15. *Dietz W., Riede W. O. and Heinzinger K.*// Z. Naturforsch.— 1982.— 37a.— P. 1038.
16. *Janscó, Heinzinger K. and Bopp P.*// Ibid. — 1985.— **40a**.— P. 1985.
17. *Robinson H. L. and Symons M. C. R.*// J. Chem. Soc. Faraday Trans. Part 1.— 1985.— 81.— P. 2131.
18. *Tanaka K., Ogita N., Tamura Y. et al.*// Z. Naturforsch.— 1977.— **42a**.— P. 29.
19. *Hawlicka E., Pálinkás G. and Heinzinger K.*// Chem. Phys. Lett.— 1989.— **153**.— P. 255.
20. *Spohr E., Pálinkás G., Heinzinger K. et al.* // J. Phys. Chem.— 1988.— **92**.— P. 6754.
21. *Szász Gy I. and Heinzinger K.*// Ibid.— 1983.— **79**.— P. 3467.
22. *Pratt K. C. and Wakeham W. A.*// J. Chem. Soc. Faraday Trans. Part 2.— 1977.— **73**.— P. 997.
23. *Heinzinger K.*// Physica.— 1985.— **131B**.— P. 196.
24. *LaPlaca S. I., Hamilton W. C., Kamb B. and Prakash A.* // J. Chem. Phys.— 1983.— **58**.— P. 567.
25. *Yamauchi S. and Kanno H.*// Chem. Phys. Lett.— 1989.— **154**.— P. 248.
26. *Probst M. M., Bopp P., Heinzinger K. and Rode B. M.*// Ibid. — 1984.— **106**.— P. 317.
27. *Tamura Y., Tanaka K., Spohr E. and Heinzinger K.* // Z. Naturforsch.— 1988.— **43a**.— P. 1103.
28. *Kleeberg H., Heinje G. and Luck W. A. P.*// J. Phys. Chem.— 1986.— **90**.— P. 4427.

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A MODELLING STUDY OF THE CONFORMATIONAL MOTIONS OF TETRAMYDROFURANE IN VARIOUS ENVIRONMENTS

Model potentials for tetrahydrofurane (THE), including inter- and intramolecular contributions and suitable for Molecular Dynamics (MD) computer simulation studies, are constructed from literature data. In one instance the CH_2-groups are treated in the united atom approximation (one force center per group) while a second model includes all intramolecular degrees of freedom. The intramolecular motions are studied mainly by MD simulations of isolated THF molecules, THF molecules entrapped in clathrate hydrates, and of aqueous solutions of THF.

1. Introduction

Molecular Dynamics (MD) computer simulations are a very powerful tool for the study of condensed phases. Accurate and reliable microscopic interaction potentials are an essential prerequisite for such studies. For small molecules it is sometimes possible to neglect the intramolecular motions and the deformations of the molecular geometry due to the environment of the molecule. For larger molecules, however, these features can no longer be ignored nor neglected. They may even play a crucial role for the structural and dynamical properties of the condensed phase [1, 2].

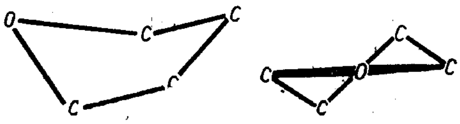

Fig. 1. The two basis conformations of THF

The properties of cyclic molecules in liquids and solids provide, among others, a good example for the importance of molecular flexibility. Tetrahydrofurane is such a molecule; many conformations of the ring are either directly. thermally accessible, or small perturbations of the intramolecular potential due to intermolecular interactions in the solid or liquid may render them accessible. There is spectroscopic evidence [3] that the equilibrium geometry of THF is nonplanar. Two such geometries can be distingushed for the THF ring: the envelope (E) form and the twisted (T) form. They are sketched in Fig. 1.

In this communication inter- and intramolecular interaction potentials for THF are presented. They are based on the combination of literature data. Two levels of approximation are used: In one instance the CH_2 groups are treated in the united atom approximation, while all intramolecular degrees of freedom are taken into account in the second instance. It is also attempted to keep the mathematical expressions for the potentials simple enough for the multiple evaluation during the simulation. The potentials are explored by normal coordinate analysis and by MD computer simulations. The motions involving changes in the intramolecular conformations are studied here for THF in various environments. The classical approximation should provide a realistic description of these motion since the masses involved are large.

2. The interaction potentials

In both cases, the total potential energy is assumed to be the sum of purely intermolecular and purely intramolecular terms:

$$V_{\text{tot}} = V_{\text{inter}} + V_{\text{intra}}$$

i. e. without interaction term. The intermolecular potentials between THF-molecules, as well as between THF and other molecules, are sums of site-site pair potentials. All sites coincide with atom positions in order to avoid the kinematic (or other) assumptions required for other types of sites if the molecular geometry is allowed to vary in the simulation. The intramolecular potentials are expressed in internal [4] and puckering [5] coordinates and thus comprise up to fivebody terms.

