Theoret. chim. Acta (Berl.) 31, 155—169 (1973)

The Influence of Solvation on $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ Transition Energies in Molecules Containing Aza or Carbonyl Groups

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Received April 16, 1973

The influence of solvation on $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ transition energies of formaldehyde, acetaldehyde, acetone, pyridine and 1,2-, 1,3-, 1,4-diazabenzenes has been investigated through CNDO calculations.

A static solvation model which distinguishes a) molecules directly involved in hydrogen bonding with solute, b) the layer of molecules in contact with the solute molecule and c) the main of molecules farther from solute, is presented.

Blue and red shifts due to solvent effects are correctly predicted by calculations for each model.

Key words: Solvent Shifts of Electronic Transitions.

1. Introduction

At present it seems that CNDO—MO theory [1] offers the most promising tool for the study of the electronic properties of large molecular systems; the same method has also been extensively and successfully used to obtain a "semi-quantitative" description of hydrogen bonded structures [2].

This method has been recently employed to study solvent effects on the activation energy of $CH_3F + F^-$ reaction [3].

In the present paper we intend to study the influence of the solvent on electronic spectra by using CNDO/2 method in its original parametrization [4].

An analogous problem has been previously investigated by Hoffman *and coworkers* [5] who focused their attention on the influence of hydrogen bond formation on different observables, including $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ transition energies, by using a more empirical approach namely the Extended Huckel Method.

The most convenient choice of solutes should meet the following two requirements: a simple geometry to favour the formulation of a model of solvation, and a well established location of the $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ transitions in gas phase and solution spectra. With this in view formaldehyde, acetaldehyde, acetone, pyridine and diazabenzenes have been considered.

The solvent should be made of small strongly polar molecules in order to save computation time and to produce remarkable shifts of the bands with respect to those obtained in gas phase or in apolar solvents. Water meets these requirements. Moreover by using the same solvent as in Ref. [5] an interesting comparison between results obtained by CNDO and EH methods is possible.

2. Calculations

The geometries and the ground state properties of the solute molecules and of water have been optimized by the energy minimizing procedure due to Powell [6], where the energy was calculated by CNDO/2 method [4].

Excited-state properties have been obtained, using the same geometry as in the ground state, by CNDO/CI method [7], where the electronic repulsion integrals were evaluated by the Pariser and Parr technique [8]. The configuration interaction included the 30 mono-excited configurations of lower energy.

Calculated spectra of isolated molecules were compared with spectra measured in vacuo. When spectra obtained in solution were considered, calculations were performed on a model for the solvated molecule. The size of calculation and the necessity of preserving the point symmetry of the solute molecule do not allow us to consider an extended solvation process. We have tried to describe solvent effects by adding to the solute molecule a few solvent molecules, namely by hydrating to different extents the proper positions of the solute. No more than five molecules of water have been located around each position. The packing with the solvent was studied for different values of the intermolecular distance ϱ (values ranged from 1.4 – 2.4 Å). This procedure was preferred to a minimizing process with respect to the intersystem distance, as it is well known that the CNDO method systematically overestimates bonding properties. In the description of the geometries of the solute-solvent systems most of the geometrical parameters found for the isolated molecules have been used. However for each intersystem distance some geometrical parameters, involving the site of interaction, which will be specified in each case, have been optimized. As an example in the case of the molecule of water, the bond angle and the O—H bond distance not involved in the intermolecular bond have been kept equal to the values optimized for the isolated molecule, while the O—H distance of the bond involved in the solvation procedure has been let vary.

Once the geometries of minimum energy of the ground state were obtained for each ϱ value, the spectrum was calculated by the CI procedure [7].

3. Results

The topology of the isolated molecules of solutes, that is formaldehyde, acetaldehyde, acetone, pyridine and 1,2-, 1,3- and 1,4-diazabenzenes are given in Fig. 1, where the optimized geometrical parameters are also reported. In the corresponding Table 1 a comparison between experimental and calculated geometries is shown. In the same table the optimized geometry of the isolated molecule of water is reported. In the case of azines all C—H bonds were assumed in the ring-plane bisecting ring-angles, with equal bond-lengths.

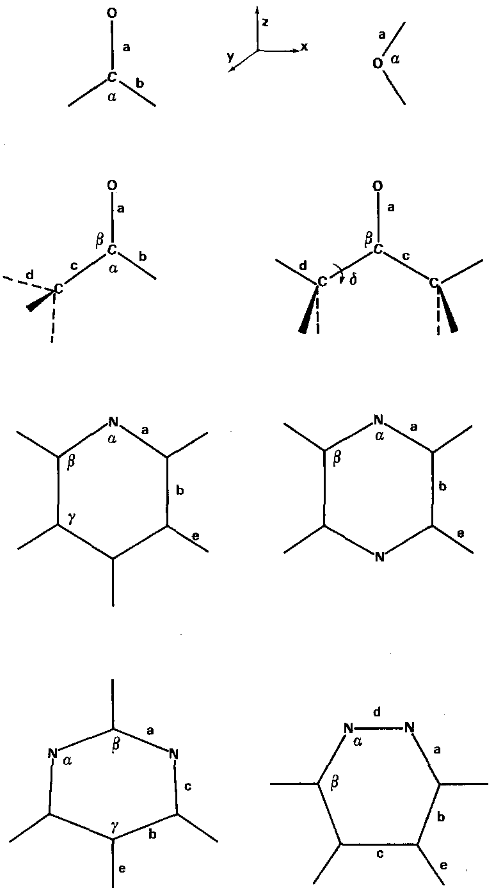

Fig. 1. Geometries and optimized parameters for isolated systems

a) *Formaldehyde*

The solvent effect on formaldehyde has been studied by considering a progressive solvation, that is several packings in which the formaldehyde molecule is bound up to six units of solvent. The more realistic situations are illustrated in Fig. 2, where the geometrical parameters which have been optimized are shown. The minimizing process has been performed for six different values of the O···H (ϱ) distance, which was varied from 1.4–2.4 Å in steps of 0.2 Å[1]. In the cases (c) and (d), where four molecules of solvent are considered, a higher stabilization is observed for (d) structure; this difference of stabilization between the two structures reaches the largest value of 24 kcal/mole for $\varrho = 2.0$ Å. If the methylene group is also solvated (on the whole six molecules of hydration), the difference in energy stabilization decreases to about 1–2 kcal/mole for all ϱ values.

