Macroscopic solvation of molecules in excited states: An MCSCF model including solvent polarization effects – I

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Abstract. An MCSCF model including the effects of solvent polarization is developed. The model is applied within the limitations of INDO approximations to look into the dominant effects of solvent polarization on the electronic structure in the excited states of a model system (e.g. $n\pi^*$ states of H_2CO). Important features of macroscopic solvation-induced reorganization of electron density and some consequence thereof are noted.

Keywords. MCSCF model; macroscopic solvation; solvent polarization model; MCSCF-reaction field solvation model: INDO-MCSCF solvation model.

1. Introduction

Environmental effect on molecular electron density and structure is an interesting area of research on many counts, and this field has been receiving considerable attention in recent years. In the quantum chemical context microscopic (specific) solvation is traditionally treated by a supermolecular approach which considers the solute–solvent pair as a single quantum mechanical system. Any nonspecific solvations arising from the interaction between the solute molecule and the electric field arising from the solvent polarization are usually taken care of by appealing to some statistical mechanical approach (e.g. the Monte Carlo or molecular dynamics methods). The execution of this step, however, requires an intermolecular potential surface which is usually modelled by the Born–Oppenheimer surface for the solute–solvent pair. This approach suffers from the problem that macroscopic solvation can sometimes have a profound influence on the electron density distribution within the solute molecule and can therefore affect the intermolecular surface itself. In addition, it could also affect intramolecular motions within the solute molecule – thereby affecting the rotational–vibrational spectra, polarizability, reactivity etc. It is, therefore important to have a clear understanding of the type and extent of electron density reorganization that macroscopic solvation can bring about. The problem of studying bulk solvent effects within the framework of quantum chemical methods has been tackled by a number of workers in recent years (Klopman 1967; Germer 1974; Constanciel and

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Tapia 1978; Miertus and Kysel 1977; Tapia 1982; Karelson *et al* 1986). The different methods differ merely in their ways of modelling the solvent reaction field potential which is incorporated in the "free molecular electronic Hamiltonian" in a suitable manner. In the image charge model of the continuum the solute is represented by an assembly of partial charges and the solvent reaction field by appropriate image charges *created* in the *bulk-solvent* by polarization. This model has shown some degree of promise (Germer 1974) and has been further refined by Constanciel and Tapia (1978). Conceptually better models based on the Kirkwood–Onsager theory of electrostatic solvation have been suggested and tested. Each of these models has a certain degree of "semiempirical content". At best, these models can be regarded as "semiclassical–semiempirical" models. However, they have never been extensively tested, a fact responsible in a big way for the lack of further systematic refinement of the available models.

In this context we have embarked upon a project for studying the macroscopic solvation of molecules in the excited electronic states. The reasons for focussing our attention on the excited states are two-fold. Firstly, these states are frequently more polar so that macroscopic solvation could be important. Secondly, a rich variety of photochemical processes do occur in molecules when electronically excited. Our theoretical understanding about the influence of solvent polarization on these reactions is rather limited. In what follows, we present a multiconfiguration self-consistent field (MCSCF) based model that incorporates the effects of solvent polarization in a self-consistent fashion within the framework of an image charge representation on the solvent reaction field. Although our primary interest has been in molecular excited states, the same methodology can be applied with equal case to investigate macroscopic solvation of molecules in the ground state.

2. Method

To account for the effects of solvent polarization in an MCSCF framework we solve a solvent-modified first order MCSCF orbital equation (cf. master equation, McWeeny 1955, 1968),

$$\tilde{V} = S\tilde{T}\tilde{\lambda}, \tag{1}$$

where $\tilde{V}$ represents the "solvent-modified" MCSCF operator, $\tilde{T}$ represents the modified coefficient matrix defining the solvent-modified MCSCF orbitals as linear combinations of the basis set of expansion (χ) as follows:

$$\tilde{\phi} = \chi\tilde{T}. \tag{2}$$

The relevant CI problem and (1) are to be solved alternately.

