202430	0.225620	–	–
1^1A_2(n-π*)	0.041872	0.066776	4.37	4.32
Acetonitrile				
1^1A_1	0.204656	0.227979	–	–
1^1A_2(n-π*)	0.042654	0.068895	4.41	4.33
Water				
1^1A_1	0.204866	0.228201	–	–
1^1A_2(n-π*)	0.042662	0.068950	4.41	4.33
Water[b]				
1^1A_1	0.205049	0.228196	–	–
1^1A_2(n-π*)	0.043076	0.068753	4.41	4.34

[a] numbers given as – (E_{total} + 114)
[b] using solvent-optimized MCSCF orbitals

The solvent effect on the excitation energy due to the use of a solvent-optimized geometry is small, though non-negligible (compare Table 1 and Table 2). For hexane one finds a decrease of 0.02 eV on going from the gas-phase geometry to the solvent-optimized geometry. For the more polar solvents acetonitrile and water the effects are greater (0.04 eV). This trend can be explained by the greater solvent effects on geometry by the more polar solvents. Therefore, geometry optimization for a given solvent becomes more important for more polar solvents. The calculated blue shift of the n-π* excitation is 0.19 eV (MR-CISD + Q values, solvent-optimized geometry) on going from gas phase to water.

Most of the calculations shown in Table 1 and Table 2 have been performed with MOs computed from a gas-phase MCSCF calculation. The last rows in Table 2 show the effect of MCSCF solvent-optimized orbitals. The use of MOs polarized in the reaction field has a very small effect on the final transition energy here.

Similar observations were made for the remaining molecules investigated in this work. However, it could be expected in cases where the solvation effect on ground geometries is more pronounced that the choice of polarized orbitals would also have more importance.

An experimental value of the blue shift for monomeric formaldehyde in water is not available due to the formation of oligomers. However it is likely to be between 0.07 and 0.23 eV, the values for oligomeric formaldehyde and acetone, respectively [13]. Several previous theoretical calculations on the blue shift of the n-π^* excitation in water have been performed. Aguilar et al. obtained a blue shift of 0.15 eV within the PCM model at the CISD level [13] and Mennucci et al. [20] reported a value of 0.12 eV at the MR-CI/6–31G** level using an integral equation formalism (IEF) of the continuum model. Yoshida and Kato [55] obtained 0.20 eV using the self-consistent field Molecular Ornstein-Zernike approach (MOZ-SCF), and Naka et al. found 0.25 eV given by RISM–SCF theory [56]. Mikkelsen et al. obtained only 0.07 eV for the blue shift of formaldehyde using a MCSCF reaction field theory [57]. In QM/MM calculations Dupuis and co-workers [58] computed a range of 0.12–0.31 eV dependent on the degree of solvation, Canuto and Coutinho [59] found a value of 0.27 eV, and Thompson [60] obtained a blue shift of 0.14 eV. Aguilar et al. [61] obtained a value of 0.18 eV using a mean field approximation for the solvent. Even though quite different methods have been used, most of the reported blue shifts agree quite well. Our computed value of 0.19 eV is also in good accord with these previous results.

Excitation to the n-π^* state leads to a decrease of the dipole moment [13, 20], which can be correlated in a first, simple picture with the blue shift of the transition. In Table 3 the dipole moments of formaldehyde in ground and excited state are collected showing the just-mentioned decrease. The calculated gas-phase dipole moment of 2.44 D agrees well with the experimental values of 2.33 D [62]. Mennucci and co-workers obtained 2.36 D and 1.55 D at the MR–CI/6–31G** level [20]. As compared to gas-phase values the dipole moments of both states increases upon solvation. The values for water as solvent agree well with those obtained by Aguilar et al. [13]. In the last two lines of Table 3 the dipole moment is given for solvent-optimized MCSCF orbitals as compared to gas phase optimized orbitals in the remaining cases. Not unexpectedly, first-order properties such as dipole moments are more sensitive to the choice of orbitals than excitation energies.