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[1] Optimized geometries are not reported, but are available on request.

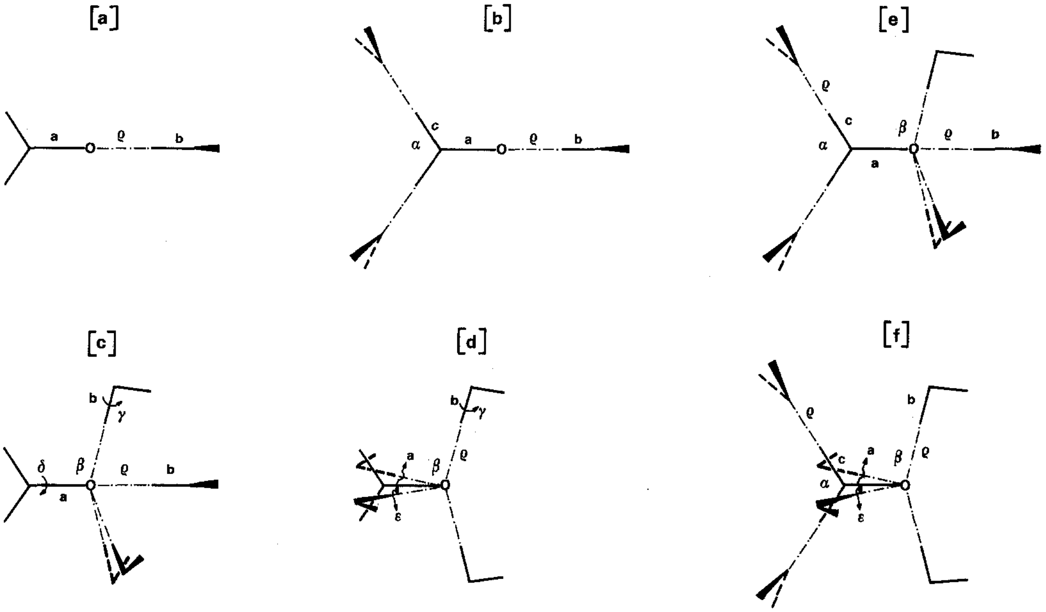

Fig. 2. Solvation model of formaldehyde with 1, 3, 4 and 6 water molecules

Table 1. Experimental and optimized geometries of the isolated molecules[a]

Molecules	Geometrical parameters							
	a	b	c	d	e	α	β	γ
HCHO	1.247	1.114				115.7		
	1.2078[b]	*1.1161*				*116.5*		
CH_3CHO	1.261	1.123	1.443	1.119		111.2	126.5	
	1.2155[c]	*1.114*	*1.5005*	*1.0861*		*117.5*	*123.9*	
CH_3COCH_3	1.274		1.455	1.119			120.2	111.6
	1.240[c]		*1.52*	*1.09*			*118.5*	*109.28*
C_5H_5N	1.342	1.382			1.116	116.3	124.9	117.5
					o – 1.0843			
	1.3402[d]	*1.3945*			*m – 1.0805*	*116.83*	*123.88*	*118.53*
					p – 1.0773			
1,4—$C_4H_4N_2$	1.344	1.381			1.121	112.0		
	1.334[e]	*1.378*			*1.05*	*115.8*		
1,3—$C_4H_4N_2$	1.342	1.380	1.343		1.119	118.5	130.2	115.9
	1.335[f]	*1.395*	*1.355*		—	*115.1*	*128.2*	*116.3*
1,2—$C_4H_4N_2$	1.351	1.374	1.384	1.280	1.116	119.5	124.0	
	—	—	—	—	—	*119.0*[f]	*123.68*	
H_2O	1.029					104.5		
	0.9571[c]					*104.5*		

[a] All the distances are in Å and the angles in (°). The upper number refers to the calculated value and the lower (in italics) refers to the experimental one.

[b] See Ref. [9]. [c] See Ref. [10]. [d] See Ref. [11]. [e] See Ref. [12]. [f] See Ref. [13].