Equation (1) can be arrived at by applying variational consideration to an energy functional (E) containing the solute–solvent interaction term (Tapia and Goscienski 1975; Constanciel and Tapia 1978),

$$\tilde{E} = \langle \Psi|H|\Psi \rangle + \lambda \langle \Psi|\Psi \rangle - \tfrac{1}{2} \langle \Psi|v|\Psi \rangle. \tag{3}$$

In (3) H represents the solute Hamiltonian and v represents the solute–solvent interaction Hamiltonian. In the image charge representation, the solvent reaction

field potential acting over the solute molecule $[\bar{V}(R)]$ is defined through an image charge density operator acting on the charged particles of the solute,

$$\bar{V}(R) = \int dR' \left\langle \Psi \frac{|\hat{\rho}_v(R')|}{|R - R'|} \Psi \right\rangle, \tag{4}$$

where $\hat{\rho}_v(R')$ is the image charge density operator defined by

$$\hat{\rho}_v(R') = f(D) \left\{ \sum_A Z_A \delta(R' - R_A) - \sum_{i=1}^{n} \delta(R' - r_i) \right\}. \tag{5}$$

In (4) the interaction has clearly been averaged over the solvent coordinates.

In (5) A represents an atom in the molecule, n is the number of electrons, $f(D) = -(1 - D^{-1})$ where the effective dielectric constant $D = \varepsilon^{\frac{1}{2}}$, ε being the macroscopic dielectric constant of the solvent. The solute–solvent interaction Hamiltonian can therefore be written as,

$$H'_{int} = \sum_A Z_A \bar{V}(R_A) - \sum_{i=1}^{n} \bar{V}(r_i).$$

In the first summation it is implicitly assumed that the self-energy components corresponding to the core-charges are of the form Z_A^2/a_A (a_A is an appropriate cavity radius). The interaction energy $\langle E' \rangle = \langle H_{int} \rangle$ is given by

$$E' = f(D) \left[\sum_{A,B} \frac{Z_A Z_B}{|R_A - R_B| + a_A \delta_{AB}} - \sum_B \sum_{\mu\nu} Z_B P_{\mu\nu} \frac{\int \chi_\mu^*(r) \chi_\nu(r) dr}{|R_B - r|} \right. \quad \rho_{2_{\mu\nu}}$$
$$\left. - \sum_A \sum_{\mu\nu}^{AO} Z_A P_{\mu\nu} \frac{\int \chi_\mu^*(r) \chi_\nu(r) dr}{|r - R_A|} + \sum_{\mu\nu\lambda\sigma} \rho_{2_{\mu\nu\lambda\sigma}} \frac{\iint \chi_\mu^*(r) \chi_\nu(r) \chi_\lambda^*(r') \chi_\sigma(r') dr \, dr'}{|r - r'|} \right],$$

$P_{\mu\nu} = [TP_1 T^+]_{\mu\nu}$, P_1 being the one-electron density matrix in the ϕ basis and P_2 the corresponding 2-electron density matrix. The solvent-modified MCSCF equation at this particular level of representation of the solvent reaction field is arrived at by making $\langle \tilde{\Psi}|H|\tilde{\Psi} \rangle + \langle H'_{int} \rangle$ stationary (w.r.t. variations in $\tilde{\Psi}$) and is given by (a more detailed derivation will be presented elsewhere),

$$\bar{V} = \bar{h} \tilde{T} \tilde{P}_1 + \bar{Z}, \tag{6}$$

where $\bar{h}$ represents the one-electron part of the MCSCF operator including solvent polarization effects, $\tilde{P}_1$ stands for the one-electron density matrix in the ϕ basis. The solvent-modified two-electron interaction matrix is represented by $\tilde{Z}$, a typical element of which reads

$$\tilde{Z}_{pi} = \sum_{jkl}^{MO} \sum_{qrs}^{AO} \tilde{T}_{jq}^+ \langle pq|rs \rangle \tilde{T}_{rk} \tilde{T}_{sl} \tilde{P}_{2kl,ij}. \tag{7}$$

$\tilde{P}_2$ represents the two-electron density matrix in the $\tilde{\phi}$ basis. Although an *ab initio* implementation of the scheme outlined is perfectly possible, it would be quite expensive in terms of computer time. To cut down computational costs, we have implemented the scheme numerically under the standard set of INDO approximations (Pople and