The dielectric energy and the solvent-screened energy ΔE_{solv} are given for formaldehyde in Table 4. ΔE_{solv} is defined according to Eq. 13 where the total energies are taken at the ground-state optimized structures for each solvent. ΔE_{solv} for the ground state is significantly larger in absolute value than that for the n-π^* state. Energy differences for the same geometry (see Table 1) are always slightly positive for the n-π^* state; in other words the non-equilibrium solvation leads to an increase in the total energy as compared to the gas phase. The same effect happens in the case of the n-π^* state of acrolein as well. This destabilization comes from the unfavorable interaction of the frozen ground-state screening charges with the electronic density of the excited state. If calculations under conditions of equilibrium solvation instead of non-equilibrium are performed for the n-π^* state, the total energy in solution is lower than the one for the gas phase. The finding of an increase in the total energy in the non-equilibrium solvation case is in contrast to the calculations reported by Mennucci et al. [20], where in the non-equilibrium case the total energies for solution are also always lower than in the gas phase.

Table 3. Dipole moment μ of formaldehyde using gas phase optimized geometries using the MR-CISD approach

States	μ [D]
Gas-phase	
1^1A_1	2.44 (2.33)[a]
1^1A_2(n-π^*)	1.28
Hexane	
1^1A_1	2.62
1^1A_2(n-π^*)	1.36
Chloroform	
1^1A_1	2.81
1^1A_2(n-π^*)	1.51
Acetonitrile	
1^1A_1	2.96
1^1A_2(n-π^*)	1.65
Water	
1^1A_1	2.98
1^1A_2(n-π^*)	1.66
Water[b]	
1^1A_1	3.05
1^1A_2(n-π^*)	1.76

[a] Exp.[62];
[b] using solvent optimized MCSCF orbitals

Table 4. Dielectric energy E_{diel} and solvent-screened energies ΔE_{solv} (MR-CISD + Q level) of formaldehyde using solvent optimized geometries

States	E_{diel} [a.u.]	ΔE_{solv} [eV]
Hexane		
1^1A_1	−0.002671	−0.0685
1^1A_2(n-π^*)	−0.004393	0.0128
Chloroform		
1^1A_1	−0.005858	−0.1453
1^1A_2(n-π^*)	−0.007869	0.0252
Acetonitrile		
1^1A_1	−0.008659	−0.2095
1^1A_2(n-π^*)	−0.010343	−0.0324
Water		
1^1A_1	−0.008947	−0.2155
1^1A_2(n-π^*)	−0.010579	−0.0339
Water[a]		
1^1A_1	−0.009342	−0.2154
1^1A_2(n-π^*)	−0.010953	−0.0286

[a] using the solvent-optimized MCSCF orbitals

Acrolein

The B3LYP/TZP approach yields a gas phase geometry in good agreement with the experimental geometry [63] (computed: $R_{C\text{–}C} = 1.473$ Å, $R_{C=C} = 1.333$ Å, $R_{C=O} = 1.210$ Å; exp.: $R_{C\text{–}C} = 1.470$ Å, $R_{C=C} = 1.345$ Å, $R_{C=O} = 1.219$ Å). A complete listing of geometry data for gas phase and solution can be found in the supplementary material. The C = O double bond increases by 0.01 Å on going from hexane to the more polar acetonitrile. From acetonitrile to water there is no change. The C–C bond decreases by the same amount. The C = C bond increases by only 0.001 Å from gas to water. These trends can be rationalized in a simple VB picture, where the ionic resonance structure with a positive charge on the terminal carbon atom and a negative charge on the oxygen atom is stabilized with increasing solvent polarity.