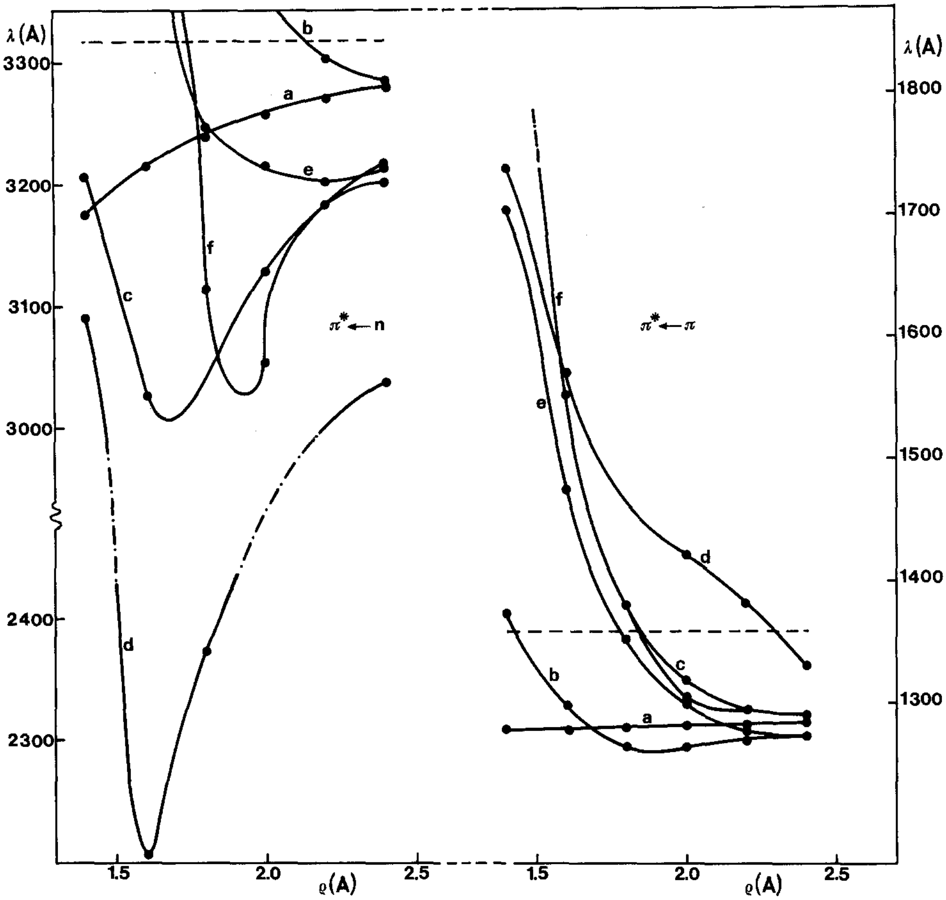

Fig. 3. Trends of $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ transition energies *vs* ϱ of the different solvation models for formaldehyde. Dot line represents transition energy for isolated molecule

The electronic spectrum of formaldehyde has been calculated by considering the molecule in the solvated situations illustrated in Fig. 2. The packings (e) and (f) correspond to (c) and (d) packings respectively, when the methylene group was hydrated. It is known from experiment that $\pi^* \leftarrow n$ transition of formaldehyde falls at 3538 Å in vacuo [14], and shifts to 2900 Å [15] in water. The trend of calculated $\pi^* \leftarrow n$ transition in different packings of solvent, for several ϱ values, is shown in Fig. 3.

A correct blue shift is predicted in the cases (a), (c) and (d) for all ϱ values. In the case (b) the blue shift is found only for the highest values of ϱ. In general it seems that the correct trend can be found when the hydration of C—O group is stronger that of CH_2 group.

The predicted red shift for $\pi^* \leftarrow \pi$ transition [16, 17] is obtained by our calculations for the higher degrees of solvation and, in general, for shorter values of ϱ. The case (d), where the red shift is found for all ϱ values, is the exception.

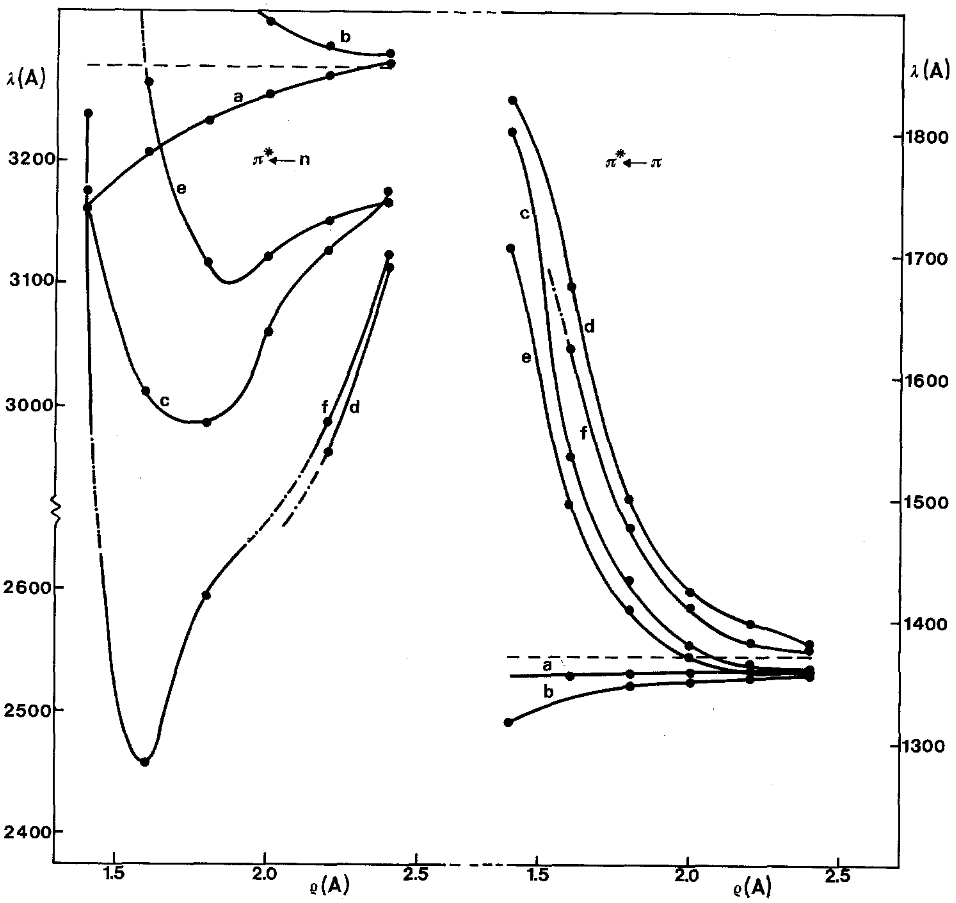

Fig. 4. Trends of $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ transition energies *vs* ϱ of the different solvation models for acetaldehyde. Dot line represents transition energy for isolated molecule

b) Acetaldehyde and Acetone

For both molecules several solvation models were considered, using one, four or five molecules of solvent in the case of acetaldehyde and one or four molecules of solvent in the case of acetone. On the basis of the experience of previous calculations on CH_3F [3], the methyl group was never hydrated. In view of this the solvent models are the same as those considered for formaldehyde.