Intermolecular Potentials. Only the THF—THF and the THF—H_2O interactions will be considered here. The way in which they are expressed allows to construct site-site intermolecular potentials with other molecules easily. The intermolecular THF—THF interaction potential consists of Coulomb and Lennard — Jones (12—6) site-site pair-potentials

$$V_{\text{inter}} = \sum_{i,j}\left(\frac{q_\alpha q_\beta}{4\pi\epsilon_0 r_{ij}} + \right.$$
$$+ 4\epsilon_{\alpha\beta}\left(\left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{12} - \right.$$
$$\left.\left. - \left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{6}\right)\right),$$

where the sum is over the sites i and j of types α and β on two molecules. The partial charges are located on the oxygen atom and on the adjacent methylene groups, or carbon atoms in the case of the model including the hydrogens. The resulting dipole moment of the molecule in the C_{2v} configuration is 1,95D, compared to an experimental value of 1,63D [9]. The partial charges and the Lennard — Jones Parameters $\sigma_{\alpha\alpha}$ and $\epsilon_{\alpha\alpha}$ are obtained from literature sources and are listed in Table 1 together with the other parameters. The simulations of THF solutions reported below are performed with the BJH model for water [10]. In order to determine the Lennard — Jones parameters for the THF-water interaction by means of combination rules, the non-Coulombic parts of the water-water intermolecular interactions of this model are reparametrized in terms of such potentials with force centers on the oxygen and hydrogen atoms. The resulting parameters are also given in Table 1. The Lennard— Jones parameters for the THF-water interactions are then obtained by applying Kong's [13] combination rule:

$$\epsilon_{\alpha\beta}\sigma_{\alpha\alpha}^{12} = (\epsilon_{\alpha\alpha}\sigma_{\alpha\alpha}^{12}/2)^{13} * (1 + (\epsilon_{\beta\beta}\,\sigma_{\beta\beta}^{12}/\epsilon_{\alpha\alpha}\sigma_{\alpha\alpha}^{12})^{1/13})^{13},$$
$$\epsilon_{\alpha\beta}\sigma_{\alpha\beta}^{6} = (\epsilon_{\alpha\alpha}\sigma_{\alpha\alpha}^{6}\epsilon_{\beta\beta}\sigma_{\beta\beta}^{6})^{1/2}$$

Table 1. Intermolecular potential parameters $\sigma_{\alpha\alpha}$ (in 10^{-19} J), $\sigma_{\alpha\alpha}$ (in Å) and partial charges (in fractions of the elementary charge) for THF, from references [6—8]

site	$\epsilon_{\alpha\alpha}$	$\sigma_{\alpha\alpha}$	q_α
O	0,01256	3,067	—0,5
CH_2^a	0,00794	3,983	0,25
C	0,00179	4,45	0,25
H	0,00132	2,2	0,0
O_{H_2O}	0,01637	3,405	—0,6596
H_{H_2O}	0,00132	2,2	0,3298

[a] united-atom

except for the parameters for the interaction between a united atom CH$_2$ group and an oxygen, which are set 0,0996 · 10^{-19}J and 3,495 Å [6].

Intramolecular Potential of THF. The intramolecular potential for THF is adapted from the work of Eyster [14] and Jorgensen [7]. The $3N-6$ ($N=5$ for the potential with united atom CH$_2$-groups, $N=13$ taking into account the hydrogens) internal degrees of freedom of the THF molecule are divided into $3N-8$ coordinates describing the motions of a ring and 2 coordinates describing deformations of the ring leading to conformational changes. Consequently, the potential energy is formulated in terms of stretching and bending internal coordinates ρ [4] and of two «puckering coordinates» q and Φ [5] as a sum of two terms, i. e. without interactions between the two:

$$V_{\text{intra}}^{\text{THE}} = \frac{1}{2}\sum_{i,j} f_{ij}\rho_i\rho_j + V_{\text{pucker}}(q,\ \Phi).$$

The first term in the equation is a usual bilinear form in terms of internal displacement coordinates. Since in the simulation the displacements are not infinitesimally small, and furthermore the internal coordinates are not orthogonal to each other, an effective coupling occurs between the coordinates. The equilibrium distances and the force constants f_{ij} for the in-plane internal coordinates are taken from ref. [14] and are collected in Tables 2 and 3 for the two models. With reference to the planar ring, the first term will be called the «in plane potential», and the second term the «out of plane» or «puckering» potential.

Table 2. **Equlibrium values (in Å and degrees) of the coordinates, diagonal (upper rows) and off-diagonal or coupling (lower rows) force constants f_{ij} for THF mith united·atom CH$_2$ groups.**

Stretching force constants and stretch-stretch coupling constants are in mdyne/Å, stretch-bend coupling constants are in mdyne, and bending and bend-bend constants are in mdyne/Å. Couplings are between adjacent angles and bonds only

	O—C	C—C	∠COC	∠OCC	∠CCC
	1,43	1,54	111,0	109,1	105,4
O—C	5,4953 0,2956	0,101	0,8752	0,4197	
C—C		4,2697 0,101		0,3656	0,417
∠COC			1,3081	0,0285	
∠OCC				1,1633	0,1139
∠CCC					1,0079 0,1139

The variables in V_{pucker} are defined in the following way: $q=(z_1^2+z_2^2+z_3^2+z_4^2+z_5^2)^{1/2}$ with z_i the distance of a ring atom from the reference plane of the molecule. This reference plane must fulfill the following requirement: It must be invariant against internal motions of the molecule as well as against translations and rotations. This is achieved if the following equations are met [5]:

$$\sum_{i=1}^{5} z_i = 0, \quad \sum_{i=1}^{5} z_i\cos(\alpha_i) = 0,$$

$$\sum_{i=1}^{5} z_i\sin(\alpha_i) = 0, \quad \alpha_i = 2\pi(i-1)/N.$$

The geometrical center of the ring P is the point $\boldsymbol{r}_p$ where $\sum_{i=1}^{5} \boldsymbol{R}_i = 0$ with $\boldsymbol{r}_i$ the positions of the ring atoms and $\boldsymbol{R}_i = \boldsymbol{r}_i - \boldsymbol{r}_p$. Two vectors $\boldsymbol{R}'$ and $\boldsymbol{R}''$ are defined:

$$\boldsymbol{R}' = \sum_{i=1}^{5} \boldsymbol{R}_i\sin(\alpha_i), \quad \boldsymbol{R}'' = \sum_{i=1}^{5} \boldsymbol{R}_i\cos(\alpha_i),$$

$\boldsymbol{R}'$ and $\boldsymbol{R}''$ span the reference $x-y$ plane with normal vector $\boldsymbol{z}_N$: $\boldsymbol{z}_N = \frac{\boldsymbol{R}' * \boldsymbol{R}''}{|\boldsymbol{R}' * \boldsymbol{R}''|}$ and the z_i finally are $z_i = \boldsymbol{R}_i * \boldsymbol{z}_N$.