The vertical excitation energies of the n-π_3* and π-π* states of acrolein for the gas phase and oscillator strengths are given in Table 5. The n-π_3* state is well described by our calculations. Our best value is 3.85 eV (MR-CISD + Q with *ref1-f*), as compared to the experimental one of 3.75 eV [64]. The π-π* state is much more difficult to describe, as one can already see from the large size-extensivity corrections. An analysis of the final MR-CISD wave function shows that the wave function had a strong multireference character with 42% of the weight of the $\ldots\pi_1^2\pi_2^1\pi_3^1$ and 30% of the $\ldots\pi_1^1\pi_2^1\pi_3^2$ configuration. Moreover, the overlap with the CAS(5,6) reference wave function is only 0.67 even though the most important CSFs of the MRCI-SD wave function are contained in the set of the reference configurations. This means that a very large relaxation of the CI expansion coefficients for the reference configurations with respect to the CASSCF wave function has occurred. Therefore, calculations using different reference spaces with particular emphasis given to the π-π* state have been performed for the gas phase first. Additionally, several basis sets also including diffuse functions have been tested.

The *ref2* (CAS(4,4)) values computed with the 6–31G* basis set show a decrease in the excitation energy of the π-π* state from 7.76 eV (MR-CISD) to 7.40 eV (MR-CISD + Q) and a further decrease to 7.25 eV with MR-AQCC. As is expected, the inclusion of the n orbital into the active space has almost no effect on the excitation energy of the π-π* state (compare *ref1* (CAS(5,6)) values with *ref2* (CAS(4,4) results). The inclusion of reference doubly occupied σ orbitals of *ref1* into the RAS space and the use of AUX σ and π orbitals (*ref3* and *ref4*) decreases the π-π* excitation energy further. From *ref2* to *ref3* it is decreased by 0.20 eV and from *ref3* to *ref4* by an additional 0.05 eV (MR-CISD + Q values). The effect of removing the interactive space restriction and allowing all reference symmetries reduces the excitation energy from 7.39 eV (MR-CISD + Q, *ref1*) to 7.32 eV (MR-CISD + Q, *ref1-f*). The basis set has an important effect as well. Using the reference configuration set *ref1*, the basis sets 6–311G**, 6–311 + G* and 6–311 + G** lead to a reduction of 0.05 eV, 0.28 eV and 0.21 eV (MR-CISD + Q values), respectively, with respect to the 6–31G* basis. These numbers demonstrate the importance of diffuse functions for the description of the π-π* state, even though it is clearly valence-like as can be seen from $<z^2>$ expectation values (z is the coordinate perpendicular to the molecular plane).

Table 5. Total energies and vertical excitation energies of acrolein for the gas-phase

States	Ref. space	E_{total} [a.u.][a]			ΔE [eV]		
		MR-CISD	MR-CISD + Q	MR-AQCC-LRT	MR-CISD	MR-CISD + Q	MR-AQCC-LRT
$1^1A'$	*ref1*[b]	0.273012	0.339285	–	–	–	–
$1^1A''(n\text{–}\pi_3^*)$		0.133802	0.193796	–	$3.79[8\times10^{-6}]$[e]	3.96	–
$2^1A''(n\text{–}\pi_4^*)$		0.009613	0.069970	–	$7.17[5\times10^{-4}]$[e]	7.33	–
$2^1A'(\pi\text{–}\pi^*)$		−0.012081	0.067852	–	7.76[0.311][e]	7.39	–
$1^1A'$	*ref1*[c]	0.373726	0.448519	–	–	–	–
$2^1A'(\pi\text{–}\pi^*)$		0.090327	0.178808	–	7.71	7.34	–
$1^1A'$	*ref1*[d]	0.386755	0.457072	–	–	–	–
$1^1A''(n\text{-}\pi_3^*)$		0.245068	0.314360	–	3.85	3.88	–
$2^1A'(\pi\text{-}\pi^*)$		0.106151	0.193322	–	7.64	7.18	–
$1^1A'$	*ref1-f*[b]	0.274847	0.342407	–	–	–	–
$1^1A''(n\text{-}\pi_3^*)$		0.137225	0.201011	–	3.74	3.85(3.75)[f]	–
$2^1A''(n\text{-}\pi_4^*)$		0.013508	0.078395	–	7.11	7.18	–
$2^1A'(\pi\text{-}\pi^*)$		−0.009427	0.073241	–	7.74	7.32	–
$1^1A'$	*ref2*[b]	0.272746	0.338935	0.343741	–	–	–
$2^1A'(\pi\text{-}\pi^*)$		−0.012469	0.066916	0.077356	7.76	7.40	7.25
$1^1A'$	*ref3*[b]	0.287640	0.346151	–	–	–	–
$2^1A'(\pi\text{-}\pi^*)$		0.011696	0.081403	–	7.51	7.20	–
$1^1A'$	*ref4*[b]	0.300519	0.351036	–	–	–	–
$2^1A'(\pi\text{-}\pi^*)$		0.028967	0.088179	–	7.39	7.15(6.41)[f]	–