The solvents shifts of $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ bands for the two molecules as a function of hydration and ϱ distance are shown in Figs. 4 and 5. The $\pi^* \leftarrow n$ transition of acetaldehyde, which falls at 3390 Å in vacuo [18], shifts to 2740 Å in water [17]. For acetone the $\pi^* \leftarrow n$ transition located at 2762 Å in vacuo [17], occurs at 2640 Å in water [19]. MO calculations in both cases give a correct interpretation of the phenomenon, showing a pronounced increase of the blue shift as more molecules of solvent are put around the carbonyl group. Moreover

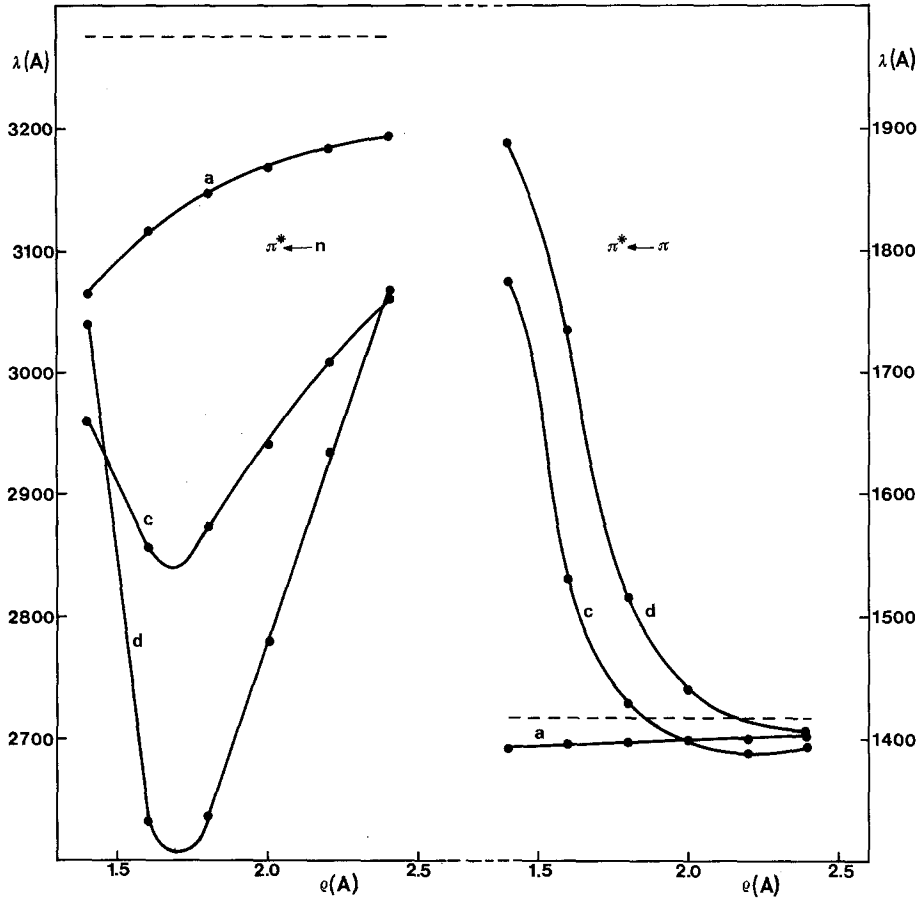

Fig. 5. Trends of $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ transition energies *vs* ϱ of the different solvation models for acetone. Dot line represents transition energy for isolated molecule

a red shift is predicted by our calculations in water for $\pi^* \leftarrow \pi$ transitions of both molecules only when a sufficient number of molecules of solvent are considered. In conclusion it seems that for these two molecules the solvent effect on electronic transitions is well interpreted by CNDO calculations only when at least four molecules are around the solute.

c) Pyridine

For water-pyridine solution several models were investigated by considering up to six units of solvents for each solute molecule. When one molecule of water has been used to represent the solvent effect, only the configuration in which one of the protons of the solvent approaches the nitrogen lone pair has been considered, having in mind the results obtained by Hoffmann and coworkers (see Fig. 3 in Ref. [5]). The models assumed when more molecules of water were considered, are shown in Fig. 6, where the optimized geometrical parameters are also reported.

