REDUCED MOMENT OF INERTIA FOR INTERNAL ROTATION AND QUANTUM-CHEMICAL DESCRIPTION OF THERMODYNAMICS OF ISOMERIC MOLECULAR COMPLEXES: STUDY OF HF–ClF SYSTEM*

Zdeněk SLANINA

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

Relations are studied between values of reduced moment of inertia I_{red} of a system consisting of a rigid frame and one asymmetric top evaluated within the exact approach and within simpler models of one symmetrical top and of two coaxial tops with particular respect to situation in the isomeric van der Waals molecules HF.ClF and ClF.HF. It has been shown that replacement of the exact approach by the model of two coaxial tops is generally more acceptable physically than that by the model of symmetrical top. For the both isomeric complexes, the error introduced by the coaxial tops approach is always lower than that introduced by transition to the second of the two basis sets (4-31G and 4-31G*) recently used for the study of structure of the complexes. Reevaluation of thermodynamics of this isomeric system using the exact approach for I_{red} has been carried out, and the problem of relative stabilities has been analyzed. According to the presented 4-31G* theoretical results, the HF.ClF isomer predominates completely in the equilibrium mixture of the two isomers up to the temperature of 40 K at least, their equimolecular ratio being not attained until at 90 K. Above this temperature, the ClF.HF isomer becomes relatively more abundant (even though not completely predominant) component of the equilibrium mixture. The paper gives proof of independence between I_{red} and the frame-top assignment. Inaccuracy in former I_{red} values and in thermodynamic characteristics of Cl_2S_2 are pointed out as a byproduct.

Quantum-chemical studies of molecular complexes, especially of the van der Waals molecules, abandon, at the present time, the description in terms of minima at the interaction energy hypersurface and their structural characteristics and tend to use the description in terms of partition functions. Thus former statements about energy of molecular complexes are replaced by theoretically generated information about their thermodynamics (*e.g.*, refs[3,4]). This change is accompanied by increasing interest in studies of movements (especially intermolecular) in molecular complexes which form a basis for construction of partition functions. In most van der Waals molecules, there are (among vibrational intermolecular normal modes) torsional modes

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of extremely low vibration frequencies (refs[5,6]), which means that from physical point of view a more justified description[7,8] of this motion can be that using the partition function of free or restricted internal rotation (rather than that using the partition function of harmonic oscillator). The theory of partition function of internal rotation was elaborated in classical papers by Pitzer and coworkers[9-11] beginning from the case of a rigid frame with attached symmetrical tops[9], continuing through the case of asymmetric tops attached to a rigid frame[10], and ending with a general formalized procedure for compound rotation[11].

In the case of study of the van der Waals molecules, the partition function in question is usually that of free internal rotation of a single top[7,8]. Recently, this way was used for evaluation[12] of thermodynamics of partial formation of isomeric molecular complexes HF.ClF and ClF.HF using an approximation of partition function of free internal rotation according to ref.[13]. The work[12] was followed by an evaluation[2] of overall thermodynamics of the HF—ClF system formation describing the internal rotation with the use of the model of two symmetrical coaxial tops[14,15]. This paper continues the study of the problems posed in refs[2,12], carrying out an analysis of consequences of various approximations of internal rotation for description of thermodynamics of van der Waals systems, especially the consequences for relations between the two isomeric structures in the HF-ClF system.

CALCULATIONS

Definitions and description of treatment. The reduced moment of inertia $I_{red}^{(a)}$ of a single asymmetric top G_2 attached to a rigid frame G_1 is given as follows. Let the given molecule of mass M has the principal central moments of inertia I_i and the principal central axes 1, 2, 3 of rotation intersecting at the centre of gravity (all the atoms are presumed to be in their equilibrium positions). The perpendicular axes x, y, z of the top are defined in such way that the internal rotation axis is denoted as z, the x axis crosses the centre of gravity of the top, and the y axis is chosen to make the orientation of the top axes (x, y, z) and molecular axes (1, 2, 3) identical (either right-handed or left-handed). Let the quantities $\lambda_{i,t}$, $(i = 1, 2, 3; t = x, y, z)$ denote the direction cosines between the axes of the top and the principal axes of the whole system. Finally, r_1, r_2 and r_3 are components on the principal axes of the vector from the centre of gravity of the molecule (*i.e.*, origin of the set of 1, 2, 3 axes) to the origin of the x, y, z coordinate system of the top. Then, the reduced moment of inertia reads as follows[10]:

$$I_{red}^{(a)} = A - \sum_{i=1}^{3} ((\lambda_{i,y}U)^2/M + \beta_i^2/I_i), \tag{1}$$

where U denotes the so called off-balance factor (2), and the terms β_i are given by Eq. (3),

$$U = \sum_{k \in G_2} m_k x_k, \tag{2}$$

$$\beta_i = \lambda_{i,z}A - \lambda_{i,y}B - \lambda_{i,y}C + U(\lambda_{i-1,y}r_{i+1} - \lambda_{i+1,y}r_{i-1}), \tag{3}$$

with the indexes $i - 1$ and $i + 1$ referring to cyclic shifts of the principal axes (*e.g.*, if $i = 1$, then

$i - 1 = 3$; if $i = 3$, then $i + 1 = 1$). Let the mass and the coordinates (in the x, y, z coordinate system) of the k-th atom of the top be denoted by the symbols m_k and x_k, y_k, z_k, respectively, and let the factors A, B, C be given by Eqs (4)—(6), respectively.

$$A = \sum_{k \in G_2} m_k(x_k^2 + y_k^2) \tag{4}$$

$$B = \sum_{k \in G_2} m_k x_k z_k \tag{5}$$

$$C = \sum_{k \in G_2} m_k y_k z_k \tag{6}$$

For stabilized asymmetric top (the axis of internal rotation coincides with a principal central axis of the top) or for symmetrical top, Eq. (1) is reduced to a simpler form[9]:

$$I_{\text{red}}^{(s)} = A - \sum_{i=1}^{3} A^2 \lambda_{i,z}^2 / I_i . \tag{7}$$

If the axis of internal rotation represents not only the symmetry axis of the top G_2 but also that of the rigid frame G_1 (and, hence, that of the whole molecule), then the system is transformed into a special case of two (symmetrical) coaxial tops[14,15] for which Eqs (1) or (7) are further reduced to Eq. (8):

$$I_{\text{red}}^{(c)} = A_1 A_2 / (A_1 + A_2) , \tag{8}$$

where A_1 and A_2 denote the moments of inertia of the groups G_1 and G_2, respectively, around the axis of internal rotation (cf. Eq. (4)).

Frame-top assignment. For usual organic molecules it is mostly evident[16,17] which of their parts represent the rigid frame and the top. This intuitive difference disappears in molecular complexes formed by two components involving few atoms (or even by two biatomic molecules). A problem thus appears (to the author's knowledge — not solved explicitly so far) whether or not the two possible frame-top assignments to the components of these complexes will result in different $I_{\text{red}}^{(a)}$ values. The classical rotational kinetic energy T of the system is given[10,18] by Eq. (9), where ω_i are components of an effective angular velocity related by Eq. (10) to components ω_i^0 of the instantaneous angular velocity of the system of the principal central axes of the whole molecule fixed in the rigid frame G_1 with respect to a reference set of axes fixed in space, and to the angular velocity Φ of the top G_2 with respect to the rigid frame G_1. Let now the component G_2 represent (in a situation otherwise equivalent dynamically) the rigid frame, G_1 being the tope. The quantities T, I_i and $\lambda_{i,z}$ are not affected by this internal change of the assignment convention; the G_1 top rotates with respect to the G_2 rigid frame with angular velocity $-\Phi$, and the ω_i^0 term of Eq. (10) is replaced by $(\omega_i^0 + \lambda_{i,z}\Phi)$; values of the other terms of Eqs (9) and (10) are denoted with apostrophe for this new frame-top assignment, *e.g.*:

$$T = \tfrac{1}{2} \sum_{i=1}^{3} I_i \omega_i^2 + \tfrac{1}{2} I_{\text{red}}^{(a)} \Phi^2 , \tag{9}$$

$$\omega_i = \omega_i^0 + \beta_i \Phi / I_i \tag{10}$$

$$\omega_i' = \omega_i^0 + \lambda_{i,z}\Phi - \beta_i' \Phi / I_i . \tag{11}$$

Comparison of the expressions (9) for the two cases gives finally the identity (12) which must apply to all choices of ω_i^0.

