FORCE CONSTANT CALCULATIONS ON DIAZINES SOLUTED IN AQUEOUS MEDIUM BY THE CNDO/FORSOL METHOD

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Summary

A program named FORSOL was elaborated for the calculation of the vibrational force constants of soluted molecules. The solute-solvent interaction was based on the solvent continuum model supposing induced electric charges (solvatons) in the solvent. Some approximations were introduced for the atom-solvaton distances and the repulsion integrals. The program is basically an extension of the CNDO-force program. As an application calculations were carried out for the pyrazine molecule.

Introduction

For the quantummechanical description of the solute-solvent interaction four models are applied frequently:

1) A supermolecule is constructed placing some solvent molecules around the solute molecule into fixed positions. For such an agglomeration the Hartree Fock operators of the isolated molecules can be applied. This method is limited by dimensions of the matrices and the computation time.

2) The solute molecule is enclosed into a solvent continuum. This model is relatively simple, but modified Hartree-Fock operator is necessary.

3) The supermolecule is embedded in a solvent continuum. This is a synthesis of the former models and yields better results than the use of those.

4) Individual solute and solvent molecules are considered, pair potentials are calculated and statistical methods are applied.

In this work employing the second model a computer program was developed for the calculations of the force constants of solute molecules. The program was applied to calculate the vibrational frequencies of the pyrazine molecule in soluted state.

Theory

For the description of the solute-solvent interaction the Hamilton operator of the solute molecule is completed with a new term ($\hat{H}_{\mathrm{corr}}$).

The model supposes electric charges ($Q_{s'}$), "solvatons" in the solvent continuum induced by the s solute atoms. The interaction is characterized by solvaton-electron and solvaton-atom potentials:

$$\hat{H}_{\text{corr}} = -\frac{\varepsilon-1}{2\varepsilon}\sum_{s'=1}^{N}\left[\sum_{i=1}^{M}\frac{Q_{s'}}{r_{s'i}} - \sum_{t=1}^{N}\frac{Q_{s'}Z_t}{r_{s't}}\right] \tag{1}$$

where ε denotes the relative dielectric constant, N stands for the number of the atoms, M stands for the electrons of the solute molecule, Z_t labels the nuclear charge of the solute atom t, $r_{s'i}$ is the solvaton-electron distance and $r_{s't}$ the solvaton-atom one.

For quantumchemical calculations at the CNDO level Miertuš and Kysel' [2] proposed the relation

$$\hat{F} = \hat{F}_0 + \hat{V} \tag{2}$$

for the correction of the Fock operator, where $\hat{F}_0$ is the Fock operator of the isolated molecule. In ZDO approximation only the diagonal matrix elements $V_{\mu\mu}$ of the correcting operator differ from zero:

$$V_{\mu\mu} = -\frac{\varepsilon-1}{2\varepsilon}\sum_{s'=1}^{N}\left\langle \chi_\mu(i)\left|\frac{Q_{s'}}{r_{s'i}}\right|\chi_\mu(i)\right\rangle \tag{3}$$

They approximate these matrix elements at the CNDO level by

$$V_{\mu\mu} = -\frac{\varepsilon-1}{2\varepsilon}\sum_{s'=1}^{N} Q_{s'}\gamma_{\mu s'} \tag{4}$$

where the repulsion integrals between the orbitals and the solvatons $\gamma_{\mu s'}$ are approximated by

$$\gamma_{\mu s'} = \begin{cases} K\gamma_{\mu\mu} & \mu \in S \\ k_{\mu t}\gamma_{\mu t} & \mu \notin t \end{cases} \tag{5}$$

with

$$K \leqq 1 \qquad k_{\mu t} = \begin{cases} 1 \\ \exp\left(-\dfrac{\varepsilon-1}{2\varepsilon r_{st}}\right) \end{cases}$$

The new quantumchemical program called FORSOL relied on the above principles. In order to reduce the matrix dimensions to those of the isolated molecules the following approximations were applied.

1) The interactions between the solvatons do not depend on the atoms of the solute, thus are omitted in the calculations.