Table 3. **Additional constants for THF with hydrogens treated explicitely. Units as in Table 2**

	C—H_a	C—H_b	∠H_aCH_a	∠H_bCH_b	∠H_aCO	∠H_aCC	∠H_bCC
1,09	1,09	109,4	109,4	109,55	109,55	110,45	
C—H_a	4,6440 —0,0652						
C—H_b		4,5709 —0,0182					
∠H_aCH_a			0,5017				
∠H_bCH_b				0,550			
∠H_aCO					0,7810 —0,0824	0,0363	
∠H_aCC					0,7346 —0,0881		—0,0664^t 0,0314^c
∠H_bCC							0,656 —0,021^{s1} 0,012^{s2} —0,443^t 0,0173^c
C—O					0,3842		
C—C						0,4288	0,328^b 0,0703^o
∠COC					0,0844		
∠OCC					—0,031	0,0158	
∠CCC						—0,31	—0,31^n —0,052^s

[b] with C—C bond defining angle; [c] angles between C—H bonds in cis positions at two adjacent carbon atoms and C—C bond;

[n] angles at neighboring carbon atoms: [o] wish C—C bond not included in angle; [s] two angles at the same carbon atom;

[s1] two angles at the same carbon atom with common C—C bond;

[s2] two angles at the same carbon atom with common H_b—C bond;

[t] angles between C—H bonds in trans positions at two adjacent carbon atoms and C—C bond.

These z_i fulfill the equations above. The relation between the puckering coordinate q and the z_i is given by: $z_i = q_m \cos(m\alpha_i)$ or $z_i = q_m \sin(m\alpha_i)$, where $m = 0, 1, 2, \ldots$ is an integer. Not all values of m are suitable for the purpose of describing the conformational motions; $m = 1$ describes, for instance, a rotation of the entire molecule. The value $m = 2$ leads to: $z_i = q_2 \cos(2\alpha_i)$, $i = 1, 2, \ldots, 5$ and $z_i = q_2 \sin(2\alpha_i)$, $i = 1, 2, \ldots, 5$ which, introducing the variable Φ, can be combined to: $z_i = q_2 \cos(2\alpha_i + \Phi)$, $i = 1, 2, \ldots, 5$.

In order to determine $q = q_2$ and Φ from the Cartesian coordinates of the ring atoms, an additional normalization condition is introduced: $\sum_{i=1}^{5} z_i^2 =$

$= q^2$ and, with $q > 0$, Φ can be obtained for instance from:

$$\Phi = \arccos\left(\left(\frac{2}{5}\right)^{-\frac{1}{2}} * \frac{z_1}{q}\right).$$

The equations for $m = 2$ describe the two basic conformations of the ring, namely the envelope and the twist form. A pseudorotation by the angle Φ transforms the one into the other. Fig. 2 shows the molecular conformations as a function of Φ (for a given value of q.) $V_{\text{pucker}}(q, \Phi)$ is taken as a series: $V_{\text{pucker}}(q, \Phi) = V_{00} + A * q^3 + B * q^4 + (C * q^2 + D * q^4) * \cos(2\Phi)$ with coefficients from reference [7]:

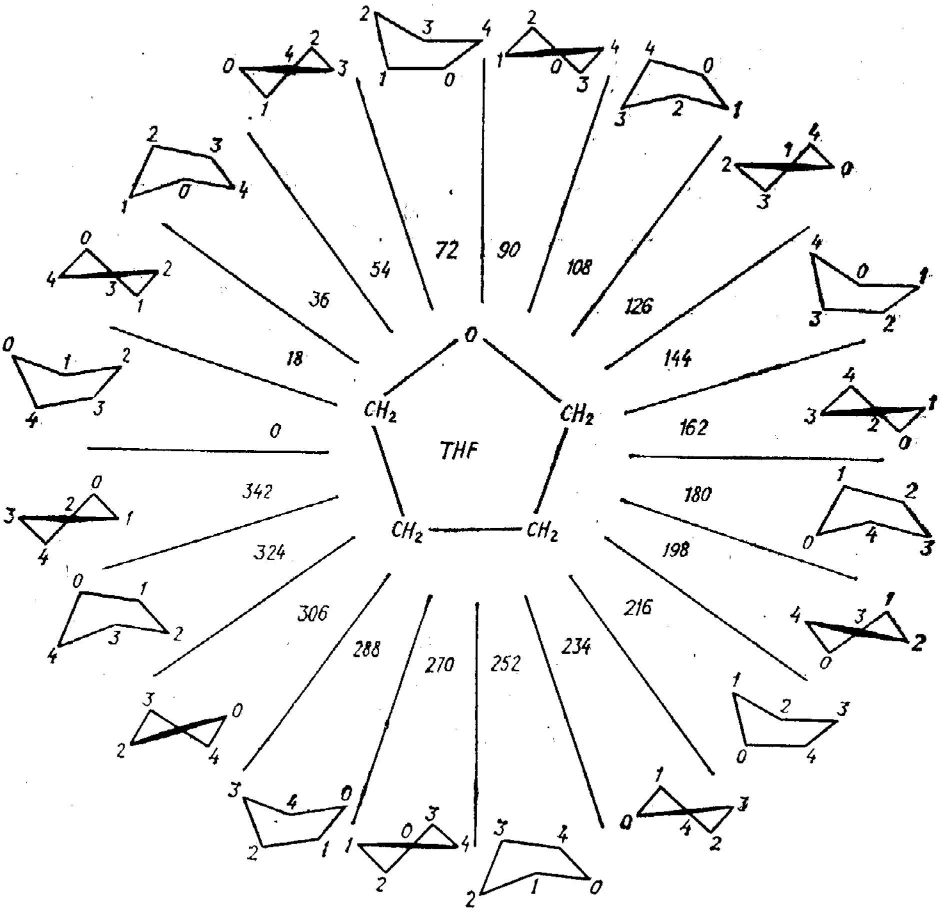

Fig. 2. Sketch of the conformations of THF as a function of Φ

$V_{00} = 0{,}24248 \cdot 10^{-19}$ J, $A = -3{,}11616 \cdot 10^{-19}\text{J Å}^{-2}$, $B = 10{,}5954 \times \times 10^{-19}\text{J Å}^{-4}$, $C = 0{,}38005 \cdot 10^{-19}\text{J Å}^{-2}$, $D = -1{,}2978 \cdot 10^{-19}\text{J Å}^{-4}$.

The resulting potential $V_{\text{pucker}}(q, \Phi)$ is shown in Fig. 3. The global minima are at $q_{\min} = 0{,}383$ Å, $\Phi = 90°$, $270°$, etc., i. e. where the molecule is in its twisted form. This is in agreement with spectroscopic evidence [3]. Conformers with $\Phi = 36°$, $72°$, $108°$, $144°$, $216°$, $252°$, $288°$ and $324°$ correspond to E-forms with methylene groups in the apex, with higher energies, while Φ-values of $0°$ and $180°$ lead to the envelope forms with the oxygen in the apex. The energy of this conformer is (at $q = q_{\min}$) 277 cm^{-1} above the minimum energy. This value is higher than the experimental estimate (50 cm^{-1} and < 170 cm^{-1} from infrared work, 57 cm^{-1} from microwave work, see refs. [3, 11] for more details), but lower than the value from ab-initio calculations with 4—31G basis (465 cm^{-1} [5]) and in reasonable agreement with the barrier height obtained more recently with a 6—31G basis (259 cm^{-1}) [12]. The planar

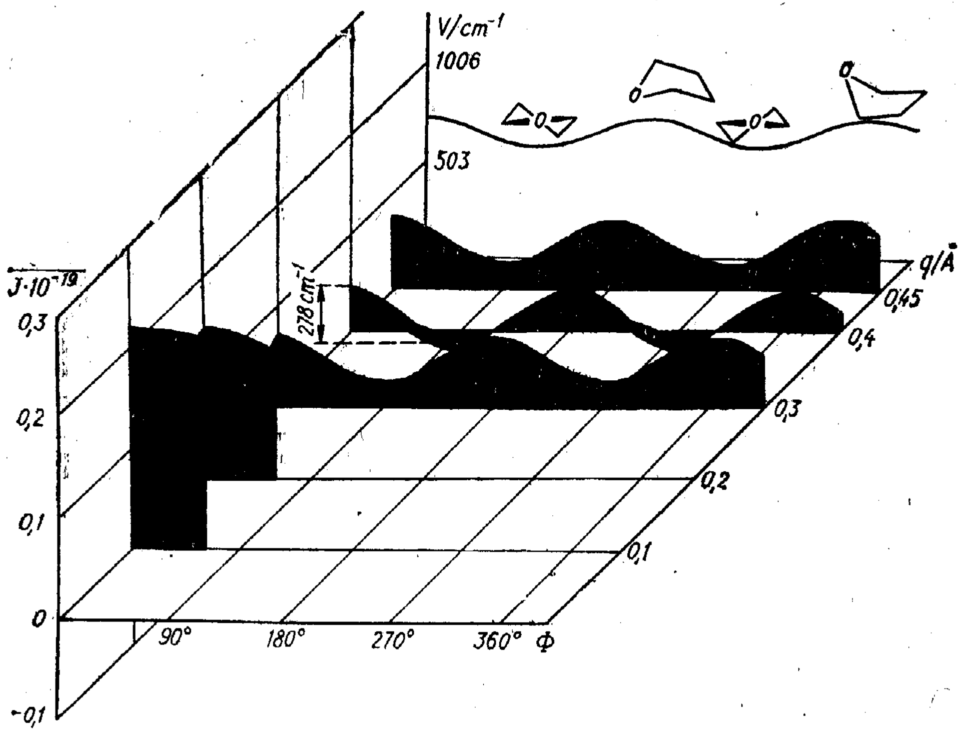

Fig. 3. The puckering potential as a function of q and Φ

conformation is 1221 cm^{-1} above the minimum energy, in good agreement with the experimental estimate [3, 11].

Other Interaction Potentials. The water molecules are assumed to be flexible, and the BJH model [10] is used to describe both the intermolecular water-water interactions and the intramolecular water potential. The other guest molecules in the clathrates simulations, N_2 and H_2S, are modelled accordingly, details will be reported elsewhere [2, 16].

