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Applications of the Virtual Charge Model to the Electronic Structures and Spectra of Benzaldehyde and Acetophenone

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Summary. The virtual charge model (Tapia model) in conjunction with the CNDO/S-CI approximation in the frame of SCF-MO theory was employed to study the effects of solvent on the electronic structures and spectra of benzaldehyde and acetophenone molecules. The CNDO/S calculations in presence of solvation indicate a satisfactory interpretation of the medium effects on the electronic structures and spectra of the molecules investigated. The prediction of our MO calculations by means of the Tapia model concerning the solvochromic shifts of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions are in accord with the observed trends which indicate a blue shift for the $n \rightarrow \pi^*$ band and a red shift for the $\pi \rightarrow \pi^*$ band upon a change of solvent from non-polar to polar solvents.

Keywords. Virtual charge model; Electronic structures; Electronic spectra; CNDO/S-CI calculations.

Anwendung des „Virtual Charge"-Modells auf die Elektronenstrukturen und Spektren von Benzaldehyd und Acetophenon

Zusammenfassung. Das „Virtual-Charge"-Modell (Tapia-Modell) im Zusammenhang mit der CNDO/S-CI-Näherung im Rahmen der SCF-MO-Theorie wurde zum Studium der Lösungsmitteleffekte auf die Elektronenstrukturen und Spektren von Benzaldehyd und Acetophenon herangezogen. Die CNDO/S-Rechnungen bei Anwesenheit von Solvens erlauben eine befriedigende Interpretation der Mediumeffekte auf Elektronenstrukturen und Spektren der untersuchten Verbindungen. Die aus MO-Rechnungen folgenden Voraussagen ergeben auf Basis des Tapia-Modells solvatochrome Verschiebungen für die $n \rightarrow \pi^*$- und $\pi \rightarrow \pi^*$-Übergänge. Die vorausgesagten Effekte stehen im Einklang mit den experimentell beobachteten Trends: Blauverschiebung für die $n \rightarrow \pi^*$-Bande und Rotverschiebung für die $\pi \rightarrow \pi^*$-Bande beim Wechsel von nichtpolarem zu polarem Lösungsmittel.

Introduction

The physical and chemical properties of molecules such as the electronic spectra are usually affected by the nature of the medium (solvent) [1, 2] which is used in the studies of their properties. In general, chemical reactions occur in aqueous or organic media (as solvents). Most of the studies of these reactions, the observed values and data of which have been cited in the literature, are related to the observed properties of the solute in the solvent. At the same time most of the theoretical calculations based on quantum theory are usually carried out for the isolated molecules neglecting medium effects. Therefore these calculations give and interpret the properties of the molecules in the gas phase. However, such calculations do not give the full picture of the electronic structures of these molecules in the presence of various media.

Therefore it is necessary to include solvent effects in the theoretical calculation in order to get a better understanding of the nature of these interactions between the solute and the solvent and to obtain results more helpful to interpret the experimental data which are frequently subject to the effects of solvent.

The interactions between the solute and the solvent are usually classified in two types:

(1) Specific interactions which arise from binding between the solute molecules and the solvent molecules by hydrogen bonding, adduct compounds and charge transfer complexes [3], etc. ...
(2) Non-specific interactions that arise from the electrostatic attraction forces between the solute and the solvent. The non-specific interactions are of different subtypes, i.e. dipole-dipole interactions, induced dipole-dipole interactions, and dispersion forces which are known as weak Van der Waals forces.

The non-specific interactions can be studied by quantum mechanics. Such studies comprise the effective charge models [1, 4–7] and the reaction field models [8–12].

The main objective of the present work is the study of non-specific interactions between the solute and the solvent and the inclusion of solvent effects in the theoretical calculations of the electronic structures and spectra of benzaldehyde and acetophenone molecules utilizing the CNDO/S-CI procedure in combination with the Tapia model based on virtual charges [6, 7, 13].