2) The interactions between the solvatons and the foreign atoms are not symmetric:

$$\gamma_{st'} \neq \gamma_{s't} \tag{6}$$

since the corresponding distances are not equal ($r_{s't} \neq r_{st'}$). We found three ways for the symmetrization:

a) according to Germer's [1] proposition

$$r_{st'}=r_{st}+\frac{r_{ss'}+r_{tt'}}{2} \tag{7}$$

b) calculation with mean distances

$$r_{st'}:=r_{s't}:=\frac{r_{s't}+r_{st'}}{2} \tag{8}$$

c) averaging of the repulsion integrals

$$\gamma_{s't}:=\gamma_{st'}:=\frac{\gamma_{st'}+\gamma_{s't}}{2} \tag{9}$$

The internal forces of the pyrazine molecule were calculated according to this approximation.

3) The solvaton-inductor atom distances can be defined in three ways:

a) Germer's suggestion [1]

$$r_{ss'}=\rho_s \tag{10}$$

where ρ_s is the van der Waals radius of the atom s.

b) All $r_{ss'}$ distances are proportional to ρ_s:

$$r_{ss'}=\sigma\rho_s \tag{11}$$

where σ is the proportionality factor.

c) Taking into account the different interactions of each atom with the solvent individual proportionality factors can be applied:

$$r_{ss'}=\sigma_s\rho_s \tag{12}$$

Pyrazine calculations were carried out employing Equ. 12.

4) For the force calculations the solvatons have to be localized. It was assumed that the solvatons are on the straight line determined by the mass center of the molecule and the atom s in a distance $r_{ss'}$ from the atom s in the direction of the solvent continuum:

$$\vec{r}_{s'}=\vec{r}_0+\frac{r_{0s}+r_{ss'}}{r_{0s}}\vec{r}_s \tag{13}$$

where the 0 index refer to the mass center.

The FORSOL program calculates internal forces, i.e. it is basically an extension of the CNDO-force program [3] to solute molecules.

Results and discussion

The FORSOL calculations on pyrazine were carried out on an R 32 computer. As reference geometry electron diffraction data were applied [4], geometry optimalization was not used.

A complet set of non-redundant coordinates were employed (see Table 1).

The effect of the solvent was taken into consideration by the following constants: $\varepsilon=78$, $\sigma_N=0.7$, $\sigma_C=1.0$ and $\sigma_H=1.0$. The results of these calculations were compared to the force constants of the isolated molecule. The force constants of the isolated molecule were scaled and the scaling factors were transferred to the solute molecule. Scaling factors are listed in Table 2.

Calculated and measured fundamentals are reported for in-plane modes in Table 3, for out-of-plane modes in Table 4. Comparing the calculated frequencies with the measured ones for solute molecules the deviations are very different. There are deviations of 3 cm^{-1} and of 95 cm^{-1}, too. The conclusion is, that better vibrational spectra are needed where all fundamentals can be assigned and the scaling factors can be fitted to the complete set of normal

Table 1

Internal coordinates of pyrazine

i	R_i	i	R_i
1	$r_{1,2}$	14	$\varphi_1-\varphi_2$
2	$r_{2,3}$	15	$\varphi_3-\varphi_4$
3	$r_{3,4}$	16	$\varphi_5-\varphi_6$
4	$r_{4,5}$	17	$\varphi_7-\varphi_8$
5	$r_{5,6}$	18	ϑ_7
6	$r_{6,1}$	19	ϑ_8
7	$r_{2,7}$	20	ϑ_9
8	$r_{3,8}$	21	ϑ_{10}
9	$r_{5,9}$	22	$\tau_{23}-\tau_{34}+\tau_{45}-\tau_{56}+\tau_{61}-\tau_{12}$
10	$r_{6,10}$	23	$\tau_{23}-0.5\tau_{34}-0.5\tau_{45}+\tau_{56}-0.5\tau_{61}-0.5\tau_{12}$
11	$\alpha_1-\alpha_2+\alpha_3-\alpha_4+\alpha_5-\alpha_6$	24	$\tau_{34}-\tau_{45}+\tau_{61}-\tau_{12}$
12	$\alpha_1-0.5\alpha_2-0.5\alpha_3+\alpha_4-0.5\alpha_5-0.5\alpha_6$		
13	$\alpha_2-\alpha_3+\alpha_5-\alpha_6$		