$$\sum_{i=1}^{3} I_i \{2\omega_i^0 \Phi(\beta_i/I_i + \beta_i'/I_i - \lambda_{i,z}) + \Phi^2[(\beta_i/I_i)^2 - (\beta_i'/I_i - \lambda_{i,z})^2]\} = \Phi^2(I_{red}'^{(a)} - I_{red}^{(a)})$$
(12)

Hence

$$\beta_i + \beta_i' - \lambda_{i,z} I_i = 0 \quad (i = 1, 2, 3)$$
(13)

which leads immediately to the identity $I_{red}'^{(a)} = I_{red}^{(a)}$. Thus the $I_{red}^{(a)}$ value is invariant with respect to choice of the frame-top assignment to individual sections of the molecule.

A certain ambiguity is introduced in the definition of top and rigid frame by the atoms lying at the axis of internal rotation. However, an analogous reasoning based again on the expression (9) for kinetic energy can easily verify that the $I_{red}^{(a)}$ value does not depend on distribution of these atoms between the rigid-frame and the top sections of the molecule. The both mentioned types of invariance can be used for simplification of data preparation before calculation of $I_{red}^{(a)}$.

Thermodynamic calculations. The reduced moments of inertia calculated in the above-mentioned way serve in this report for construction of the usual classical partition function of free internal rotation (e.g., ref.[17]); partition functions of the other motions are constructed in terms of the conventional approximation[17] of rigid rotator and harmonic oscillator. Isomerism of reaction component, *i.e.* transition from partial to overall thermodynamic characteristics, is taken into account by means of weighting treatment[4,19]. Throughout the paper the set of fundamental physical constants[20] and atomic masses[21] are employed.

RESULTS AND DISCUSSION

It is recommended to simplify the calculation of reduced moment of inertia in the case of a single asymmetric top (especially for groups with a small off-balance factor[9,10]) by applying the same procedure as in the case of symmetrical top; further simplification is achieved by the treatment of asymmetric top in terms of two co-axial tops (refs[2,20]). With the aim of systematic evaluation of behaviour of all three approximations, we chose a set of ten molecules (involving three van der Waals molecules) exhibiting one internal-rotational degree of freedom, one of the rotating groups — at least — being of the type of asymmetric top. Table I summarizes the I_{red} values calculated for these systems by the approximations (1), (7), and (8). The used structural characteristics of most members of this set of molecules are derived from experiment or from assessment, except for the isomeric complexes ClF.HF and HF.ClF whose geometry parameters were taken from the quantum-chemical study[12] carried out in terms of the *ab initio* SCF approach within 4-31G and 4-31G* basis sets. From Table I it is seen that (except for the HF.ClF, HCl_2C–$CClH_2$, and Cl_2S_2 systems) the $I_{red}^{(c)}$ values are very close to $I_{red}^{(a)}$ values: for calculation of thermodynamic characteristics of these seven systems it would be quite sufficient to replace the reduced moment of inertia determined in the approach of one asymmetric top by mere approximation of two coaxial tops. Behaviour of $I_{red}^{(c)}$ (as compared with $I_{red}^{(a)}$) of HF.ClF, HCl_2C–$CClH_2$, and Cl_2S_2 is surprisingly uniform: for all the three systems the $I_{red}^{(c)}$

value is approximately twice as high as the reference value $I_{red}^{(a)}$. Whether or not the calculation of reduced moment of inertia of a molecule with one asymmetric top can be approximated by treatment in terms of two coaxial tops, it is generally determined by mutual relations of all the parameters appearing in formulas for determination of $I_{red}^{(a)}$. It is, of course, obvious that a considerable difference between the $I_{red}^{(a)}$ and $I_{red}^{(c)}$ can be expected with systems having a relatively large value of the off-balance factor U for at least one of the two possible frame–top assignments.