3. Simulations

The MD simulations are carried out in the NVE ensemble. The forces are computed from the analytical derivatives of the potentials in all cases, and since all molecules are flexible, integration is carried out in Cartesian coordinates. The long range electrostatic interactions are treated by Ewald-summation (see e. g. ref. [15]). More details about the simulations as well as further results can be found elsewhere [2] and in a forthcoming publication [16]. Only the conformational motions of the THF molecules in various environments will be discussed here.

4. Results and discussion

Normal mode frequencies of planar THF have been reported by Eyster [14]. Table 4 gives these frequencies together with the ones obtained with the present model in the united-atom approximation, and the ones from the MD-simulations obtained from the positions of the peak maxima in the Fourier cosine transforms of the autocorrelation functions of the particle velocities in the center of mass frame of the molecule. The influence of the united atom approximation is seen by comparing lines A and B in Table 4. It is small, except for the lowest frequency, where a coupling to a wagging type motion of the hydrogens is probably responsible for the difference of 40 cm^{-1}. Lines C to F, compared to line B, show the influence of the puckering motion and of the environment on these modes. Only small shifts, both to the red and to the blue, are seen for the high frequency modes. These shifts do not depend on

Table 4. **Vibrational frequencies of THF in cm^{-1}, from normal coordinate analyses and from MD- simulations. The error margin for cases C to F is estimated to be about ± 5 cm^{-1}. The attributions are from ref. [14], MD results are attributed on the basis of the frequencies**

	C—O ring			C—C C—O ring			
	as. str	str.	as. str	sy. str.	breath.	bend	bend
A	1196	1093	958	954	904	960	604
B	1198	1121	969	954	906	652	563
C	1185	1106	979	960	927	635	604
D	1184	1107	977	967	932	637	555
E	1186	1105	980	963	934	638	653
F	1184	1105	982	963	930	638	553

A: normal modes, from ref [14] fom a C_{2v} molecule. *B*: this work, normal mode analysis with united atoms and the force field form Table 2. *C*: from the Fourier transform of the **autocorrelation** function of the particle velocities, solution of THF in water, 293 K. *D*: same as *C* for THF in a clathrate cage at 242 K. *E*: same as *D*, 138 K. *F*: same as *D*, 73 K.

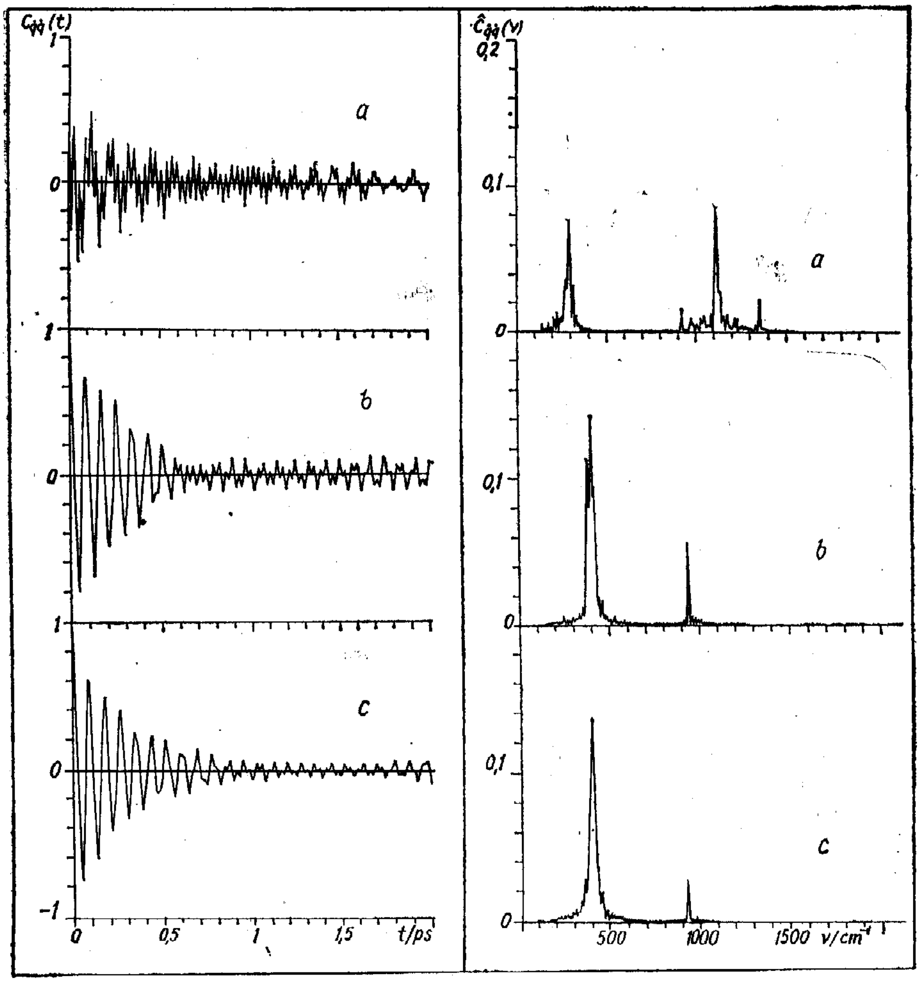

Fig. 4. Autocorrelation functions $C_{qq}(t)$ (left) and their Fourier cosine transforms $\hat{C}_{qq}(\nu)$ (right). All-atom THF in a clathrate cage at 264 K (*a*); united-atom THF in a clathrate cage at 242 K (*b*); and united atom THF in aqueous solution at 293 K (*c*)