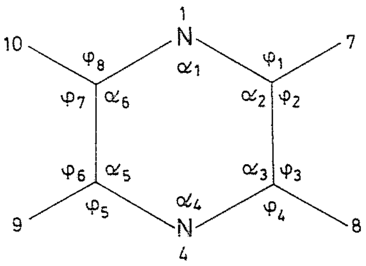

Table 2

Scaling factors of pyrazine

Coordinate		Scaling factor
$r_{(CN)}$	(1, 3, 4, 6)	0.33
$r_{(CC)}$	(2, 5)	0.39
$r_{(CH)}$	(7, 8, 9, 10)	0.39
$\beta_{(ring)}$	(11, 12, 13)	1.05
$\beta_{(CH)}$	(14, 15, 16, 17)	0.44
$\gamma_{(CH)}$	(18, 19, 20, 21)	0.64
$\gamma_{(ring)}$	(22, 23, 24)	0.50

Table 3

Calculated and measured in-plane fundamentals of pyrazine[a] (cm^{-1})

Species	Fundamental	Isolated molecule		Solute molecule	
		calc.	meas.	meas.[b]	calc.[c]
A_g	2	3038	3055	–	2976
	8a	1599	1580	1585	1560
	9a	1225	1233	1240	1199
	1	986	1016	1024	979
	6a	625	602	–	623
B_{1u}	13	3021	3012	–	2993
	19a	1465	1475	1492	1397
	18a	1153	1133	1130	1144
	12	1007	1018	1035	1005
B_{2g}	7b	3036	3040	–	3106
	8b	1532	1525	1532	1529
	3	1339	1346	1293	1329
	6b	692	704	704	688
B_{3u}	20b	3046	3066	–	3018
	19b	1458	1418	1420	1444
	14	1148	1145	1157	1150
	15	1016	1056	1074	1029
Average deviation:		17.9		33.8	

[a] Raman spectra of isolated molecule and numbering of the fundamentals from [5]

[b] solvent 1 mol/l NaOH

[c] $\varepsilon = 78$

Table 4

Calculated and measured out-of-plane fundamentals of pyrazine[a] (cm^{-1})

Species	Fundamental	Isolated molecule		Solute molecule	
		calc.	meas.	meas.[b]	calc.[c]
A_u	17a	963	960		955
	16a	356	350		350
B_{1g}	10a	901	927		886
B_{2u}	11	768	785	801	798
	16b	451	417		452
B_{3g}	5	998	983		988
	4	767	756		720

[a, b, c] for footnotes see Table 3.

Table 5

Scaled diagonal force constants of pyrazine (10^2 N m^{-1}, 10^{-8} N and 10^{-18} N m, respectively)

Type of coordinate		Calculated		Experimental [6]
		$\varepsilon=1$	$\varepsilon=78$	
r(CN)		7.237	6.840	6.97
r(CC)		6.311	6.313	6.34
r(CH)		5.311	5.355	5.12
β(ring)	(11)	1.586	1.640	
	(12)	0.774	0.904	
	(13)	2.126	2.156	
β(CH)		0.251	0.242	
γ(CH)		1.945	1.765	
γ(ring)	(22)	0.294	0.294	
	(23)	0.184	0.171	
	(24)	0.255	0.255	

frequencies and/or the model has to be refined (e.g. the $r_{ss'}$ distances have to be rescaled).

Table 5 contains the calculated diagonal force constants for isolated and soluted pyrazine together with the corresponding experimental force constants [6]. In spite of the different definition of the internal coordinates the agreement of the calculated and experimental force constants is satisfactory.

It is interesting that considerable deviation between the calculated force constants of the isolated and solute molecule is observed only for the r(CN) mode and for the ones in which the CH group moves.

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