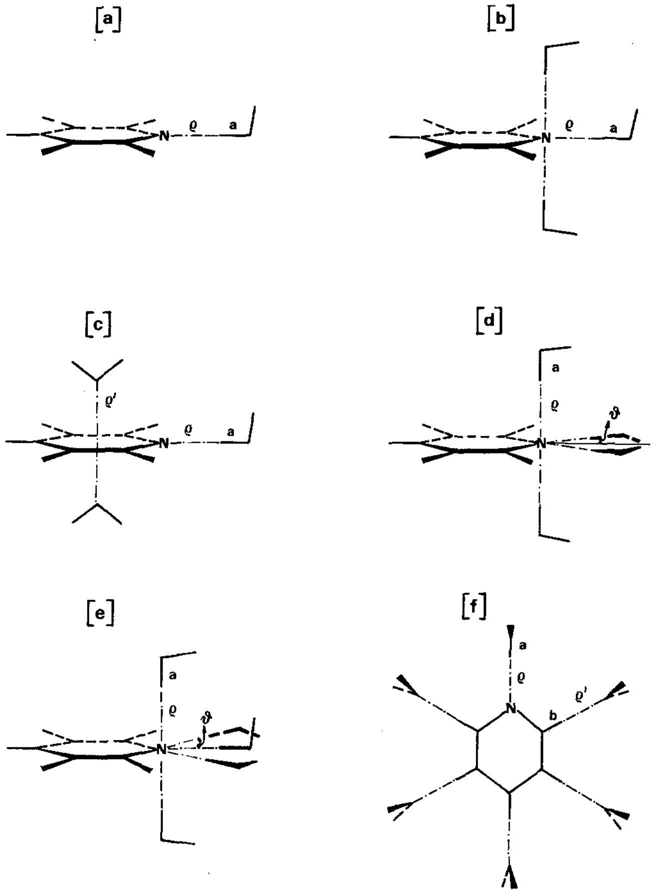

Fig. 6. Solvation model for pyridine with 1–6 water molecules

The calculated solvent shifts of electronic bands of pyridine in different solvent situations are shown in Fig. 7 as a function of the ϱ distance. A blue shift of about 300–400 Å is expected for $\pi^* \leftarrow n$ transition in water [20, 21]. Our results give the correct answer for all the considered models and the quantitative agreement with experiment is the better the greater the number of molecules of water around the nitrogen. Likewise the observed red shift of the p band of pyridine, which was found at 2500 Å in vacuo [22] and at 2530 Å [21] (or 2570 Å [20]) in water, is correctly predicted by calculations for all ϱ values and in this case the agreement is excellent also on a quantitative basis, with the exception of (c) model, where the red shift is overestimated.

d) Diazabenzenes

Solvation models with two, six, eight and ten molecules of water were studied for 1,4-, 1,3- and 1,2-diazabenzenes. Owing to its topology in the case of 1,2-isomer only the models with two and six molecules of water have been

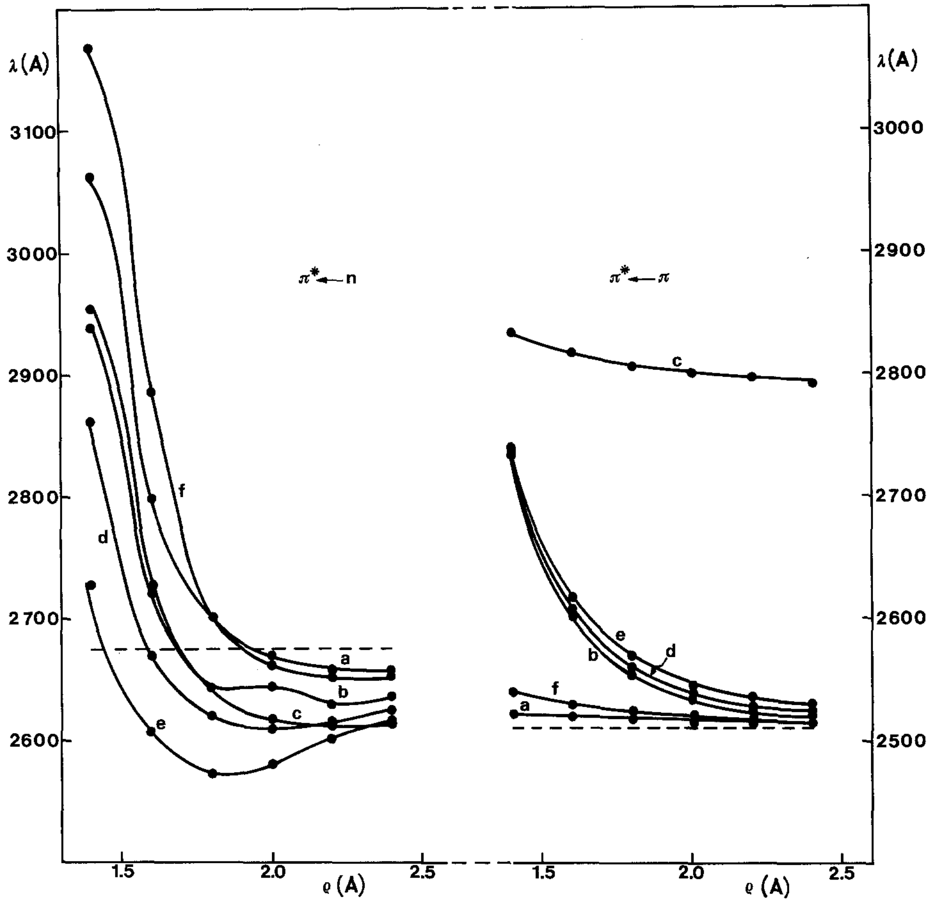

Fig. 7. Trends of $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ transition energies *vs* ϱ of the different solvation models for pyridine. Dot line represents transition energy for isolated molecule

considered. The structures of hydrated pyridine were used as reference models, keeping in mind that in diazabenzenes two nitrogens are present.

As found for the former molecules the solvent shifts for $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ are well predicted by calculations. Now the agreement with experiment for $\pi^* \leftarrow n$ is even better, while in the case of $\pi^* \leftarrow \pi$ transitions the red shift, which is experimentally found to be very low in all cases and practically zero for 1,2-diazabenzene, is slightly overestimated. The trend of transition energies for the three molecules in different solvent structures, for different values of ϱ, is shown in Figs. 8, 9 and 10.

