

STABILIZATION ENERGY OF COLLISION COMPLEXES AND ITS SEMIEMPIRICAL CALCULATIONS*

M.HORÁK^a, S.HILGARD^b and P.HOBZA^c

^a *J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 121 38 Prague 2,*

^b *Institute of Organic Chemistry, Charles University, 128 40 Prague 2 and*

^c *Institute of Hygiene and Epidemiology, 100 42 Prague 10*

Received July 16th, 1974

Interaction energy between a molecule of acetic acid monomer and hexafluoroethane, tetrachloromethane, and carbon disulphide molecules was determined as a sum of dispersion, repulsion, coulomb, and polarization energy. Potential curves exhibit minima of energy over the range of separations 2.3—3.2 Å for various mutual spacial orientations of the molecules. The shape of the potential curve with the minimum found for these model systems supports the concept of formation of very weak collision complexes in solutions of polar solutes in non-polar solvents. The stabilization energy of the collision complexes is very small and its occurrence is to a considerable extent governed by the entropy effects. Thus, the collision complexes exhibit a significantly statistical character.

The previous paper described our experimental study of the dimerization of acetic acid in the gaseous phase and in the solutions of non-polar solvents¹. From the difference of the stabilization enthalpies of dimerization in the gaseous phase and in the solutions we estimated the value of the stabilization enthalpy of formation of the so called "collision complexes"^{2,3} of the molecules of the acetic acid monomer and molecules of non-polar solvents. In this communication we have calculated the values of this stabilization enthalpy by means of semiempirical methods. Moreover, we studied the role of energetic and entropic factors in the formation of the collision complexes in solutions.

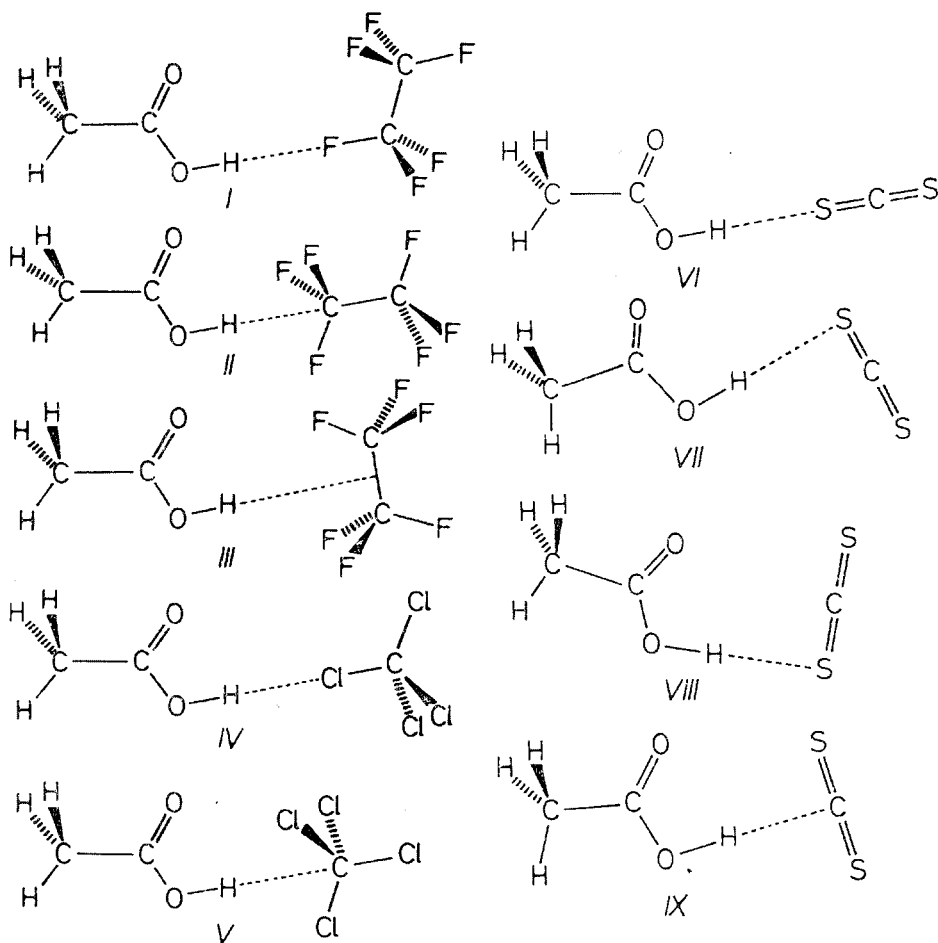
EXPERIMENTAL

The compounds used in this study were dry substances of analytical purity. The methods of their preparation, purification, and the data on their quality were summarized in our previous communication⁴. This paper described also the preparation of solutions, techniques of spectra measurement, and the procedure used to mathematically separate overlapping bands.