TABLE I

Reduced moments of inertia I_{red} (in 10^{-39} g cm^2) of selected systems calculated by asymmetric top ($I_{red}^{(a)}$), two coaxial tops ($I_{red}^{(c)}$) and symmetric top ($I_{red}^{(s)}$) approximations

System	$\dfrac{|U|}{10^{-31} \text{ g cm}}$^{a,b}	$I_{red}^{(a)}$	$I_{red}^{(c)}$	$I_{red}^{(s)}$^{b}	Source of structural data
ClF.HF	0·022^c	0·00282^c	0·00291^c	0·00291^c	ref.[12]
	8·61^c			−43·6^c	
	0·019^d	0·00206^d	0·00213^d	0·00213^d	
	9·57^d			−42·6^d	
(H$_2$O)$_2$	0·155	0·0823	0·0857	0·0832	ref.[7]
	0·083			0·0802	
HF.ClF	0·110^c	0·00662^c	0·0126^c	0·00633^c	ref.[12]
	0·300^c			0·0123^c	
	0·143^d	0·0168^d	0·0310^d	0·0192^d	
	0·494^d			0·0296^d	
CH$_3$OH	0·149	0·0998	0·107	0·107	ref.[23]
	0			0·0998^e	
H$_2$O$_2$	0·158	0·0703	0·0750	0·0697	ref.[24]
HDO$_2$	0·159	0·0917	0·101	0·0943	ref.[25]
	0·318			0·0751	
HNO$_3$	0·161	0·142	0·151	0·151	ref.[26]
	0			0·142^e	
C$_6$H$_5$SH	0·219	0·273	0·281	0·281	ref.[27]
	0			0·273^e	
HCl$_2$C–CClH$_2$	9·54	4·91	10·9	8·64	ref.[28]
	9·17			2·27	
Cl$_2$S$_2$	11·4	5·76	11·1	− 1·56	ref.[22]

^{a} Off-balance factor, see Eq. (2). ^{b} The upper line — the lighter group considered as a top, the lower line — the heavier group considered as a top (points on the axis of internal rotation ignored). ^{c} 4−31G basis set values. ^{d} 4-31G* basis set values. ^{e} Exactly equal to $I_{red}^{(a)}$, a consequence of symmetry of the top.

However, it should be stressed that relatively high value of $|U|$ is not a necessary prerequisite for such a difference between $I_{red}^{(a)}$ and $I_{red}^{(c)}$, and, moreover, it even does not represent a sufficient condition. This conclusion can be documented by some examples of Table I. Thus *e.g.* HF.ClF belongs (especially so if the H atom is denoted as the top) to systems having the lowest values of $|U|$ factor among the set considered, but, nevertheless, it belongs to the three critical systems for which the approximation of $I_{red}^{(a)}$ value by $I_{red}^{(c)}$ value fails. If, on the contrary, the Cl atom is taken as the top in ClF.HF, then the $|U|$ factor is comparable with the values of $HCl_2C-CClH_2$ or Cl_2S_2, the agreement between $I_{red}^{(a)}$ and $I_{red}^{(c)}$ being perfect all the same. These results obtained for the van der Waals molecules show that the problem of possibility of approximation of the $I_{red}^{(a)}$ calculation by simpler models cannot be reduced to the criterion of values of the off-balance factor U.

The data of Table I also lead to an unexpected result when comparing quality of $I_{red}^{(s)}$ and $I_{red}^{(c)}$. It must be admitted that, except for ClF.HF system, all the systems having close $I_{red}^{(a)}$ and $I_{red}^{(c)}$ values show the same or even better agreement between $I_{red}^{(a)}$ and $I_{red}^{(s)}$ values. Naturally, the $I_{red}^{(s)}$ and $I_{red}^{(c)}$ values can even be exactly the same, if the $I_{red}^{(s)}$ approach is applied to a system whose one group is symmetrical and is considered to be the top, too. But we found two substantial serious deficiencies of the approximation of $I_{red}^{(a)}$ by $I_{red}^{(s)}$ as compared with the approximation of $I_{red}^{(a)}$ by $I_{red}^{(c)}$. Firstly, in contrast to $I_{red}^{(a)}$ (and essentially to $I_{red}^{(c)}$), the $I_{red}^{(s)}$ term depends (when evaluated for a system of two groups G_1 and G_2, at least one of them being asymmetric) on frame–top assignment. This can easily be understood in view of the above-given proof of independency between $I_{red}^{(a)}$ and this assignment. The proof is based on identity of the classical rotational kinetic energy in the two possible frame-top assignments; this identity follows immediately from the scheme[10] of $I_{red}^{(a)}$ derivation. Now if we artificially let B, B', C, C', U, and U' for a pair of asymmetric tops be equal to zero, so that formula for $I_{red}^{(s)}$ reduces formally to that for $I_{red}^{(s)}$, the conditions (13) will read as follows:

$$\lambda_{i,z}(A + A' - I_i) = 0 \quad (i = 1, 2, 3).\qquad(14)$$

Obviously, Eqs (14) cannot generally hold for a pair of asymmetric tops. Consequently, if a pair of tops, at least one of which is an asymmetric one, are treated as symmetrical tops, then the resulting values $I_{red}^{(s)}$ and $I_{red}'^{(s)}$ are generally different. The second deficiency of approximating $I_{red}^{(a)}$ by $I_{red}^{(s)}$ for an asymmetric top is that the resulting reduced moment of inertia may be negative (Table I), which essentially prevents its application in partition function of internal rotation. None of these two deficiences is encountered with the approximation of $I_{red}^{(a)}$ by $I_{red}^{(c)}$. Thus, in some cases the calculation of reduced moment of inertia of a system with one asymmetric top carried out in terms of the $I_{red}^{(s)}$ approximation provides a closer agreement with the exact value $I_{red}^{(a)}$ than that carried out by the $I_{red}^{(c)}$ approximation, but, with respect

to the mentioned two defects, it is advisable to replace the $I_{red}^{(a)}$ value (if it had to be replaced by a value from a simpler model) by $I_{red}^{(c)}$ rather than by $I_{red}^{(s)}$.

In the particular case of the van der Waals molecules ClF.HF and HF.ClF, the results of Table I indicate considerably low values of $I_{red}^{(a)}$: for example, those values are even lower than reduced moment of inertia[8,29,30] of D_{2d} form of $(H_2)_2$. This fact is undoubtedly connected with the arrangements of FClF and FHF atoms (in the HF.ClF and ClF.HF complexes, respectively) being not much deviated from linearity. Figure 1 presents dependence of $I_{red}^{(a)}$ and products $I_1 I_2 I_3$ of the two complexes on the respective deviation from linearity (the angles ClFF and HFF, respectively), values of the other structural parameters being kept at their $4-31G$ values[12]. The values $I_{red}^{(a)}$ were found to be extremely sensitive to these deviations from linearity. Especially sensitive is the $I_{red}^{(a)}$ value of HF.ClF which is doubled and lowered to about
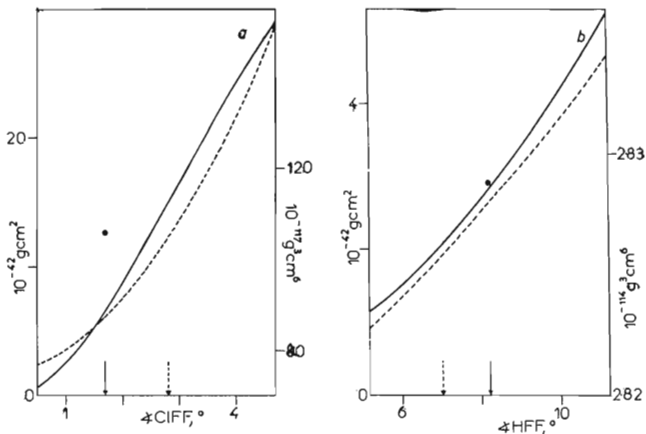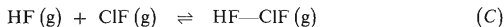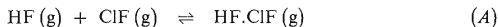

Fig. 1

Dependences of reduced moment of inerta $I_{red}^{(a)}$ (solid lines) and of product of principal central moments of inertia $I_1 I_2 I_3$ (dashed lines) on the deviation from linearity (angle ClFF and angle HFF for HF.ClF (a) and ClF.HF (b) structure, resp.) of quasilinear triad of atoms in the isomers; solid and dashed arrows indicate the equilibrium value of the angle in 4-31G and 4-31G* approach[12], resp., and ● indicates the value of $I_{red}^{(c)}$. For the purpose of this figure, all the structural parameters were taken from 4-31G calculations and only the angle ClFF or HFF was varied