4. Discussion

In a static model of solvation three types of solvent molecules can be distinguished: A) molecules directly involved in hydrogen bonding to the solute; B) the layer of molecules in contact with the solute molecule, that is

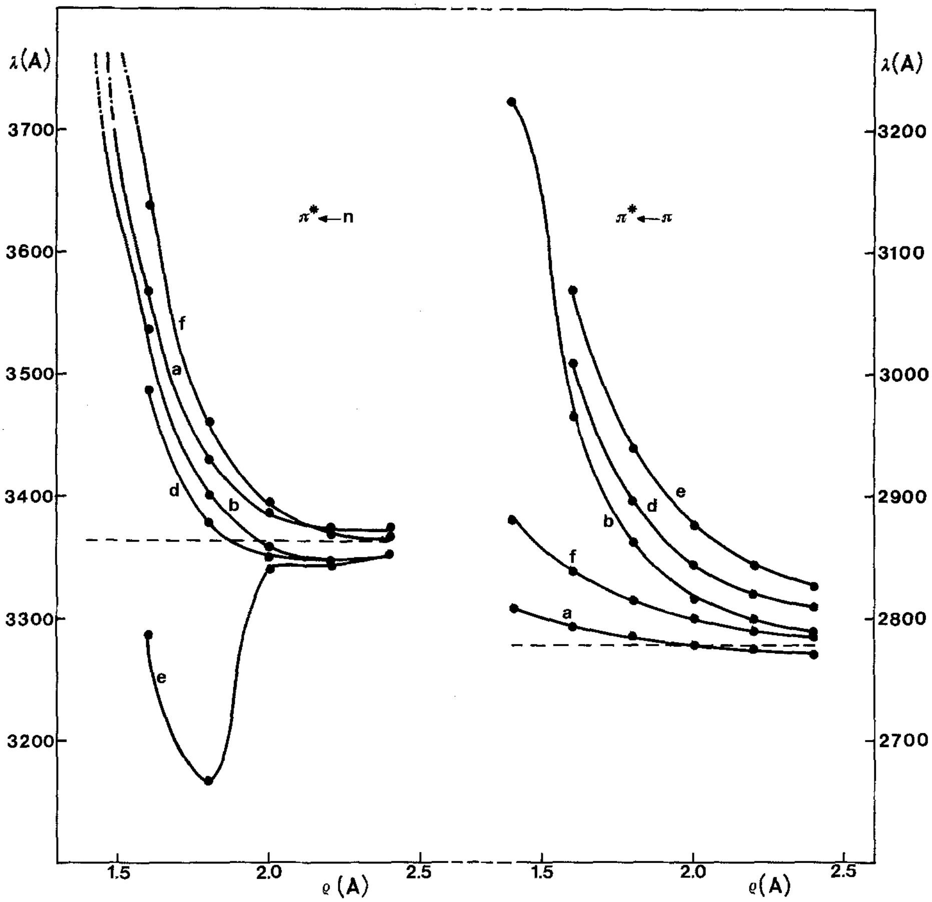

Fig. 8. Trends of $\pi^*\leftarrow n$ and $\pi^*\leftarrow\pi$ transition energies *vs* ϱ of the different solvation models for 1, 4-diazabenzene. Dot line represents transition energy for isolated molecule

directly interacting with it, but without forming hydrogen bonds, and C) the surrounding molecules farther from the solute.

In our theoretical model as few as possible water molecules of type B have been considered, and the effect of the molecules of type C has been considered negligible. The geometries of the models for the different solutes are shown in Fig. 1 and have been previously discussed. By inspection of Table 1 a very satisfactory agreement between geometries calculated by CNDO method and those obtained by experiment for all isolated molecules can be verified.

When only one molecule of water is considered, as is usually done when studying hydrogen bonding [5], a stabilization energy ranging between 7 and 10 kcal/mole, is found. This order of magnitude reproduces well the extimated value for a hydrogen bond of such type [17]. The maximum stabilization energy for the different molecules, interacting with one unit of water (*a* case) are collected in Table 2, where the corresponding ϱ distances are also shown.