Theoretical Methods

A model was suggested by Klopman [4] in order to study the non-specific interactions between the solute and the solvent. Germer [5] implemented this model adding the solvent interaction with the solute to the elements of the Fock matrix in corporation with the SCF procedure. Tapia and Constanceil criticised the Germer method of adding the non-specific solute-solvent interactions to the Fock matrix and introduced an alternative model [1, 6, 7], known as the virtual charge model (Tapia model). Tapia and Constanceil proposed that there are virtual charges "solvatons" and each solvaton has an oppostie charge to that of the atom it is related to, according to the relation

$$\bar{q} = -fq, \tag{1}$$

where f is a function of the dielectric constant (ε) of the medium, and q is the net charge of the atom to which the solvaton is connected. Tapia suggested the following formula for function f,

$$f = 1 - (\varepsilon^{-1/2}). \tag{2}$$

This model assumes that the solute molecule includes a number of fixed point charges Z_A close over electric core and the solvaton as a sum of virtual point charges ($-fZ_A$). The total energy of the systems is expressed as the sum of the inherent total energy of the solute ε^{Σ} (in the absence of the solvent), the interaction energy between the solute molecule and the solvent E^{Σ}, and the interactions between the solvatons themselves E^{S}, i.e.

$$E_{T} = \varepsilon^{\Sigma} + E^{\Sigma} + E^{S}, \tag{3}$$

and the Hamiltonian operator is written as

$$\hat{H} = \hat{H}^{\Sigma} - f\hat{V}^{\Sigma} + f^{2}\hat{V}^{SS} \tag{4}$$

where

$$\begin{aligned} \langle \psi, | \hat{V}^{\Sigma} | \psi_1 \rangle &= -\sum_{A} Z_A V_A + \sum_{\mu} \sum_{r} \rho^{H}_{\mu r} V_{\mu r}, \\ \langle \psi_1 | \hat{V}^{SS} | \psi_1 \rangle &= \frac{1}{2} \left[\sum_{A} Z_A V_A - \sum_{\mu} \sum_{r} \rho_{\mu r} V_{\mu r} \right] . \end{aligned} \tag{5}$$

If the variational principle is used, the Hartree-Fock matrix elements can be given by

$$\hat{F} = \hat{F}^{0} + f\hat{V}, \tag{6}$$

where

$$\hat{V} = \sum_{B} \frac{Z_B}{|R_B - r|} - \int \frac{\rho(r')\,\mathrm{d}r'}{|r - r'|} . \tag{7}$$

F^{0} is the Fock matrix in the absence of solvents.

When this model is used together with the CNDO/S-CI, then at this level of approximation we obtain the following relations [14, 15],

$$\begin{aligned} V_{\mu r} &= 0, \qquad \text{if} \qquad \mu \neq \nu \\ V_{\mu\mu} &= \sum_{B} \left[Z_B - \sum_{\lambda}^{B} \rho_{\lambda\lambda} \right] \gamma_{AB} \\ &= \sum_{B} q_B \gamma_{AB}, \qquad \mu \in A; \\ V_A &= \sum_{B} \left[Z_B \gamma_{SA\cdot SA} - \sum_{\lambda}^{B} \rho_{\lambda\lambda} \gamma_{\lambda\cdot SA} \right] \equiv V_{SA\cdot SA}, \end{aligned} \tag{8}$$

where q_B is the net charge on the atom B, $\rho_{\lambda\lambda}$ is the electronic density on orbital λ and γ_{AB} is the two-centre electronic repulsion integral.

In the present study, the aromatic carbonyl molecules which include benzaldehyde and acetophenone are subject of this investigation. For this purpose standard geometries are used [16].

All the calculations have been carried out by using the NEC computer ACOS 6 version of the Computer Centre of University of Basrah.