one fifth, respectively, when changing the 4-31G equilibrium value of the ClFF angle by $\pm 1°$. The angles ClFF and HFF (in the complexes HF.ClF and ClF.HF, respectively) play a unique role with respect to the $I_{red}^{(a)}$ values: similar variation of the other bond angle (i.e. HFF and ClFF in the HF.ClF and ClF.HF complexes, respectively) has a negligible effect on the $I_{red}^{(a)}$ value. Moreover, it should be stressed that the products of principal moments of inertia $I_1 I_2 I_3$ (in contrast to the $I_{red}^{(a)}$ values) show a substantially smaller sensitivity to deviations from linearity: whereas ratio of the greatest and the smallest values (within the interval of values considered in Fig. 1) $I_{red}^{(a)}$ for HF.ClF and ClF.HF is about 45 and 5, respectively, the corresponding ratios of the $I_1 I_2 I_3$ products are only about 2 and 1·004, respectively. Structural characteristics of the two complexes depend essentially on choice of basis[12,31]. Although changes of these characteristics themselves with changes of the basis set need not necessarily be dramatic, they can even cause changes in order of mangitude of the $I_{red}^{(a)}$ value (cf. $I_{red}^{(a)}$ of HF.ClF evaluated within the 4-31G and 4−31G* basis sets, respectively). Considering results in Fig. 1 and Table I, it can be concluded that the error caused by the evaluation of reduced moment of inertia of either of the complexes within the $I_{red}^{(c)}$ approach (instead of $I_{red}^{(a)}$ approach) is smaller than the error due to application of values of different basis set.

So far the thermodynamic characteristics of formation of the complexes HF.ClF (A) and ClF.HF (B) have been obtained[2,12] with the use of approximative I_{red} values of the two associates (e.g., $I_{red}^{(c)}$ values[2]). Therefore, this paper presents a reevaluation of thermodynamics of the processes (A) and (B) as well as of the overall process (C) (in which the both isomeric complexes are considered side by side) with application of the correct $I_{red}^{(a)}$ values.

$$HF\,(g)\;+\;ClF\,(g)\quad\rightleftharpoons\quad HF.ClF\,(g) \qquad\qquad (A)$$

$$HF\,(g)\;+\;ClF\,(g)\quad\rightleftharpoons\quad ClF.HF\,(g) \qquad\qquad (B)$$

$$HF\,(g)\;+\;ClF\,(g)\quad\rightleftharpoons\quad HF{-\!-}ClF\,(g) \qquad\qquad (C)$$

Parallel thermodynamic calculations were carried out for two quality levels of structural and energy characteristics of the two complexes as suggested in ref.[12]. We used (i) the structural, vibrational, and energy data obtained[12] in terms of 4-31G basis set and (ii) a modified set of these parameters in which the 4-31G terms of potential energy changes accompanying the processes (A) and (B) were replaced by the 4-31G* values. Relative stability of the two isomeric complexes can easily be studied in terms of the weighting factors[4,19,32] w_i which will be used further for transition from the characteristics of the partial processes (A), (B) to total values connected with the

overall process (C). The temperature dependences of the weighting factors are presented in Fig. 2 for a broad temperature range. Obviously, the replacement of $I_{red}^{(c)}$ by $I_{red}^{(a)}$ value causes an increase in relative stability of the ClF.HF isomer to the detriment of relative stability of the HF.ClF isomer. However, these changes in values of the weighting factors do not exceed 0·08 for any of the two considered sources of molecular parameters.

Analysis of mutual stabilities of the two isomers is significant with respect to inter-pretation of experimental data on the HF–ClF system. At the present time, the non--hydrogen-bonded complex (HF.ClF) is the only form which has been observed[33,34], while its hydrogen-bonded counterpart (ClF.HF) has gone undetected. With the aim of evaluation of results of all reasonable combinations of existing theoretical data on the two complexes, the above-given sets (i) and (ii) of the molecular data used in refs[2,12] were extended by a third set involving both structural and energy characteristics derived from 4-31G* calculations[12] (Table II). If all the molecular parameters come from the 4-31G calculation, then the hydrogen-bonded structure appears distinctly more stable in the whole broad temperature range of Fig. 2, which contradicts experimental findings[33,34]. However, possibility of higher stability of the
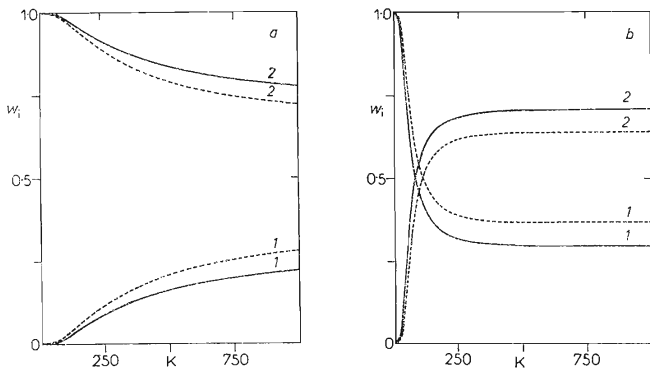