[a] numbers given as − (E_{total} + 191)
[b] 6–31G*
[c] 6–311G**
[d] 6–311 + G**
[e] calculated oscillator strength
[f] Exp. [64]

Combining the individual effects – basis set (0.21 eV), extension of the reference space (0.25 eV), all reference symmetries/no interactive space (0.07 eV) and MR-AQCC-LRT (0.15 eV) – gives an approximate total correction of 0.68 eV with respect to the *ref1*/6–31G* calculation, leading to an estimate of 6.71 eV for the π-π^* excitation energy from our calculations. The experimental value is 6.41 eV [64].

To our knowledge, there exist very few previous calculations of this kind. Valenta and Grein [65] obtained 7.53 eV for the vertical excitation energy of the π-π^* state using the MRD-CI approach and Dunning's ($9s5p/4s2p$) contracted basis set for C and O, and the ($4s/2s$) basis for H. Davidson and Nitzsche [66] obtained a similar high value of 7.52 eV using a CISD calculation with symmetrically orthogonalized π and π^* orbitals obtained from a non-orthogonal SCF procedure.

Vertical excitation energies for acrolein are given for several solvents using gas-phase (Table 6) and solvent-optimized (Table 7) geometries. The geometries have a relatively small effect on calculated vertical excitation energies. A decrease of 0.08 eV is obtained for the n-π_3^* and of 0.03 eV for the π-π^* excitation when going from the gas-phase optimized to the solvent optimized geometries. A quantitative agreement between the calculated and experimental excitation energies in solvent is not to be expected, since the CAS(5,6) reference space is not large enough for a completely satisfactory description of the π-π^* state. Therefore, we concentrate on the comparison of computed solvent shifts with experimental ones. The n-π_3^* state is red-shifted by 0.04 eV for hexane and blue-shifted by 0.19 eV for water (for experimental values, see Table 5 and Table 7). The computed shifts can be obtained as the difference of the solvent-screened energies ΔE_{solv} (see Table 8) between excited state and ground state. In this table, dielectric energies for the individual states are also given. The respective computed solvatochromic shifts of the n-π_3^* state for hexane and water are 0.10 eV and 0.21 eV. Therefore, a blue shift is found for hexane in contrast to the small red shift observed experimentally. The shifts for water agree very well. For the π-π^* excitation the experimental red shifts are 0.45 eV (hexane) and 0.51 eV (water) (see Table 5 and Table 7). Respective computed values are 0.24 eV (hexane) and 0.43 eV (water). The large experimental shift of the π-π^* excitation for hexane is reproduced only partially by our calculations. Agreement for water is good. To our knowledge only one previous calculation on the solvatochromic effects for acrolein exists (refer-

Table 6. Total energies and vertical excitation energies of acrolein using the gas-phase optimized geometry and the *ref1*/6–31G* approach