Results and Discussion

Electronic Spectra

The results for benzaldehyde and acetophenone obtained by the CNDO/S-CI method are listed in Table 1 [17]. For benzaldehyde, the results reveal that an

Table 1. CNDO/S-CI Singlet transitions of benzaldehyde and acetophenone molecules without solvation

Energy (ev)	Wave length (nm)	Oscillator strength	Main M.O. transition
Benzaldehyde			
2.93	423	0	$18\,n \rightarrow 21\,\pi^*$
4.62	268	0.0045	$19\,\pi \rightarrow 21\,\pi^*$
5.35	231.8	0.1877	$20\,\pi \rightarrow 21\,\pi^*$
6.30	196.5	0.2757	$19\,\pi \rightarrow 21\,\pi^*$ $19\,\pi \rightarrow 22\,\pi^*$
6.42	193.0	0.4616	$20\,\pi \rightarrow 22\,\pi^*$
Acetophenone			
2.97	417.8	0.000016	$21\,n \rightarrow 24\,\pi^*$
4.64	267	0.0038	$22\,\pi \rightarrow 24\,\pi^*$
5.40	230.0	0.1695	$23\,\pi \rightarrow 24\,\pi^*$
6.34	195.4	0.3125	$22\,\pi \rightarrow 24\,\pi^*$ $22\,\pi \rightarrow 25\,\pi^*$
6.46	191.7	0.4845	$23\,\pi \rightarrow 25\,\pi^*$

electronic transition of energy 2.93 ev is related to the $18\,n \rightarrow 21\,\pi^*$ transition. The corresponding observed energy value of this transition (3.14 ev) [18] is in qualitative agreement with the predicted one. The second calculated transition is of weak intensity (4.6 ev) and is related to the $19\,\pi \rightarrow 21\,\pi^*$ transition. It involves molecular orbitals of π-type delocalized over the whole molecule and the calculated energy for this transition is not much different from the experimental value (4.3 ev) [19]. Another more intense transition of energy calculated (5.34 ev) and referred to $20\,\pi \rightarrow 21\,\pi^*$ transition includes molecular orbitals of π-type localized on the benzene ring. This energy value can be correlated to the observed one at 5.1 ev [20]. The calculated results for acetophenone are also seen in Table 1. They indicate the

Table 2. CNDO/S results as a function of dielectric constant (ε) for ${}^1(n\pi^*)$ states of benzaldehyde and acetophenone molecules

ε	Ground state		Acetophenone	
	Energy (ev)	Oscillator strength	Energy (ev)	Oscillator strength
1.0	2.93	0	2.97	$16 \cdot 10^{-6}$
1.25	2.96	0	3.03	$17 \cdot 10^{-6}$
1.50	3.03	0	3.12	$18 \cdot 10^{-6}$
200	3.12	0	3.23	$20 \cdot 10^{-6}$
300	3.24	0	3.34	$25 \cdot 10^{-6}$
4.00	3.38	0	3.50	$37 \cdot 10^{-6}$
10.0	3.68	0	3.79	$41 \cdot 10^{-6}$
25.0	3.80	0	3.88	$132 \cdot 10^{-6}$

Table 3. The observed results of solvent effects on the n → π* band [19, 25]

a. Benzaldehyde

Solvent	Cyclohexane	CCl_4	C_6H_6	Dioxane
Wavelength (nm)	370	366	364	360
Energy (ev)	3.34	3.38	3.40	3.44

a. Benzaldehyde

Solvent	*n*-Hexane	CCl_4	C_6H_6	CH_3COOH	CH_3CN	$CHCl_3$
Wavelength (nm)	2.23	321	320	320	317	316
Energy (ev)	3.84	3.86	3.91	3.87	3.87	3.92

existence of a very weak intensity transition at 2.97 ev attributed to the 21 n → 24 π* transition, whereas the observed energy of this transition from the electronic spectra is 3.77 ev [20]. The observed spectrum [20] for this molecule shows a band of medium intensity at 4.42 ev. This can be compared to the calculated value obtained here, which has an energy of 4.62 ev, attributable to the 22 π → 24 π* transition which is comprising π-type molecular orbitals and delocalized over the whole molecule. A third band was obtained experimentally at 5.30, this value is in good