Segal 1966). This particular mode of parametrization is adopted on the basis of its very satisfactory performance in the calculation of molecular electronic structures of small- and medium-sized excited-state molecules in the absence of any solvation (Das *et al* 1986, 1989). The different matrix elements are defined as,

$$h_{pq}^{core} = (h_{INDO}^{core})_{pq} - v_{pq},$$
(8)

where (h_{INDO}^{core}) represents the standard INDO core matrix elements and v_{pq} represents the solvent correction term in the image charge model of the solvent reaction field. The different matrix elements of v are parametrized as follows:

$$v_{pp}^{A} = f(D) \sum_{B} (Z_B - \tilde{P}_B) g_{AB}^{0}, \quad \left(P_B = \sum_{\mu \in B} \tilde{P}_{\mu\nu} \right),$$
(9)

$$v_{pq}^{AA} = 0, \quad (\chi_p, \chi_q, \text{ both on A}),$$
(10)

$$v_{pq}^{AB} = \tfrac{1}{2} S_{pq}^{AB} \{ v_{pp}^{A} + v_{qq}^{B} \}, \quad \{\chi_p \text{ on A}, \chi_q \text{ on B}\}.$$
(11)

The diagonal elements of v incorporate standard INDO correction terms which means that the g_{AA}^{0} term will depend on the AO index p. The off-diagonal (two-centre elements of v) are evaluated by invoking Mulliken's approximation. The matrix $\tilde{P}$ is defined as follows

$$\tilde{P} = \tilde{T} P_1 \tilde{T}^{+}.$$

The master equation (2) is solved by adopting a variant of the orthogonal gradient technique developed in our laboratory (Mukherjee 1978; Bhattacharyya and Mukherjee 1979, 1981; Das *et al* 1986, 1989).

3. Results and discussion

We report here some interesting results obtained by applying the model outlined in the preceeding section to the study of the effects of macroscopic solvation on the molecular electronic structure of a prototypical system e.g. formaldehyde in the $n\pi^*$ states. The trial wavefunction ($\tilde{\Psi}$) used has been

$$\tilde{\Psi} = \frac{1}{2^{\frac{1}{2}}} \{ |\phi_1 \bar{\phi}_1 \cdots \phi_i \bar{\phi}_j \cdots \phi_n \bar{\phi}_n| + (-1)^S |\phi_1 \bar{\phi}_1 \cdots \phi_j \bar{\phi}_i \cdots \phi_n \bar{\phi}_n| \},$$

where ϕ_i represents the nonbonding orbital and ϕ_j is a π^* orbital. $S = 0$ for the singlet $n\pi^*$ state and 1 for the corresponding triplet. Molecular structural parameters for H_2CO in the $^{1,3}n\pi^*$ states have been taken from the work of Das *et al* (1986). Actual bond lengths and angles used are the averages of the corresponding quantities in the singlet and triplet $n\pi^*$ states. The planar configuration of the molecule is used throughout.

3.1 *Solvation-induced changes on the electron-density distribution and their effects*

Table 1 reports net electron densities on different atoms in $n\pi^*$ states of the form-aldehyde molecule in media of widely different macroscopic dielectric constant (ε).

Table 1. Macroscopic solvation induced reorganization of electron density in the $^{1,3}n\pi^*$ states of formaldehyde (planar).

Dielectric constant of the solvent (ε)	Net electron density on different atoms ($^3n\pi^*$ states)				Net electron density on different atoms ($^1n\pi^*$ state)			
	H_1	H_2	C	O	H_1	H_2	C	O
1·0	0·9600	0·9600	4·0005	6·0793	0·9627	0·9627	3·9715	6·1031
10·0	0·9404	0·9404	3·9761	6·1430	0·9443	0·9443	3·9375	6·1738
20·0	0·9334	0·9334	3·9780	6·1552	0·9411	0·9411	3·9340	6·1837
30·0	0·9321	0·9321	3·9697	6·1661	0·9362	0·9362	3·9292	6·1984
40·0	0·9302	0·9302	3·9685	6·1711	0·9344	0·9444	3·9276	6·2036
50·0	0·9288	0·9288	3·9677	6·1745	0·9033	0·9033	4·0226	6·1707
60·0	0·9320	0·9320	3·9257	6·2102	0·9320	0·9320	3·9257	6·2102
70·0	0·9269	0·9269	3·9667	6·1795	0·9312	0·9312	3·9251	6·2125
80·0	0·9262	0·9262	3·9663	6·1813	0·9305	0·9305	3·9245	6·2144