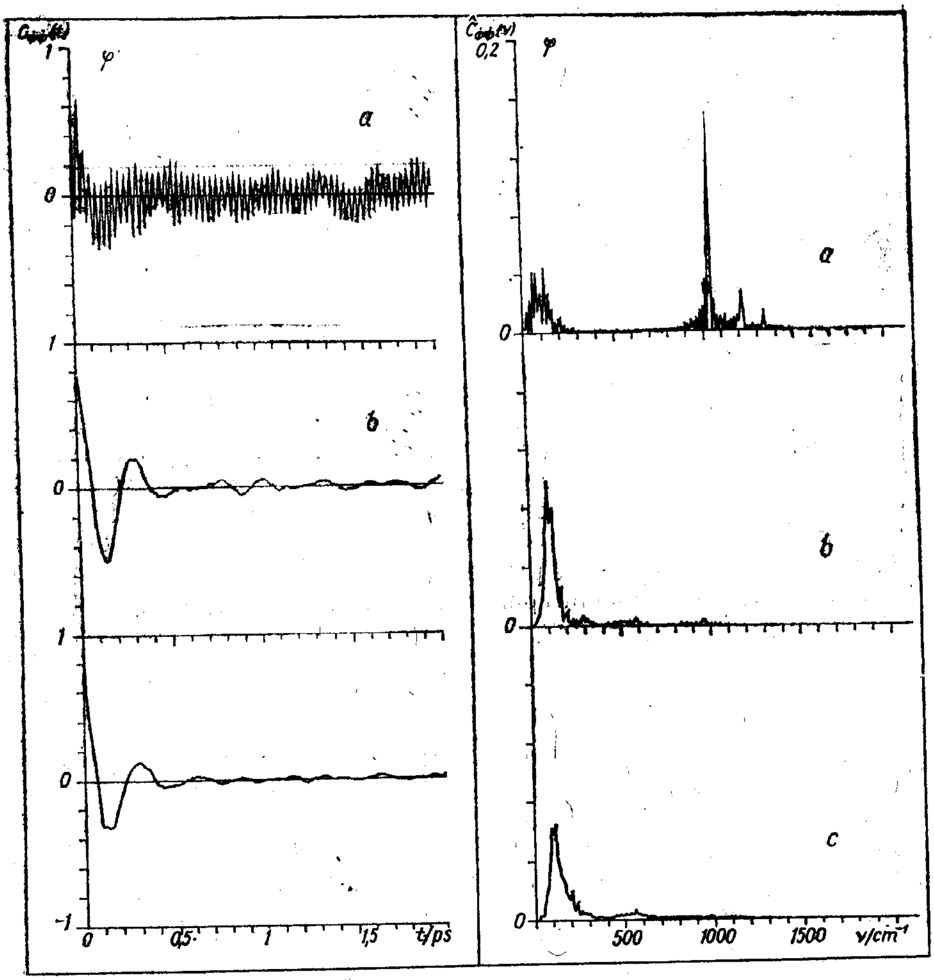

Fig. 5. Same as Fig. 4 for $C_{\dot\Phi\dot\Phi}(t)$ and $\hat C_{\dot\Phi\dot\Phi}(\nu)$

the type of environment (liquid or clathrate) and also do not depend on temperature. The two low frequency bending modes, on the other hand, have shifts of up to sevepal 10 cm^{-1}, which depend on the environment of the molecule.

In analogy with the technique employed for the «in-plane» motions, the puckering motions are analyzed in terms of the normalized autocorrelation functions of the time derivatives of the puckering coordinates, $\dot q$ and $\dot\Phi$:

$$C_{\dot q\dot q}(t) = \langle \dot q_i(\tau) * \dot q_i(\tau + t)\rangle_{i,\tau} / \langle \dot q_i(\tau) * \dot q_i(\tau)\rangle_{i,\tau},$$

$$C_{\dot\Phi\dot\Phi}(t) = \langle \dot\Phi_i(\tau) * \dot\Phi_i(\tau + t)\rangle_{i,\tau} / \langle \dot\Phi_i(\tau) * \dot\Phi_i(\tau)\rangle_{i,\tau},$$

$\dot q$ and $\dot\Phi$ are computed numerically from the simulation data. Fig. 4 and 5 shows these functions together with their Fourier cosine transforms (spectral densities) for three cases. The frequencies of the peak maxima are reported in Table 5.

The q—q-correlation can be interpreted as describing essentially the oscillatory motions of the molecule at fixed conformer, while the Φ—Φ-correlation can be seen as the librational motions of the pseudorotation that transforms one conformer into another one, see Fig. 2. The correlations for both types of motions decay within about 1 ps in the environments studied here, except for the fast motions of the hydrogens that couple with the puckering in the all — atom approximation (curves a in Figs. 4 and 5).