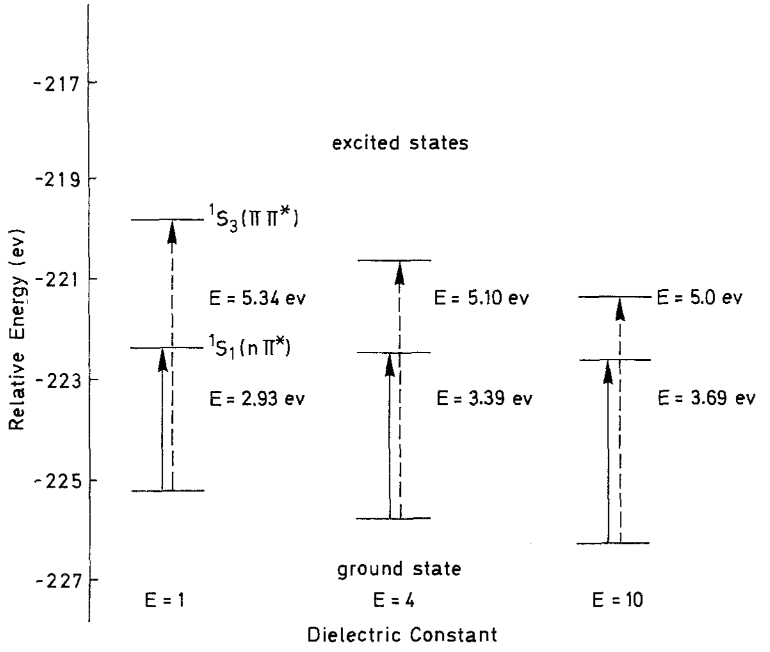

Fig. 1. CNDO/S results of solvent effects on the ground state and $^1(n\pi)$, $^1(\pi\pi^*)$ excited state energies of benzaldehyde

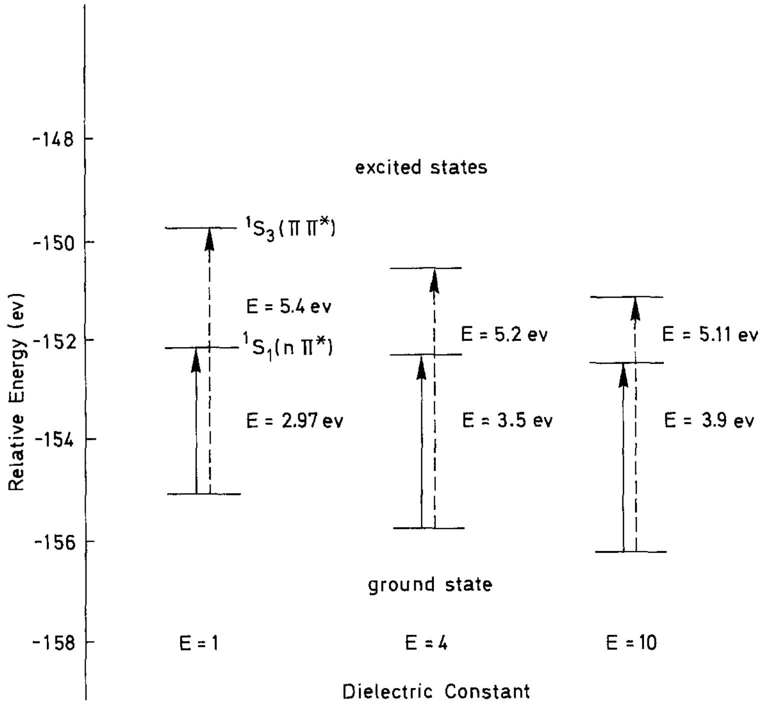

Fig. 2. CNDO/S results of solvent effects on the ground state and $^1(n\pi^*)$, $^1(\pi\pi^*)$ excited state energies of acetophenone

agreement with the predicted value (5.39 ev) and is related to the $23\pi \rightarrow 24\pi^*$ transition including π-type molecular orbitals localized on the benzene ring only.