* Part VII in the series Studies of Solute-Solvent Interactions; Part VI: This Journal 39, 3215 (1974).

CALCULATIONS

In view of the complexity of the interacting molecules, the simplest method of the interaction energy calculation was used — the empirical Buckingham potential in the Eliel parametrization⁵. This was because at the present time it is not possible to use some of the more advanced procedures



for systems of such complexity. To the dispersion and repulsion energy determined in this way, the contribution of the coulomb and polarization energy was then added. As the input data, the charge densities as determined by the CNDO/2 method⁶, the van der Waals atomic radii⁵, and the bond polarizabilities^{7,8} were used. Further information on the method used in these calculation of interaction energy can be found in ref.⁹. The interaction energy of the molecular pairs was determined for configurations I–IX.

RESULTS

The interaction of pairs of molecules which were assumed¹ to form collision complexes was subjected to a theoretical investigation. As the polar molecule, the monomer of acetic acid was used; the interaction partners were then tetrachloromethane, carbon disulphide, and hexafluoroethane molecules. Hexafluoroethane served in the calculations as a substitution for molecules of perfluorocycloalkanes which — even though used in the experiments — would considerably complicate the calculations because of their complexity. Table I summarizes the values of the calculated interaction energy for all the studied pairs and for various orientations, the particular contributions of dispersion, repulsion, coulomb, and polarization energies, and the intermolecular separation at which the energy minimum on the potential energy curve occurred (Fig. 1).

The usually shallow minima were found to occur at fairly large intermolecular separations. If this separation was expressed as $r_{H...F}$, *i.e.* the separation between the hydrogen of the hydroxyl of the acetic acid monomer and the nearest atom X of the second molecule, the minima lay between 2.3 and 3.2 Å. If the separation was expressed as usual for two molecules bound by the hydrogen bond, *i.e.* as the separation of the two heavy atoms bound by the hydrogen atom, the minima fell between 3.4 and 4.3 Å. In any case, the separation between the molecules at the peak of interaction

TABLE I

Calculated Interaction Energies^a E and its Contributions, Dispersion E_d , Repulsion E_r , Electrostatic E_e , Polarization E_p , for Vapours of Molecules of Acetic Acid Monomer-Solvent

Solvent	Orientation	r^b	E_d	E_r	E_e	E_p	E	ΔH^c
C ₂ F ₆	I	2.3	-0.64	0.28	-0.21	-0.01	-0.58	-0.2 ^d
	II	2.7	-1.22	0.38	0.30	-0.02	-0.57	
	III	3.2	-1.03	0.25	0.29	-0.01	-0.50	
CCl ₄	IV	2.8	-0.77	0.31	-0.04	-0.01	-0.50	-1.9
	V	2.8	-2.92	1.32	0.18	-0.08	-1.50	
CS ₂	VI	2.9	-0.65	0.25	-0.06	-0.01	-0.48	-2.7
	VII	2.8	-0.98	0.40	0.04	-0.02	-0.55	
	VIII	2.7	-1.43	0.64	0.28	-0.18	-0.69	
	IX	2.5	-1.92	0.92	-0.23	-0.21	-1.44	

^a kcal mol⁻¹; ^b separation $r_{H...X}$ in Å at the potential energy minimum; ^c experimentally determined stabilization enthalpies from ref.¹; ^d value determined for the collision complex acetic acid monomer-perfluoromethyldecane.

is well beyond the range of chemical forces so that the delocalization contributions of the hydrogen bond do not have to be considered. This is why in our method of the interaction energy calculation the charge-transfer (delocalization) term was not explicitly considered¹⁰.