Table 5. Frequencies of the peak maxima in the spectral densities of $C_{\dot q \dot q}$ and $C_{\dot\Phi\dot\Phi}$, in cm^{-1}. The error margin is estimated to be ±5 cm^{-1}

			$C_{\dot q\dot q}$		$CC_{\dot\Phi\dot\Phi}$	
clath.	all atom	264 K	293	1113	140	1039
clath.	all atom	64 K	294	1117	136	1034
clath.	un. atom	242 K	399	934	99	—
clath.	un. atom	138 K	402	934	122 115	—
clath.	un. atom	73 K	503	932	133 138	—
solut.	un. atom	293 K	393	928	119	—

This influence of the hydrogens on the puckering motion is obvious from Table 5 and the Figures. The lower frequency obtained from $C_{\dot q\dot q}$ is lowered by about 100 cm^{-1} and the higher frequency is increased by almost 200 cm^{-1} if the hydrogens are treated explicitely. In this case, the spectral density shows intensity also at other frequencies, indicating complex couplings between the hydrogen motions and the puckering. This is also seen from the Φ—Φ-correlation. In the united-atom approximation, the only coupling of the puckering is with the ring breathing motion at 932 cm^{-1}. From the relative in-

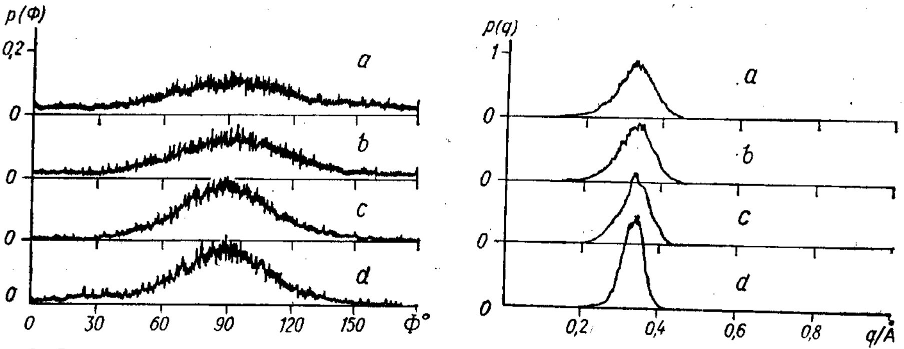

Fig. 6. Distribution of the puckering coordinates q and Φ, in arbitrary units, from the simulations of THF in a clathrate at:
a — 242 K; *b* — 190 K; *c* — 138 K; *d* — 73 K

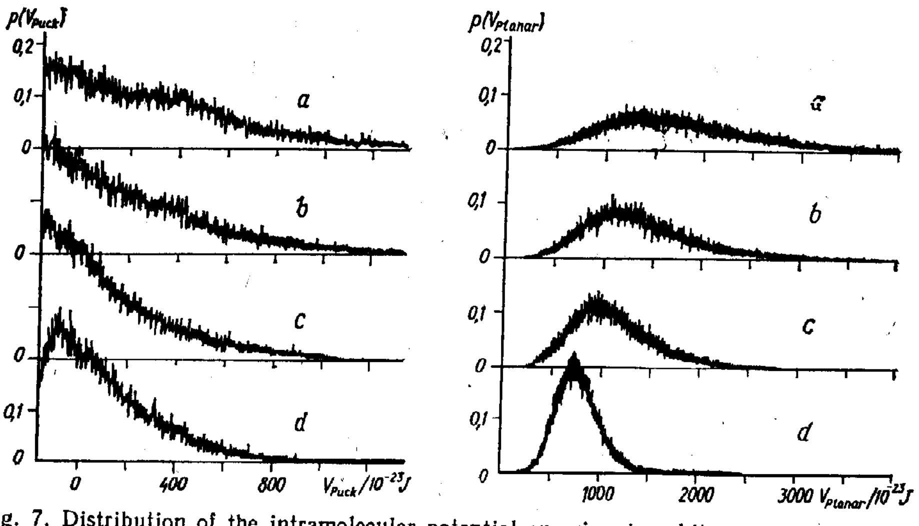

Fig. 7. Distribution of the intramolecular potential energies, in arbitrary units, separately for pucker and inplane interactions, from the simulations of THF in a clathrate at:
a — 242 K; *b* — 190 K; *c* — 138 K; *d* — 73 K

tensity of the peaks, it seems that this coupling is reduced by the solvation of the molecule in aqueous solution. In this case, a shoulder appears in $\hat{C}_{\Phi\Phi}$ (ν) around 550 cm^{-1}, which could be due to the librational motions of the water.

From normal coordinate analyses out-of-plane modes at 214 cm^{-1} and 277 cm^{-1} are reported for the C_{2v} molecule [14]. These values are lower than the ones found here for the main peak in the transform of the q—q-correlation, but higher than the one from the Φ—Φ-correlation. Values similar to the ones reported here are also found in MD-simulations of isolated THF molecules with the present intramolecular potential [2]: 120 cm^{-1} and 400 cm^{-1}. The widths of the bands are much smaller in this case than the ones in Fig. 4 and 5. These frequencies are thus only slightly shifted by the environment, which essentially leads to a broadening of the peaks.

The distribution of the puckering coordinates is seen in Fig. 6. This mirrors both the thermal motions of the molecule ant its deformations under the influence of its neighborhood. The distributions show the expected behaviour as a function of temperature. Note that p (Φ) is nonzero over the entire range of Φ, even at the lowest temperature studied, showing that interconversion between the conformers takes place. The q-distribution shows that, as expected from the potential, this interconversion does not occur through the planar conformation ($q = 0$).

Fig. 7 finally shows distributions of the in-plane and pucker potential energy of THF at various temperatures. Here also, the behaviour as a function of temperature is broadly as expected. Features in p (V_{pucker}) indicate again that couplings occur in these strongly anharmonic potentials. The distributions both in Fig. 6 and 7 also indicate that the potentials are sufficiently sampled by the MD-simulations and one should thus expect the frequencies and spectral densities reported above to be reliable.