Solvent Effects on Electronic Spectra

It is known that positions and intensities of the absorption bands in UV region depend on the nature of the solvent used [21]. Kasha et al. [22–24] concluded that

Table 4. CNDO/S results as a function of dielectric constant (ε) for the first $^1(\pi\Pi^*)$ states of benzaldehyde and acetophenone molecules

ε	Benzaldehyde		Acetophenone	
	Energy (ev)	Oscillator strength	Energy (ev)	Oscillator strength
1.0	4.626	0.0045	4.642	0.00380
1.25	4.616	0.00617	4.638	0.00524
1.50	4.606	0.00798	4.632	0.00675
2.00	4.595	0.00957	4.624	0.00787
3.00	4.592	0.00983	4.622	0.00778
4.00	4.590	0.01064	4.615	0.00972
10.0	4.550	0.02200	4.585	0.01590
25.0	4.500	0.02280	4.575	0.01820

Table 5. CNDO/S results as a function of dielectric constant (ε) for the second $^1(\pi\Pi^*)$ states of benzaldehyde and acetophenone molecules

ε	Benzaldehyde		Acetophenone	
	Energy (ev)	Oscillator strength	Energy (ev)	Oscillator strength
1.0	5.348	0.1877	5.398	0.1695
1.25	5.330	0.1924	5.392	0.1738
1.50	5.320	0.1987	5.375	0.1802
2.00	5.280	0.2083	5.342	0.1897
3.00	5.220	0.2242	5.289	0.1969
4.00	5.100	0.2331	5.202	0.2017
10	5.010	0.2241	5.115	0.2020
25.0	4.98	0.2782	5.034	0.2038

the carbonyl group containing compounds such as aldehyde, ketones, etc.... have electronic transitions of $n \rightarrow \pi^*$ type that can be easily distinguished from the electronic transition of $\pi \rightarrow \pi^*$ type by using solvent effects. It was found that if the non-polar solvent is replaced by a polar one, a measurable increase takes place in the energy of $n \rightarrow \pi^*$ transitions of the solute (blue shift) while the $\pi \rightarrow \pi^*$ transitions are liable to a decrease in energy (red shift). This effect is attributed to the specific and non-specific interactions between the solute and the solvent.

The theoretical results concerning solvent effects on the $n \rightarrow \pi^*$ transitions in benzaldehyde and acetophenone are shown in Table 2. They denote that a blue shift accompanies the increase of the polarity (ε) of the solvent. These results are found to be in good agreement with the observed ones taken from a study of solvent effects on the excited state $^1(n\pi^*)$ for benzaldehyde and acetophenone (Table 3) [19, 25].

The stability of the ground state and the excited states for benzaldehyde and acetophenone are depicted in Figs. 1 and 2, respectively. These figures exactly clarify the behaviour if the solvent is changed. They show a decrease in the energy of the ground state as the polarity of the solvent (ε) increases. This means that the

Table 6. CNDO/S results of dipole moments as a function of dielectric constant (ε) for the ground state and the $^1(n\pi^*)$, $^1(\pi\Pi^*)$ excited states of benzaldehyde and acetophenone molecules (in Debye)

ε	Benzaldehyde				Acetophenone			
		$^1(n\pi^*)$	$^1(\pi\Pi^*)_{1st}$	$^1(\pi\Pi^*)_{2nd}$		$^1(n\pi^*)$	$^1(\pi\Pi^*)_{1st}$	$^1(\pi\Pi^*)_{2nd}$
	μg	μe	μe	μe	μg	μe	μe	μe
1.0	3.37	3.67	5.57	5.80	3.97	3.82	5.13	5.12
1.5	4.23	3.34	6.52	6.73	4.49	3.54	6.13	6.16
3.0	4.86	3.28	7.31	8.11	5.12	3.37	6.65	6.84
25.0	6.53	2.97	9.63	9.71	6.74	3.20	9.13	8.77