The magnitude of the stabilization enthalpy depends on the mutual orientation of the interacting molecules. An exception represents hexafluoroethane: three different orientations of the acetic acid monomer molecule and the hexafluoroethane molecule, *I–III*, give very similar values between -0.5 and -0.6 kcal mol⁻¹. In the system with tetrachloromethane, two orientations were considered (*IV* and *V*); in one of them, the hydrogen atom of the monomer hydroxyl was directed against the chlorine atom, in the other one against the carbon atom of the tetrachloromethane molecule. The values of the stabilization enthalpy of these two orientations are very different, the latter one is three times larger. Differences of a similar magnitude were found for the pair acetic acid monomer–carbon disulphide, too. Four different

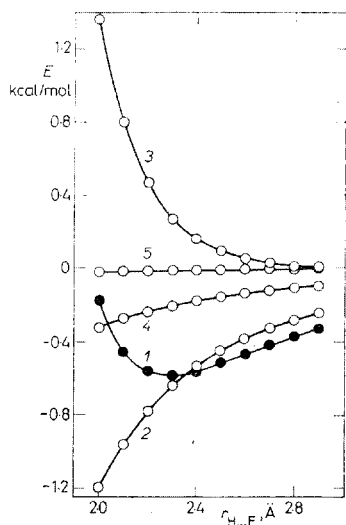


FIG. 1

Dependence of Calculated Total Interaction Energy *1* (full points/of) the Molecule of Acetic Acid Monomer with C₂F₆ in Orientation (*I*), and Particular Contributions of Dispersion *2*, Repulsion *3*, Coulomb *4*, and Polarization *5* Energy on Intermolecular Separation $r_{H...F}$.

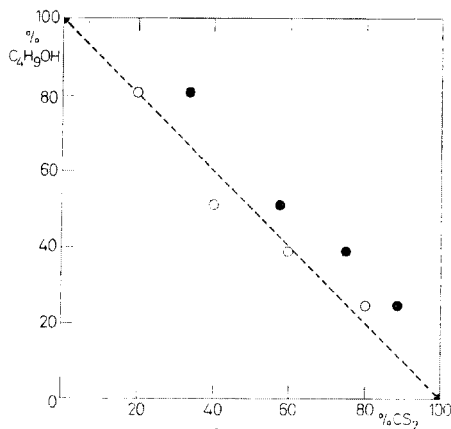


FIG. 2

Dependence of Concentration of *t*-Butyl Alcohol–1,2-Difluorotetrachloroethane Collision Complex on Molar ● and Volume ○ Composition of the Solvent Mixture (1,2-difluorotetrachloroethane–CS₂)

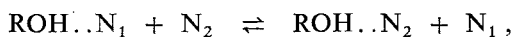
orientations were investigated here (VI–IX) with the conclusion that the most stable was that one in which the O–H bond of the monomer was perpendicular to the linear molecule of carbon disulphide and directed towards the carbon atom.

DISCUSSION

There is a fair agreement between the experimental values of the stabilization enthalpy¹ of formation of the collision complex of the acetic acid monomer with tetrachloromethane, carbon disulphide, and perfluoromethyldecaline (Table I) and the values calculated for the most stable orientations of the molecular pairs. The largest deviations were found in the interactions with carbon disulphide; however, the considerable bigger experimental value is evidently due to the fact that carbon disulphide is not an entirely inert solvent (as it follows from its other properties, too¹¹).

The minima on the potential energy curves occur in the region of reasonable intermolecular separations. The occurrence of the minima as well as the calculated equilibrium separations provide a considerable support for the reliability of the concept of the collision complex formation in these systems. However, small values of the interaction energy raise the question in which way the formation of so weak collision complexes can be accomplished. First, let us regard the formation of the collision complexes as an equilibrium process (collision equilibria were described in the previous communication¹).

The processes taking place in a system composed of two non-polar solvents, N₁ and N₂, and a very small amount of a polar solute ROH (whose concentration is kept so low that the interaction ROH..ROH does not play a role) can be described as an equilibrium reaction by the equation



where ROH..N₁ and ROH..N₂ are collision complexes of the ROH molecule with the solvent molecules N₁ and N₂, respectively. The equilibrium constant *K* is – according to the law of mass action – expressed as

$$K = [\text{ROH}..N_2][N_1]/[\text{ROH}..N_1][N_2], \quad (1)$$

where the quantities in parentheses represent the molar concentrations. The equilibrium constant is simply related to the thermodynamic quantities of complex formation

$$-RT \ln K = \Delta G = \Delta H - T \Delta S. \quad (2)$$

Here, ΔG , ΔH , ΔS are the free enthalpy, enthalpy, and entropy changes, respectively; *R* is the gas constant, and *T* the absolute temperature.