An increase in solvent polarity is seen to reduce the electron density on the carbonyl carbon atom and increase it on the carbonyl oxygen. It essentially means that macroscopic solvent polarization increases the polarity of the carbonyl group in the $n\pi^*$ state. The increased polarity of the $>C^{\delta+}=O^{\delta-}$ group in more polar media indirectly suggests that the intensity of $n\pi^*$ transition should increase with solvent polarity. This is in agreement with experimental findings (Liptay 1966; Robinson 1967; Senthilnathan and Singh 1973). A perusal of table 1 also indicates that the $>C=O$ group is more polar in the $^1n\pi^*$ state irrespective of the presence or absence of macroscopic solvation. The polarity as noted already, increases monotonically with increase in solvent polarity. The relative rate of increase of the polarity, however, is different in the singlet and triplet states. We have monitored this by calculating the increase in $>C=O$ group moment (the charge-separation component only) relative to its solvent-free counterpart in the corresponding $n\pi^*$ states as functions of solvent dielectric constant (figure 1). The rate of increase is seen to be higher in the
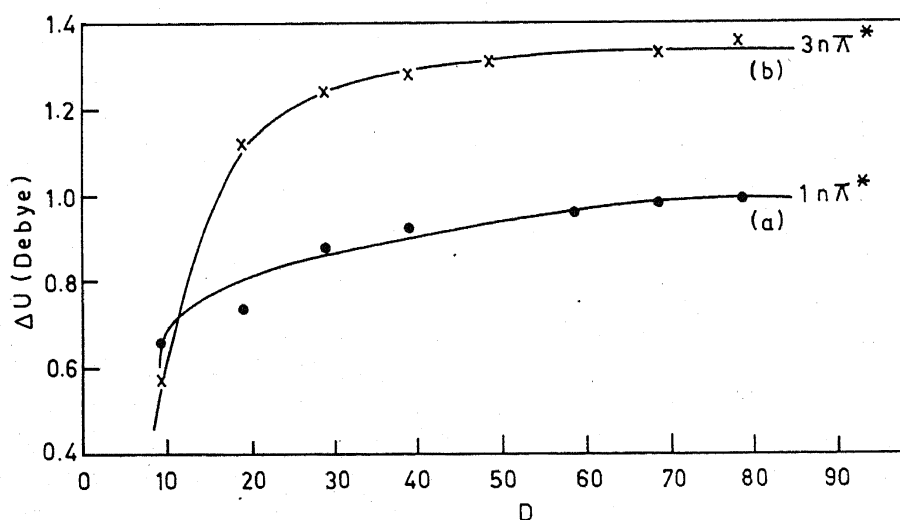
Figure 1. Variations in the macroscopic solvation induced changes in the carbonyl group moment as functions of solvent polarity, (a) H_2CO in $^1n\pi^*$ states, and (b) H_2CO in $^3n\pi^*$ state.
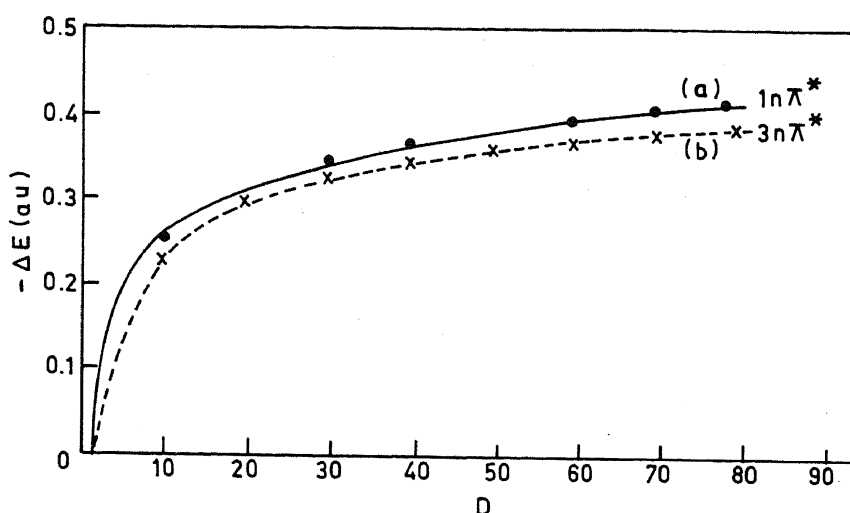
Figure 2. Variations in the macroscopic solvation energy as functions of solvent polarity, (a) H_2CO in a $^1n\pi^*$ state, and (b) H_2CO in a $^3n\pi^*$ state.