Table 7. CNDO/S results of net charges as a function of dielectric constant (ε) for the ground state and the $^1(n\pi^*)$, 1st $^1(\pi\Pi^*)$ excited states of benzaldehyde and acetophenone molecules (carbonyl group)

a. Benzaldehyde *Ph*-C^1HO^2

ε	Ground state		Excited states			
	C^1	O^2	$^1(n\pi^*)$		$^1(\pi\Pi^*)_{1st}$	
			C^1	O^2	C^1	O^2
1.0	0.216	−0.365	0.045	0.242	0.102	−0.402
1.5	0.272	−0.436	0.083	0.179	0.130	−0.482
3.0	0.347	−0.528	0.147	0.088	0.182	−0.568
25.0	0.592	−0.791	0.371	−0.273	0.372	−0.833

b. Acetophenone *Ph*-C^1O^2-CH_3

ε	Ground state		Excited states			
	C^1	O^2	$^1(n\pi^*)$		$^1(\pi\Pi^*)_{1st}$	
			C^1	O^2	C^1	O^2
1.0	0.242	−0.401	0.082	0.230	0.147	−0.042
1.5	0.300	−0.476	0.130	0.163	0.179	−0.502
3.0	0.380	−0.570	0.197	0.064	0.237	−0.593
25.0	0.625	−0.826	0.431	−0.315	0.442	−0.854

stability of these molecules increase as the dielectric constant of the medium increases. A similar trend is predicted for the stability of the $^1(n\pi^*)$ excited states in various solvents but the increase in the stability of the latter state is less than what occurs in the stability of the ground state for the same increase in (ε). Thus, the final effect of the solvent is to increase the difference between the energy of the ground state and that of the $^1(n\pi^*)$ excited state producing the blue shift.

The calculated results for the effects of the solvents upon $\pi \rightarrow \pi^*$ transitions in benzaldehyde and acetophenone are presented in Table 4 for the first $^1(\pi\pi^*)$ excited state, and in Table 5 for the second $(\pi\pi^*)$ excited state. Tables 4 and 5 indicate that a red shift arises in these molecules as the dielectric constant (ε) increases (Fig. 1 and 2); this is also associated with an increase in the oscillator strength. This seems in good accordance with the observed results [26, 27].

Dipole Moments and Electronic Charge Distribution

Generally it is known that the interactions between a solute and a solvent depend upon the polarity of the medium. When an electronic transition takes place, the electronic charge densities on the atoms of the molecule redistribute themselves leading to a change in the dipole moment values of that molecule. It is of interest to compare the dipole moment values of the ground state with those of the excited states in order to get an accurate understanding of polar solvent effects on these states. If the dipole moment of the ground state is greater than that of the excited state i.e. $Mg > Me$, this means that the presence of the polar solvent causes an increase in the stability of the ground state larger than the increase occurring in the excited state.

Thus, the ground state energy is reduced in polar solvents by an amount larger than that which occurs in the excited states (Figs. 1, 2) leading to a blue shift for $n \rightarrow \pi^*$ transition.

In contrast to what has been mentioned above, a red shift takes place for $\pi \rightarrow \pi^*$ transition, where $\mu e > \mu g$.

Our calculated results for the dipole moments of the ground and excited states of benzaldehyde and acetophenone are given as a function of the dielectric constant (ε) of the medium (Table 6). For both molecules consideres, the calculations reveal that the dipole moment of the excited state $^1(n\pi^*)$ is less than that of the ground state. Hence a blue shift is predicted by our calculations. It can also be seen from Table 6 that the dipole moment values for both $^1(\pi\pi^*)$ excited states are greater than that of the ground state which gives an evidence for the red shift.

In order to interpret the variations in the dipole moment values in different solvents, Table 7 presents the net charges on the oxygen and carbon atoms of the carbonyl group in benzaldehyde and acetophenone as a function of the dielectric constant (ε) of the medium.

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