States	E_{total} [a.u.][a]		ΔE [eV]	
	MR-CISD	MR-CISD + Q	MR-CISD	MR-CISD + Q
Hexane				
$1^1A'$	0.275789	0.342014	–	–
$1^1A''(n\text{-}\pi_3^*)$	0.132886	0.192882	3.89	4.06
$2^1A'(\pi\text{-}\pi^*)$	−0.003558	0.079457	7.60	7.14
Water				
$1^1A'$	0.280905	0.347230	–	–
$1^1A''(n\text{-}\pi_3^*)$	0.132497	0.192836	4.04	4.20
$2^1A'(\pi\text{-}\pi^*)$	0.005787	0.090698	7.49	6.98

[a] numbers given as – (E_{total} + 191)

Table 7. Total energies and vertical excitation energies of acrolein using the solvent optimized geometries and the *ref1* approach

States	Basis set	E_{total} [a.u.][a]		ΔE [eV]		
		MR-CISD	MR-CISD + Q	MR-CISD	MR-CISD + Q	Exp.
Hexane						
$1^1A'$	6–31G*	0.275915	0.342118	–	–	–
$1^1A''(n\text{-}\pi_3^*)$		0.133821	0.193711	3.87	4.04	–
$2^1A'(\pi\text{-}\pi^*)$		−0.003048	0.079568	7.59	7.14	–
Acetonitrile						
$1^1A'$		0.281194	0.347476	–	–	–
$1^1A''(n\text{-}\pi_3^*)$		0.136260	0.196153	3.94	4.12	–
$2^1A'(\pi\text{-}\pi^*)$		0.007939	0.091773	7.44	6.96	–
Water						
$1^1A'$		0.281415	0.347708	–	–	–
$1^1A''(n\text{-}\pi_3^*)$		0.136330	0.196240	3.95	4.12	–
$2^1A'(\pi\text{-}\pi^*)$		0.008227	0.092114	7.43	6.95	–
Hexane						
$1^1A'$	6–311 + G**	0.38968739	0.460047	–	–	–
$1^1A''(n\text{-}\pi_3^*)$		0.2446395	0.313889	3.95	3.98	3.71[b]
$2^1A'(\pi\text{-}\pi^*)$		0.1157666	0.2048513	7.45	6.94	5.96[b]
Acetonitrile						
$1^1A'$		0.3949562	0.465675	–	–	–
$1^1A''(n\text{-}\pi_3^*)$		0.2461761	0.315536	4.05	4.08	–
$2^1A'(\pi\text{-}\pi^*)$		0.12689237	0.217417	7.29	6.75	–
Water						
$1^1A'$		0.3951856	0.465926	–	–	–
$1^1A''(n\text{-}\pi_3^*)$		0.2462173	0.3156000	4.05	4.09	3.94[c]
$2^1A'(\pi\text{-}\pi^*)$		0.12718841	0.2177749	7.29	6.75	5.90[d]

[a] numbers given as −(E_{total} + 191)
[b] ref. [75]
[c] ref. [76]
[d] ref. [77]

Table 8. Dielectric energy E_{diel} and solvent-screened energies ΔE_{solv} (MR-CISD + Q level) of acrolein using solvent optimized geometries and the CAS(5,6)/6–311 + G** approach

States	E_{diel} [a.u.]	ΔE_{solv} [eV]
Hexane		
$1^1A'$	−0.003086	−0.0810
$1^1A''(n\text{-}\pi_3^*)$	−0.005031	0.0128
$2^1A'(\pi\text{-}\pi^*)$	−0.006093	−0.3137
Acetonitrile		
$1^1A'$	−0.009764	−0.2341
$1^1A''(n\text{-}\pi_3^*)$	−0.011705	−0.0320
$2^1A'(\pi_2\text{-}\pi_3^*)$	−0.012829	−0.6556
Water		
$1^1A'$	−0.010087	−0.2409
$1^1A''(n\text{-}\pi_3^*)$	−0.011969	−0.0337
$2^1A'(\pi\text{-}\pi^*)$	−0.013051	−0.6654