Fɪɢ. 2

Temperature dependences of weights w_i of the isomers HF.ClF 1 and ClF.HF 2 for the 4-31G (a) and 4-31G* (b) energetics: solid lines w_i based on $I_{red}^{(a)}$, dashed lines w_i based[2] on $I_{red}^{(c)}$. The structural data were in all cases taken from the 4-31G calculations[12]

HF.ClF structure is brought by the transition from description of energy of the processes (A), (B) in terms of 4-31G to a description in larger basis sets[2,12,31]. Let us, therefore, restrict our further description of energy to the more perfect basis set 4-31G*; the results given in Fig. 2 and Table II can then be summarized as follows. At very low temperatures (at least below 40 K), HF.ClF forms predominant component (at least 90%) of equilibrium mixture of the two isomers. The various approaches tested in Table II agree in giving relatively close values of this critical temperature (the greatest difference makes 20 K). Further increase in temperature results in mutual approaching of concentrations of the two isomers, equal concentrations being not attained until at 90 K (there are, however, considerable differences between individual used approximations in localization of this point of stability inversion). Further increase in temperature above this inversion point results in an only very slow increasing of relative concentration of the hydrogen-bonded isomer ClF.HF which appears to be relatively more stable but not distinctly predominant component of the equilibrium mixture above the inversion temperature. However, the absolute stabilities of the two isomers decrease systematically with increasing temperature. In the context of the paper it is interesting that the temperature at which the non-hydrogen-bonded isomer forms about 90% of the equilibrium mixture of isomers depends but little on type of approximation of I_{red}, whereas the temperature of inversion (50% of each isomer) depends on the source of I_{red} much more distinctly (Table II). The experimental generation itself of the HF—ClF system[33,34] was carried out by supersonic expansion of a mixture of HF, ClF, and Ar. Temperature in such experiments depends on several factors and can reach very low values[35]

TABLE II

Temperatures leading to some distinct relative concentrations (90, 50, and 40%) of the non--hydrogen-bonded isomer HF.ClF in the equilibrium mixture of both isomers

Quality of molecular structure	Quality of potential energy	Approximation of I_{red}	T, K[a]		
			90%	50%	40%
4-31G	4-31G*	$I_{red}^{(c)}$	40	120	210
		$I_{red}^{(s)}$	40[b]	90[b]	130[b]
		$I_{red}^{(a)}$	40	90	130
4-31G*	4-31G*	$I_{red}^{(c)}$	60	—	—
		$I_{red}^{(s)}$	50[b]	540[b]	—
		$I_{red}^{(a)}$	50	300	—

[a] The temperature interval 10—1 000 K was examined and the critical temperatures rounded off to tens. [b] H atom considered as a top.

which may decrease far below the mentioned 40 K predicted in this paper as the temperature under which the non-hydrogen-bonded isomer should form more than 90% of the equilibrium mixture. If, in addition to it, the relative high signal-to-noise ratio (ref.[34]) is taken into account, then the agreement between experimental findings and theoretical data on HF—ClF system can be considered reasonable within the 4—31G* term of potential energy.