Let us consider now the following three cases: the value of K equals unity, the value of K is smaller and larger than unity. For $K = 1$, ΔG is zero and $\Delta H = T\Delta S$. In this case ΔH is of a purely entropic origin and the distribution of the two collision complexes is linearly dependent on the molar fractions of the solvents. If K is larger than unity, ΔG is negative; if K is smaller than unity, ΔG is positive. In both cases the abundance of one of the collision complexes is higher than the abundance of the corresponding solvent in the mixture.

We studied experimentally the systems composed of two non-polar solvents, N_1 (1,2-difluorotetrachloroethane), N_2 (carbon disulphide), and a solute (t-butyl alcohol or phenol). The distribution of the t-butyl alcohol collision complexes is shown in Fig. 2. A similar distribution dependence was found for the collision complexes of phenol, too. If the abundance of the collision complexes is plotted against the volume fraction of the solvents in the mixture, an approximately linear dependence results. In the correlation with the mole fraction a positive deviation from linearity (concave curvature) of the plot is apparent which indicates that in the mixture under study $K < 1$ and ΔG is positive. This in fact means that the molar abundance of the collision complex of the solute with 1,2-difluorotetrachloromethane is larger for any composition of the mixture than the corresponding abundance of 1,2-difluorotetrachloroethane in the mixture of the solvents. This finding seemingly disagrees with the ratio of the values of the stabilization enthalpies for the collision complex formation, as its value is larger for the carbon disulphide complex.* However, one has to realize that the sense of the distribution curve curvature is determined by the sign of ΔG and this is determined in a system with a low interaction energy by the sign of the entropic term.

The influence of the entropy effects is projected into the statistical nature of the collision interactions. This factor causes the collision complex distribution in a binary solvent mixture to depend linearly on its volume rather than on its molar composition. This is because the collision probability depends not only on the number, but also on the volume (*i.e.* collision cross-section) of the colliding molecules. The statistical character of the distributions will be restricted by decreasing temperature; below a certain temperature the interaction energy might assume the role of the determining factor and the distribution could be treated as a stoichiometric distribution.

The statistical nature of the collision complex formation results from the experiments with sterically hindered solutes, too. These compounds form collision complexes with the same abundance, regardless of the extent of the steric hindrance of the interacting group (hydroxyl, in this case) in the solvent mixture (here: 1,1,2-trifluorotrchloroethane-carbon disulphide in the ratio 6 : 4). This statement holds

* The experimentally determined ratios of the values for the acetic acid monomer are transferred here to phenol and t-butyl alcohol.

for the collision complex distribution of phenol, 2-methyl phenol, 2,6-dimethyl phenol, 2,6-diisopropyl phenol, and 2,6-di-t-butyl-4-methyl phenol within the limits of the experimental error in the determination of collision complex concentrations ($\pm 5\%$). On the other hand, the same solutes in the mixture tetrachloromethane + 3% acetonitrile (Fig. 3) or in the solution of n-heptadecyl bromide exhibit a strong dependence of the abundance of various forms on the sterical hindrance of the phenolic hydroxyl. In these cases, however, specific interactions of the hydroxyl group play a significant role and in the solutions there occur also donor-acceptor complexes besides the collision complexes of phenol. As the stability of the donor-acceptor complexes decreases strongly with the increasing steric hindrance, the steric hindrance causes extensive changes in the distribution of the solution entities.

The occurrence of the collision complexes is also supported by the following experiment. The bands of a collision complex of a certain type, *e.g.*, formed by the acetic acid monomer and tetrachloromethane, exhibit a slightly different wave-number values depending on the environment in which they were measured. The wave-numbers of these bands are described by the Kirkwood-Magat-Bauer (KMB) equation adjusted for non-polar solvents¹² to the form

$$\nu = \nu_0 - C(n^2 - 1)/(n^2 + 1), \quad (3)$$

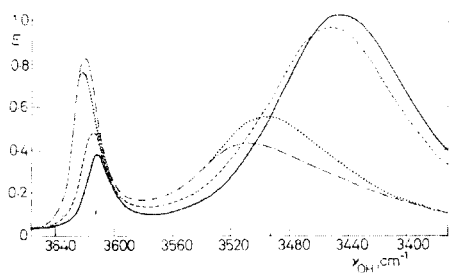


FIG. 3

Bands $\nu(\text{O—H})$ of Complexes Phenol (—), 2-Methyl Phenol (---), 2,6-Dimethyl Phenol (.....), and 2,6-diisopropylphenol (-.-.-) in the Solvent Mixture 97% CCl_4 + 3% CH_3CN