Table 9. Dipole moment μ of acrolein for the gas phase optimized geometry and the MR-CISD/CAS(5,6)/6–311 + G** approach

State	μ [D]
Gas-phase	
$1^1A'$	3.09
$1^1A''(n\text{-}\pi_3^*)$	0.85
$2^1A'(\pi\text{-}\pi^*)$	5.67
Hexane	
$1^1A'$	3.34
$1^1A''(n\text{-}\pi_3^*)$	0.90
$2^1A'(\pi\text{-}\pi^*)$	6.71
Acetonitrile	
$1^1A'$	3.84
$1^1A''(n\text{-}\pi_3^*)$	1.28
$2^1A'(\pi\text{-}\pi^*)$	7.51
Water	
$1^1A'$	3.89
$1^1A''(n\text{-}\pi_3^*)$	1.30
$2^1A'(\pi\text{-}\pi^*)$	7.53

ence interaction site model (RISM)-SCF calculations [67]). The computed shift of 0.19 eV for the n-π_3* excitation in water agrees well with our result.

The lowering of the dipole moment for the n-π_3* state and its increase for the π-π* state (see Table 9) illustrate the computed blue and red shifts, respectively. The contribution of the dipolar valence structure discussed in connection with the geometry changes on solvation leads to a greater stabilization of the π-π* state as compared to the n-π_3* state on going from hexane to water. The former is stabilized by 0.35 eV while the latter is stabilized by just 0.05 eV (see Table 7). Similarly, the importance of conjugation on the stability of the π-π* state has been stressed by Morukuma et al. [68].

Pyrazine

The optimized geometries of pyrazine computed with the B3LYP/TZP approach and the experimental gas-phase geometry are given in the supplementary material. The calculated gas-phase geometry is in very good agreement with the experimental one [69]. The solvent effect on the pyrazine geometry is almost negligible with bond distances changing by at most 0.001 Å and bond angles by at most 0.3°.

For the gas phase, five states have been calculated using the *ref1*/6–31G* method (Table 10). Besides the ground state, these are the π-π* state and three states arising from excitations of symmetric/antisymmetric combinations of the lone pair orbitals into the π* orbitals. In the remaining calculations only the two lowest excitations (n_+-π_4* and π-π*) have been treated. The π-π* state has significant multireference character. The configuration $\ldots\pi_3^1\pi_4^1$ has a weight of 54% and the next important configuration $\ldots\pi_2^1\pi_5^1$ has a contribution of 16% in the MR-CISD wave function. The calculated gas-phase excitation energy of the n_+-π_4* state (best value 4.21 eV (MR-AQCC, *ref2*/6–311G**) is in good agreement with the value of 4.15 eV obtained by

Table 10. Total energies and vertical excitation energies of pyrazine for the gas-phase