triplet $n\pi^*$ states. It should be pointed out here that the computed $>C=O$ group moment in the $^1n\pi^*$ state is much higher than its triplet state counterpart in the absence of a solvent. It is only the solvent-induced increase of the polarization of the $>C=O$ group that increases faster with the increase in solvent polarity in the $^3n\pi^*$ states. A look at table 1 suggests that the major component of solvation energy in the present model would come from the solvation of the $>C=O$ moiety. Figure 2 shows the variation of solvation energy in the $n\pi^*$ states with changes in the dielectric constant of the media. As expected, the profiles of $\Delta E_{solvation}$ versus dielectric constant plots are very similar to the corresponding plots for ΔU versus D. The singlet–triplet splitting is seen to be rather insensitive to variation in the solvent dielectric constant which is in conformity with experimental results.

3.2 *Solvation and degree of localization of the n and π* orbitals*

$n\pi^*$ transition in formaldehyde involves the promotion of an electron from an orbital (n) predominantly localized on the oxygen atom to an orbital (π^*) delocalized over the $>C=O$ moiety with higher amplitude on the carbon atom. This means that this transition has an element of intramolecular charge transfer character which opposes the normal polarization ($C^{\delta+}=O^{\delta-}$) of the carbonyl group. Since macroscopic solvation tends to polarize the carbonyl group in the normal direction, solvation could have important effects on the "localization-characteristics" of the n and π^* orbitals.

Table 2 reports the per cent localization of the n orbital on the oxygen atom and that of the π^* orbital on the carbonyl carbon atom in $^{1,3}n\pi^*$ states as functions of solvent polarity. Both in singlet and triplet $n\pi^*$ states, increase of solvent polarity is seen to reduce the degree of localization of the nonbonding orbital on the oxygen atom. Simultaneously, the per cent localization of the π^* orbital on the carbonyl carbon atom increases. While the degree of localization of the n orbital appears to be almost spin-independent, the degree of localization of the π^* orbital on the carbonyl carbon atom in the $^3n\pi^*$ state is substantially less pronounced as compared to that observed in the $^1n\pi^*$ state. This difference is seen to persist when solvent polarity is

Table 2. Influence of macroscopic solvation on the degree of localization of the n and π^* orbital in the singlet and triplet $n\pi^*$ states of planar H_2CO.

Solvent dielectric constant (ε)	Percentage of localization of the n orbital of the carbonyl oxygen atom		Percentage of localization of the π^* orbital on the carbonyl carbon atom	
	$^1n\pi^*$	$^3n\pi^*$	$^1n\pi^*$	$^3n\pi^*$
1·0	91·5	91·4	85·2	80·6
10·0	90·4	90·5	87·7	83·8
20·0	90·0	90·0	88·0	84·3
30·0	89·6	89·8	88·2	84·5
40·0	89·4	89·6	88·3	84.6
50·0	89·2	89·5	88·4	84·7
60·0	89·3	89·4	88·4	84·8
70·0	89·1	89·3	88·4	84·8
80·0	89·1	89·3	88·4	84·8

gradually increased. A higher degree of localization of the carbonyl π^* orbital on the carbon centre essentially means that it is more antibonding. Solvents of higher polarity therefore appear to enhance the antibonding character of the π^* system of the carbonyl group. This is in agreement with the general experimental finding that solvents of higher polarity tend to stabilize a π^* system (Basu 1964).

4. Conclusion

The model described appears to handle macroscopic solvation reasonably well. The increase in polarization of the $>C=O$ group in solvents of higher dielectric constants indicates that macroscopic solvation can have important effects on the structural characteristics of a carbonyl in $n\pi^*$ states. Of special importance in this context is the possibility of macroscopic solvation affecting molecular inversion in $n\pi^*$ states of simple carbonyls or thiocarbonyls. This as well as the influence of solvation on the photochemical decomposition pathways of $X_2CO \rightarrow X_2 + CO$ in $n\pi^*$ states are presently under study. We hope to return to these aspects in the near future.

Acknowledgements

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