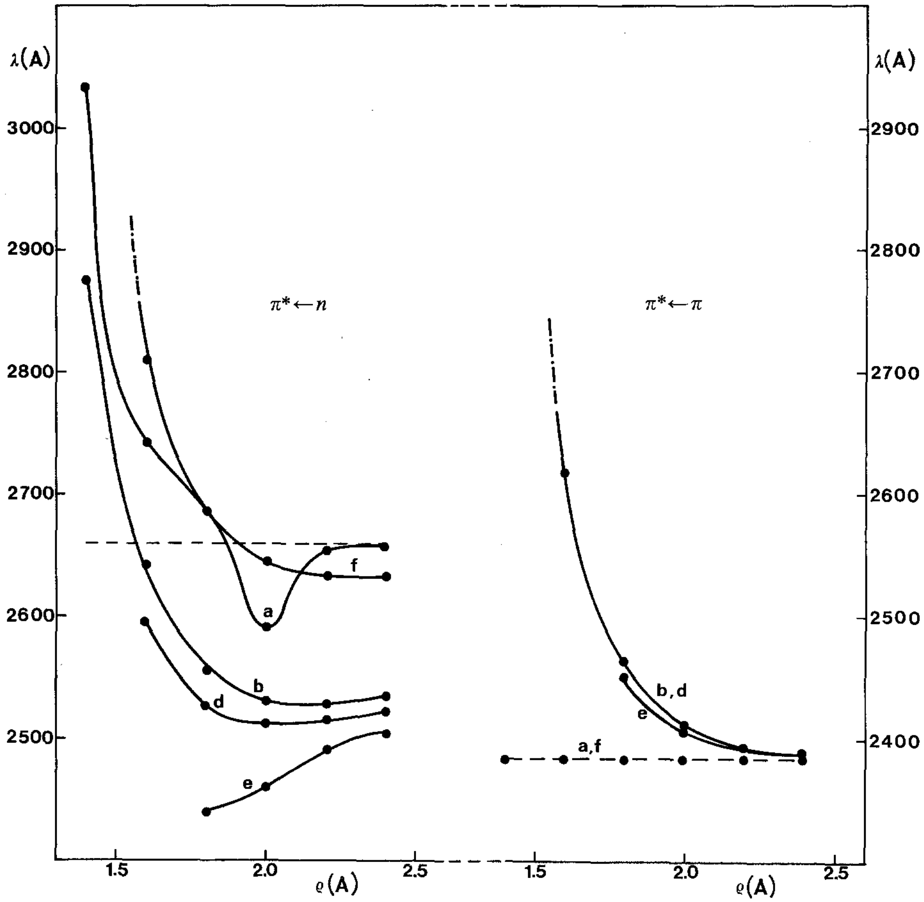

Fig. 9. Trends of $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ transition energies *vs* ϱ of the different solvation models for 1, 3-diazabenzene. Dot line represents transition energy for isolated molecule

For the considered molecules the distance that minimizes the energy is 1.6 Å. The exception is acetone – water system for which a ϱ value of 1.4 Å is obtained. CNDO results for pyridine, that is a stabilization energy of −10.7 kcal/mole for an equilibrium distance between oxygen and nitrogen atoms of 2.65 Å, can be compared with −2.3 kcal/mole obtained by EH method with an equilibrium distance of 2.76 Å [5].

When more units of solvent are packed around the solute, the solute – solvent mean distance rises to values between 1.8 and 2.0 Å and the corresponding stabilization energy of solvation model is 30−50 kcal/mole. The relevant numerical data are reported in Table 2.

The solvent effect on transition energies has been studied considering different packings at several solvent – solute distances. The relevant data are shown in Figs. 3−5, 7−10. When a sufficient number of water units are packed around the solute a satisfactory interpretation of the solvation effect can be obtained by CNDO calculations if a favourable ϱ value is chosen. The

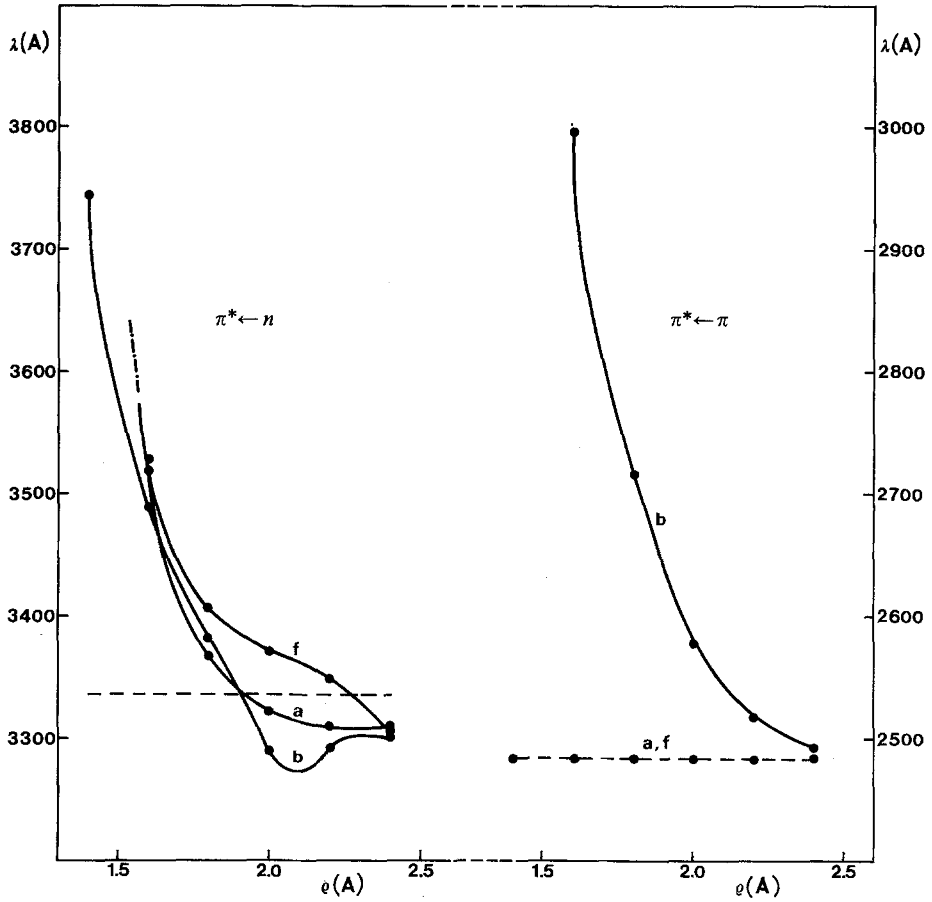

Fig. 10. Trends of π*←n and π*←π transition energies *vs* ϱ of the different solvation models for 1, 2-diazabenzene. Dot line represents transition energy for isolated molecule

situation is illustrated in Table 3 where a qualitative agreement between measured and calculated blue and red shifts for π*←n and π*←π transitions respectively, can be observed for all molecules when a proper amount of solvation is included; the ϱ values at which the best agreement is obtained are also shown.