Ref. space	States	E_{total} [a.u.][a]			ΔE [eV]		
		MR-CISD	MR-CISD + Q	MR-AQCC	MR-CISD	MR-CISD + Q	MR-AQCC
ref1[b]	1^1A_g	0.409086	0.509696	0.531929	–	–	–
	$1^1B_{3u}(n_+\text{-}\pi_4^*)$	0.240931	0.346515	0.373715	4.58	4.44[9.05×10^{-3}][d]	4.31
	$1^1B_{2u}(\pi\text{-}\pi^*)$	0.217567	0.317556	0.340228	5.21	5.23[5.13×10^{-2}][d]	5.22
	$1^1A_u(n_+\text{-}\pi_5^*)$	0.202455	0.315232	–	5.62	5.29[0.00][d]	–
	$1^1B_{2g}(n_-\text{-}\pi_4^*)$	0.188607	0.292063	–	6.00	5.92[5.65×10^{-2}][d]	–
ref2[b]	1^1A_g	0.407721	0.508233	–	–	–	–
	$1^1B_{3u}(n_+\text{-}\pi_4^*)$	0.240612	0.346145	–	4.55	4.41	–
	$1^1B_{2u}(\pi\text{-}\pi^*)$	0.216711	0.316540	–	5.20	5.22	–
ref2-f[b]	1^1A_g	0.415588	0.521799	–	–	–	–
	$1^1B_{3u}(n_+\text{-}\pi_4^*)$	0.249908	0.363343	–	4.51	4.31	–
	$1^1B_{2u}(\pi\text{-}\pi^*)$	0.224288	0.329939	–	5.20	5.22	–
ref2[c]	1^1A_g	0.515336	0.626740	0.653433	–	–	–
	$1^1B_{3u}(n_+\text{-}\pi_4^*)$	0.350110	0.466631	0.498665	4.50	4.36	4.21
	$1^1B_{2u}(\pi\text{-}\pi^*)$	0.325331	0.435962	0.462846	5.17	5.19(4.81)[e]	5.19

[a] numbers given as – (E_{total} + 263);
[b] 6–31G* basis;
[c] 6–311G** basis;
[d] oscillator strengths are given in brackets;
[e] exp. ref. [71]

Table 11. Total energies and vertical excitation energies of pyrazine in solution using solvent-optimized geometries

Ref. space	States	E_{total} [a.u.][a]		ΔE [eV]	
		MR-CISD	MR-CISD + Q	MR-CISD	MR-CISD + Q
Isooctane					
ref1[b]	1^1A_g	0.412538	0.513069	–	–
	$1^1B_{3u}(n_+\text{-}\pi_4^*)$	0.241827	0.347455	4.65	4.51
	$1^1B_{2u}(\pi\text{-}\pi^*)$	0.221672	0.321630	5.19	5.21
ref2[c]	1^1A_g	0.5187033	0.629988	–	–
	$1^1B_{3u}(n_+\text{-}\pi_4^*)$	0.3507484	0.467267	4.57	4.43(3.92)[d]
	$1^1B_{2u}(\pi\text{-}\pi^*)$	0.3292656	0.439837	5.15	5.17(4.75)[e,f]
Acetonitrile					
ref1[b]	1^1A_g	0.418158	0.518759	–	–
	$1^1B_{3u}(n_+\text{-}\pi_4^*)$	0.245225	0.351239	4.71	4.56(3.94)[d]
	$1^1B_{2u}(\pi\text{-}\pi^*)$	0.227952	0.328071	5.18	5.19(4.75)[f]
ref2[c]	1^1A_g	0.524180	0.635472	–	–
	$1^1B_{3u}(n_+\text{-}\pi_4^*)$	0.353838	0.470649	4.63	4.48
	$1^1B_{2u}(\pi\text{-}\pi^*)$	0.335347	0.446013	5.14	5.15
Water					
ref1[b]	1^1A_g	0.418389	0.518997	–	–
	$1^1B_{3u}(n_+\text{-}\pi_4^*)$	0.245410	0.351446	4.71	4.65
	$1^1B_{2u}(\pi\text{-}\pi^*)$	0.228177	0.328305	5.18	5.19
ref2[c]	1^1A_g	0.524402	0.635698	–	–
	$1^1B_{3u}(n_+\text{-}\pi_4^*)$	0.354019	0.470847	4.64	4.49(4.11)[d]
	$1^1B_{2u}(\pi_3\text{-}\pi_4^*)$	0.335557	0.446229	5.14	5.16(4.75)[f]

[a] numbers given as $-(E_{\mathrm{total}} + 263)$
[b] 6–31G* basis
[c] basis 6–311G**
[d] ref [78]
[e] in cyclohexane
[f] ref [79]

Sobolewski et al. [70] using a Davidson-corrected MR-CI approach and a DZP basis set. For the π-π^* state our best calculated (MR-AQCC and 6–311G** basis set) value is 0.38 eV higher than the experimental value of 4.81 eV [71], but in good agreement with the value of 5.14 eV obtained in ref [70]. Larger basis set/CI expansions would certainly improve the excitation energies further. Our calculated oscillator strength values of 9.05×10^{-3} and 5.13×10^{-2} for the n_+-π_4^* and π-π^* states (see Table 10) are in good agreement with the experimental values of 5.7×10^{-3} and 6.2×10^{-2} [71].