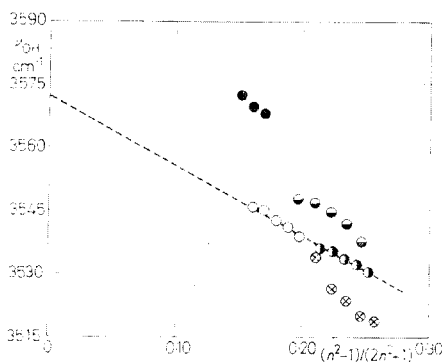


FIG. 4

Dependence of Wave-Number of Separated Bands $\nu(\text{O—H})$ of Collision Complexes Acetic Acid Monomer with CCl_4 \circ and with $\text{C}_{11}\text{F}_{20}$ \bullet in the Mixture of these Solvents, with CCl_4 in the Mixture $\text{CCl}_4\text{—CS}_2$ \ominus and with $(\text{CFCl}_2)_2$ \oplus and with CS_2 \otimes in the Mixture of these Solvents on the Refractive Index of these Solvent Mixtures

TABLE II

Wave-Numbers of $\nu(\text{O}-\text{H})$ Band of the Collision Complex Acetic Acid Monomer-Tetrachloromethane and Their Correlation with the Refractive Index of the Mixtures^a

Mixture	Component ratio ^b	n^c	$\nu(\text{O}-\text{H})^d$	$\Delta\nu(\text{O}-\text{H})^e$
$\text{C}_{11}\text{F}_{20}^f + \text{CCl}_4$	80 : 20	1.3096	3 545.8	+0.02
	60 : 40	1.3338	3 545.2	+1.01
	40 : 60	1.3581	3 542.5	-0.14
	20 : 80	1.3823	3 540.7	-0.47
	0 : 100	1.4066	3 539.0	-0.74
$\text{CCl}_4^g + \text{CS}_2$	100 : 0	1.4582	3 536.2	-0.69
	80 : 20	1.4913	3 535.7	+0.54
	60 : 40	1.5244	3 534.0	+0.47
	40 : 60	1.5576	3 532.1	+0.13
	20 : 80	1.5906	3 530.4	-0.09

^a Wave-numbers of doublet components after the mathematical separation, cm^{-1} ; ^b component ratio in volume percent; ^c experimental refractive index of mixtures at 78.5°C or 25°C; ^d wave-number of the band maximum of the complex in cm^{-1} ; ^e difference between experimental and calculated wave-numbers from equation $\nu = 3572.9 - 167.8(n^2 - 1)/(2n^2 + 1)$ in cm^{-1} ; ^f $\text{C}_{11}\text{F}_{20}$ - perfluoromethyldecaline, measurements at 78.5°C; ^g measurements at 25°C.

where ν is the wave-number* of the band of the O—H bond stretching vibration in the collision complex, ν_0 and C constants characterizing the solute molecule, and n the refractive index of the solvent mixture. The wave-numbers of the bands of the collision complex under investigation fit equation (3) (Table II, Fig. 4); the wave-numbers of the bands of a different complex formed by the acetic acid monomer and, e.g., perfluoromethyldecaline or carbon disulphide lie on different straight lines. Thus, it is evident that the constants ν_0 and C belong to a certain collision complex, i.e. to an entity formed from the original solute in the solution. If it were not the case, all the values of wave-numbers should fit one expression and the constants ν_0 and C would hold for the free molecule of the acetic acid monomer.

The calculated value ν_0 of the collision complex of the acetic acid monomer with tetrachloromethane, $3572.9 \pm 1.3 \text{ cm}^{-1}$, has the meaning of the wave-number of a hypothetical collision complex whose molecule is subjected to no external influence. The calculated value is by 9.7 cm^{-1} smaller than the value $\nu(\text{O}-\text{H})$ of the

* The bands of the collision complexes in the investigated systems lie very close to each other and had to be mathematically separated before being used.

isolated acetic acid monomer molecule in the gaseous phase. The lower wave-number of the collision complex band is in agreement with the sense and with the extent of the interaction of its components.