In Table 4 oscillator strengths (*f*) for π*←n and π*←π transitions, calculated for isolated molecule and for the same hydrated models as presented in Table 3, are shown; *f* values for π*←n transitions of isolated molecules are always higher than the values obtained for solvated molecules, however very small *f* values are always obtained. On the contrary an increasing of *f* values for π*←π transitions is found for hydrated molecules compared to isolated ones. The few available experimental data confirm this finding, apart from the exception of the π*←π band of acetone, where a lowering of oscillator strength of π*←π band for isolated molecule respect to hydrated one is theoretically and experimentally found.

Table 2. Stabilization energies for several solvation models

Molecule	Model[a]	ϱ (Å)	ΔE (kcal/mole)
HCHO	a	1.6	7.09
	d	2.0	39.09
CH_3CHO	a	1.6	7.59
	d	1.8	38.72
CH_3COCH_3	a	1.4	9.29
	d	2.0	31.12
C_5H_5N	a	1.6	10.67
	e	1.8	21.15
1,4—$C_4H_4N_2$	a	1.6	19.14
	e	1.8	41.73
1,3—$C_4H_4N_2$	a	1.6	20.46
	e	1.8	38.28
1,2—$C_4H_4N_2$	a	1.6	19.20
	b	2.0	37.84

[a] The models (a), (b), (d) and (e) refer to the corresponding structures in Figs. 2 and 6.

Table 3. Experimental and calculated blue and red shifts for $\pi^*\leftarrow n$ and $\pi^*\leftarrow\pi$ transitions

Molecule and model	ϱ (Å)	$\pi^*\leftarrow n$ transition blue shift (nm)		$\pi^*\leftarrow\pi$ transition red shift (nm)	
		calc.	exp.	calc.	exp.
HCHO (d)	2.0	70.4	63.8	6.3	
CH_3CHO (d)	1.8	68.1	65.0	5.4	
CH_3COCH_3 (d)	2.0	49.3	12.2	2.6	
C_5H_5N (e)	1.8	9.8	30.0–34.0	5.9	3.0–7.0
1,4—$C_4H_4N_2$ (e)	1.8	19.7	17.5–23.9	16.3	3.9
1,3—$C_4H_4N_2$ (e)	1.8	21.9	18.8–24.9	6.9	1.5
1,2—$C_4H_4N_2$ (b)	2.0	4.5	25.0–35.6	23.3	$\sim$0

In the case of pyridine, for which the change in the electric dipole moment upon excitation to the lowest energy singlet $\pi^*\leftarrow n$ excited state has been measured [26] to be $\Delta\mu = 3.2$ D, a quantitative agreement with experiment has been found. The measured ground state dipole moment of pyridine is 2.19 D [27], consequently the excited state dipole moment is -1.0 D. Our CNDO calculation predicts 2.94 D for the ground state dipole moment and -1.44 D for excited state dipole, with a substantial decreasing of the moment upon excitation, as predicted by solvent effect theory when a blue shift is observed [28]. The calculated dipole moment for the excited state, associated with the first $\pi^*\leftarrow\pi$ transition is 3.06 D, according to observed red shift. Moreover for the other diazabenzenes CNDO calculations predict for an observed blue or red shift, a corresponding lower or higher value of the dipole of the involved excited state, with respect to the ground state dipole moment. In the case of formaldehyde, acetaldehyde and acetone for a calculated blue shift of $\pi^*\leftarrow n$ transition a decrease of the value of dipole moment of excited π^* state (with respect to the n

Table 4. Calculated and observed oscillator strengths (f) of $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ transitions

Molecule	$\pi^* - n$		$\pi^* - \pi$	
	in vacuo	in water	in vacuo	in water
HCHO	—	—	0.228	0.354
	—	—	*0.57*[a,h]	—
CH_3CHO	—	—	0.383	0.278
	—	—	*0.20*[b,h]	—
CH_3COCH_3	—	—	0.360	0.352
	—	—	*0.16*[c,h]	*0.00*[d,h]
C_5H_5N	0.005	0.003	0.083	0.100
	—	—	—	*0.07*[e,h] – *0.06*[f,h]
1,4—$C_4H_4N_2$	0.009	0.003	0.206	0.249
	0.012[g]	*0.017*[f,h]	*0.10*[g]	*0.12*[f,h]
1,3—$C_4H_4N_2$	0.000	0.003	0.080	0.102
	0.0076[g]	*0.01*[f,h]	*0.052*[g]	*0.06*[f,h]
1,2—$C_4H_4N_2$	0.012	0.011	0.071	0.080
	0.008[g]	*0.006*[f,h]	*0.020*[g]	—

[a] See Ref. [23]. [b] See Ref. [24]. [c] See Ref. [25]. [d] See Ref. [19]. [e] See Ref. [21]. [f] See Ref. [20]. [g] See Ref. [22]. [h] Calculated from ε_{max} through the relationship $f = 2 \cdot 10^{-5} \cdot \varepsilon_{max}$.

state dipole moment) is found. On the other hand for $\pi^* \leftarrow \pi$ transitions, for which a correct red shift is obtained, the calculated dipole moments for excited π^* states associated with transitions are again lower than ground state dipole moments. However it is well known that not all frequency shifts are caused entirely by dipole interactions, but other types of interaction may give important or even dominant contributions in certain cases [28].

In conclusion we feel that the present hydration model gives an adequate description of solvent effect, keeping in mind the limits imposed by the complexity of the problem. It is noteworthy that the observed shift of transition energy is correctly predicted only when the ϱ values are in the range of the experimental finding and a sufficient number of water molecules is put around the solute. This fact suggests that hydrogen bond model alone cannot explain observed trends of the UV spectra due to solvent effect. It is the first time to our knowledge that the blue and red shifts due to solvent effects can be correctly predicted by one calculation.

Acknowledgements. One of us (P.C.) thanks Professor C. Moser for hospitality at C.E.C.A.M. laboratories in Orsay.

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