Excitation energies for different solvents are documented in Table 11. Dielectric energies and solvent-screened energies ΔE_{solv} are given in Table 12. As in the previous cases, we discuss solvent shifts in comparison to experimental values. All computed solvatochromic shifts discussed below are derived from the largest calculation (ref2/6–311G**) collected in Table 12. For experimental data see Table 11. In case of the n_+-π_4^* transition, experimental solvatochromic shifts with respect to the gas phase cannot be given because of the ambiguities of the assignment in the gas phase. We compute a shift of 0.07 eV from gas-phase to isooctane. The experimental shift from isooctane to acetonitrile is 0.02 eV as compared to the computed value of 0.05 eV. Our value is in good agreement with the value of 0.04 eV obtained by Ågren et al. [72] by using a multiconfiguration self-consistent reaction field theory. From acetonitrile to water an experimental shift of 0.17 eV is found, whereas a value of only 0.01 eV is computed. This discrepancy is certainly due to the lack of specific, hydrogen-bonded interactions in the continuum model. An explicit inclusion of solvent molecules forming hydrogen bonds with the N atoms would be required for a more quantitative agreement [73] in this case. For the π-π^* state practically no shift is observed both experimentally and in our calculations. This is different to the situation found in acrolein where a large increase of the dipole moment and a concomitant solvatochromic shift was found.

Table 12. Dielectric energy E_{diel} and solvent-screened energies ΔE_{solv} (MR-CISD + Q level) of pyrazine, using solvent-optimized geometries and the *ref2*/6–311G** approach

States	E_{diel} [a.u.]	ΔE_{solv} [eV]
Isooctane		
1^1A_g	−0.003475	−0.0884
$1^1B_{3u}(n_+\text{-}\pi_4^*)$	−0.004305	−0.0173
$1^1B_{2u}(\pi\text{-}\pi^*)$	−0.003519	−0.1054
Acetonitrile		
1^1A_g	−0.009603	−0.2376
$1^1B_{3u}(n_+\text{-}\pi_4^*)$	−0.010364	−0.1093
$1^1B_{2u}(\pi\text{-}\pi^*)$	−0.009643	−0.2735
Water		
1^1A_g	−0.009873	−0.2438
$1^1B_{3u}(n_+\text{-}\pi_4^*)$	−0.010609	−0.1147
$1^1B_{2u}(\pi\text{-}\pi^*)$	−0.009911	−0.2794

Conclusions

The continuum solvation model COSMO has been implemented into the COLUMBUS program system at the MCSCF and MR-CISD levels. Both equilibrium and non-equilibrium solvation processes for electronic excitations can be treated. Systematic investigations concerning various reference spaces, basis sets, solvent-optimized geometries and MOs have been performed for a multitude of excited valence states of formaldehyde, acrolein and pyrazine. In the cases treated here, the solvent effect on geometries was non-negligible but rather small. The same conclusions could be made concerning solvent-optimized MOs. The computed solvatochromic shifts were in good agreement with experimental shifts within the limits of the continuum solvation model.

The largest CI dimensions treated in this work were about 74 million. The computations were performed on standard Linux PCs. In the next step the COSMO implementation will be included in the parallel CI program [74] currently allowing calculations with CI dimensions of 400–500 million on Linux PC clusters. Implementation of COSMO into the MR-AQCC approach is also straightforward.

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