The KMB equation, based on the validity of Onsager's theory of the reaction field (see discussion in ref.^{2,3}), can be used in the investigation of non-specific interactions in solutions. Therefore, in the treated case it describes well the non-specific influence of the solvent mixture on the collision complex molecule. Specific effects of the collision complex formation show themselves explicitly in the values of the constants ν_0 and C .

An incorrect use of the KMB equation (3) can be demonstrated on the example of the correlation between the wave-number of the $\nu(\text{O—H})$ of the acetic acid monomer in the solutions of pure solvents and the refractive indexes of these solvents. This correlation (Table III) should describe simultaneously — against the concept of Onsager's theory of the reaction field — both the non-specific and the specific interactions of the collision complex formation. The erroneous interpretation of the Onsager's model manifested itself by the increase of the calculated value of ν_0 by $52.2 \pm 6.8 \text{ cm}^{-1}$ in comparison with the $\nu(\text{O—H})$ value of the gaseous monomer. At the same time, the over-all quality of the correlation became considerably worse.

As both the experiments and the semiempirical calculations show, the formation of collision complexes of polar solutes in solutions of non-polar solvents has to be

TABLE III

Wave-Numbers of $\nu(\text{O—H})$ Bands of the Collision Complexes Acetic Acid Monomer–Non-Polar Solvents and their Correlation with the Refractive Index of the Solvents

Solvent	Temperature ^a °C	$\nu(\text{O—H})^b$	n^c	$\Delta\nu(\text{O—H})^d$
Perfluoromethylcyclohexane	60	3 572.8	1.2540	+0.4
Perfluoromethyldecaline	95	3 572.0	1.2730	+3.3
Perfluorobenzene	40	3 557.8	1.3606	+4.7
1,1,2-Trifluorotrichloroethane	45	3 556.0	1.3375	−1.0
1,1,1-Trifluorotrichloroethane	45	3 551.1	1.3382	−5.8
1,2-Difluorotetrachloroethane	60	3 549.6	1.3851	+0.6
1,1-Difluorotetrachloroethane	60	3 548.7	1.3851	−0.3
Tetrachloromethane	50	3 537.4	1.4343	−4.1
Carbon disulphide	45	3 521.4	1.6057	+2.4
—	—	3 582.6	1.0000	—

^a Temperature during spectra measurement; ^b experimental wave-numbers in cm^{-1} ; ^c refractive index of the solvent used, at the temperature of measurement; ^d difference between experimental and calculated wave-numbers from equation $\nu = 3634.8 - 451.5(n^2 - 1)/(2n^2 + 1)$ in cm^{-1} .

taken into consideration. The decisive role in the balance of their formation plays the entropic component and this is why the collision complexes exhibit a significantly statistical character. However, one has to have in mind that by a change in the conditions (temperature, pressure) the energetic component might prevail in which case the formation of collision complexes could acquire a stoichiometric character.

REFERENCES

1. Hilgard S., Horák M., Vystrčil A.: *This Journal* 39, 3215 (1974).
2. Horák M., Plíva J.: *Spectrochim. Acta* 21, 911 (1965).
3. Horák M., Moravec J., Plíva J.: *Spectrochim. Acta* 21, 919 (1965).
4. Hilgard S.: *Thesis*. Charles University, Prague 1973.
5. Eliel E. L., Allinger N. L., Angyal S. J., Morrison G. A.: *Conformational Analysis*, Chapter 7. Interscience, Wiley, New York 1965.
6. Pople J. A., Beveridge D. L.: *Approximate Molecular Orbital Theory*. McGraw-Hill, New York 1970.
7. Le Févre R. J. W.: *Advan. Phys. Org. Chem.* 3, 1 (1965).
8. Denbigh K. G.: *Trans. Faraday Soc.* 36, 936 (1940).
9. Hobza P., Zahradník R.: *This Journal* 39, 2857 (1974).
10. Pimental G. C., McClellan A. L.: *The Hydrogen Bond*. Freeman, San Francisco 1960.
11. Koningstein J. A.: *Rec. Trav. Chim.* 83, 315 (1964).
12. Josien M. L., Fuson N.: *J. Chem. Phys.* 22, 1264 (1954).

Translated by Z. Hermann.