5. Summary and conclusions

A united-atom and all-atom flexible model for THF is developed from literatures data. They are used in MD-simulations of THF in clathrate hydrates and in aqueous solution at various temperatures as well as in normal coordinate analyses. The intramolecular vibrational frequencies of THF, which are analyzed here, display frequency shifts, compared to the normal mode frequencies of the isolated molecule, of up to a few 10 cm^{-1} in aqueous solutions and, surprisingly, also in clathrate cages. Frequency shifts of up to 100 cm^{-1} are found for the puckering motions between the united-atom and the all-atom models. Distributions of the puckering coordinates and of the intramolecular potential energies confirm the interpretation given from the analysis of the spectral densities of the intramolecular motions. The conformational motions discussed here have been shown [2] to make important contributions to the decorrelation of the intramolecular proton-proton vectors mainly responsible for the NMR relaxation rates; measurements of these rates on THF in clathrate hydrates have been reported recently [17].

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1. *Nickel E.* // Computersimulation von 18-Krone-6, thesis, RWTH-Aachen.— 1990.
2. *Meier W.* // Molekulardynamische Computersimulation von Clathrathydraten, thesis, RWTH-Aachen.— 1992.
3. *Engerholm G. G., Luntz A. C., Gwinn W. D., Morris D. O.* // J. Chem. Phys.— 1969.— **56**.— P. 2446; *Greenhouse J. A., Strauss M. L.* // Ibid.— 1969.— **50**.— P. 124.
4. *Wilson E. B., Decius J. C., Cross P. C.* // Molecular Vibrations, McGraw-Hill, New York.— 1955.

5. *Cremer D., Pople J. A.* // J. Amer. Chem. Soc.— 1975.— **97**.— P. 1354; *Cremer D.* // J. Phys. Chem.— 1990.— **94**.— P. 5502.
6. *Jorgensen W. L., Ibrahim M.* // J. Amer. Chem. Soc.— 1973.— **107**.— P. 2464.
7. *Chandrasekhar J., Jorgensen W. L.* // J. Chem. Phys.— 1982.— **77**.— P. 5073.
8. *Lemberg H. L., Stillinger F. H.* // Ibid.— 1975.— **62**.— P. 1677.
9. Handbook of Chemistry and Physics, edited by Weast, R. C., CRC Press, 1988.
10. *Bopp Ph., Jancso G., Heinzinger K.* // Chem. Phys. Lett.— 1983.— **98**.— P. 129; see also: *Ruff I., Diestler D. J.* // J. Chem. Phys.— 1990.— **93**.— P. 2032.
11. *Rosas R. L., Cooper C., Laane J.* // J. Phys. Chem.— 1990.— **94**.— P. 1830.
12. *Cremer D.* // Isr. J. Chem.— 1983.— **23**.— P. 72.
13. *Kong C. L.* // J. Chem. Phys.— 1973.— **59**.— P. 2464.
14. *Eysler J. M. Prohofsky E. W.* // Spectrochim. acta.— 1974.— **30A**.— P. 2041.
15. *Allen M. P., Tildesley D. J.* Computer Simulation of Liquids // Clarendon Press, Oxford, 1987.
16. *Meier W., Zeihler M. D.* and *Bopp Ph.*, in preparation.
17. *Albayrak C., Zeidler M. D., Kuchler R., Kanert O.* // Ber. Bunsenges phys. Chem.— 1989.— **93**.— P. 1119.

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АНАЛІТИЧНИЙ РОЗВ'ЯЗОК СЕРЕДНЬОСФЕРИЧНОЇ ЗАДАЧІ ДЛЯ БАГАТОСОРТНОЇ ІОННО-ДИПОЛЬНОЇ МОДЕЛІ

Розглядається багатосортна іонно-дипольна модель з довільними розмірами, валентностями і дипольними моментами частинок. Знайдено загальний розв'язок рівнянь Орнштейна — Церніке в середньосферичному наближенні з використанням факторизаційної техніки, впровадженої Вертхаймом і застосованої до несферичних взаємодій Блюмом.

Наявність густого полярного середовища, яке інтенсивно взаємодіє з іонами, відіграє визначну роль для багатьох властивостей розчинів електролітів. Тому розвиток у рамках статистичної теорії електролітів послідовного іонно-молекулярного підходу, який базується на рівноправному врахуванні всіх частинок розчину, відкриває принципово нові можливості для розкриття природи і кількісного опису явищ іонної сольватації, формування ефективних міжіонних взаємодій у розчинах, утворення іонного порядку та інших ефектів, а також для дослідження характеру їх зміни при зміні концентрації іонів та інших параметрів (температури, густини і полярності розчинника, характеру міжчастинкових взаємодій) [1—6].

Основна проблема в задачі опису і послідовного врахування рідкої молекулярної підсистеми виникає внаслідок наявності орієнтаційних ступенів вільності у молекул. Врахування орієнтаційних залежностей у потенціалі міжмолекулярних взаємодій здійснюється звичайно за допомогою розкладу за узагальненими сферичними функціями. У результаті орієнтаційно залежні функції зображуються в орієнтаційно-інваріантній формі [7—10].

Найпростішою моделлю в рамках іонно-молекулярного підходу є іонно-дипольна, що складається із твердих сфер, які мають або заряд, або дипольний момент. Останнім часом ця модель досліджувалась у рамках гіперланцюжкового наближення, модифікованого рівняння Пуассона — Больцмана, а також середньосферичного наближення. Особливе місце тут займають дослідження в рамках середньосферичного наближення [2, 3, 11—15], яке не лише допускає аналітичний розв'язок для ряду модельних систем, але й приводить до порівняно простих і достатньо коректних результатів при порівнянні з більш точними теоріями, а також результатами комп'ютерного моделювання.