Let us now deal with the problem of prediction of partial and total thermodynamic characteristics of the HF and ClF associates. The first step is calculation of the partial characteristics, i.e. those connected with the processes (A) and (B) creating the individual associates. Partial $\Delta H_{T,i}^0$ terms are not essentially affected by transition from
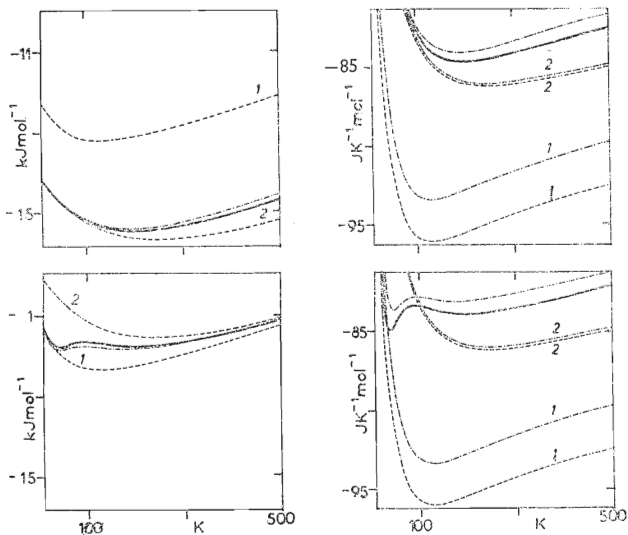

Fig. 3

Temperature dependences of the standard enthalpy ΔH_T^0 and entropy ΔS_T^0 for the partial (1 or 2 — see Fig. 2) and overall associations of HF and ClF: the upper figures 4-31G energetics, the lower figures 4—31G* energetics, solid lines total values based on $I_{red}^{(a)}$, dashed lines partial values based on $I_{red}^{(a)}$, dash-dotted lines partial and/or total values based[2] on $I_{red}^{(c)}$. The structural data were in all cases taken from the 4-31G calculations[12]. Standard state in ideal gas phase at 101 325 Pa pressure

$I_{red}^{(c)}$ to $I_{red}^{(a)}$. However, total values ΔH_T^0, *i.e.* the values belonging to the overall process (C) and found on the basis of $\Delta H_{T,i}^0$ and w_i values through the weighting treatment[4,19,32] are, in principle, dependent in the I_{red} values by means of the weight factors w_i. Nevertheless, the results given in Fig. 3 show an only very indistinct difference between the $\Delta H_T^{(c)}$ values obtained from the $I_{red}^{(c)}$ approach and those obtained from the correct $I_{red}^{(a)}$ values. However, the results obtained from the (ii) source of molecular parameters are intersting from the point of view of general investigation of properties of the weighting treatment. Curves of temperature dependences of the total ΔH_T^0 term obtained with the use[2] of both $I_{red}^{(c)}$ and $I_{red}^{(a)}$ show, in the temperature interval studied, an unusual $(cf.^{36})$ course with two local minima and one local maximum. Unusual increase in difference between overall enthalpy and the partial term due to the more stable structure with increasing temperature is also maintained within a certain temperature range (which has already been reported[2] with application of the $I_{red}^{(c)}$ term) even in the case of employing the correct $I_{red}^{(a)}$ values and the (ii) set of molecular parameters. These phenomena at the curves of temperature dependence of the total term ΔH_T^0 are obviously connected[37,38] with the already mentioned (Fig. 2) change of relative stability order of the two isomeric structures in the region of low temperatures.

In contrast to the partial enthalpy values, the partial entropy terms $\Delta S_{T,i}^0$ are affected by transition from $I_{red}^{(c)}$ to $I_{red}^{(a)}$, the effect being not always negligible; the change itself, however, is represented by a shift by a temperature-independent factor. This factor is insignificant in the process (B), due to close values $I_{red}^{(c)}$ and $I_{red}^{(a)}$ in the both approaches (i) and (ii). But in the case of the partial entropy term connected with the equilibrium (A), the decrease accompanying the transition from $I_{red}^{(c)}$ to $I_{red}^{(a)}$ is about $2 \cdot 7 \text{ J K}^{-1} \text{ mol}^{-1}$ for the two approaches (i) and (ii). This represents the most significant change in the thermodynamics of the association of HF and ClF caused by application of correct $I_{red}^{(a)}$ instead of former[2] $I_{red}^{(c)}$. The total ΔS_T^0 term is affected by this modification less distinctly than the mentioned partial term. In accordance with the ΔH_T^0 term, the temperature dependence of ΔS_T^0 term shows (with application of the (ii) parameters) three stationary points as well as a region where difference between the ΔS_T^0 term and the partial value belonging to the more stable structure is decreased with increasing temperature. Thus it can be concluded by stating that replacement of $I_{red}^{(c)}$ values by more correct $I_{red}^{(a)}$ values maintains all qualitative features of thermodynamics of the processes $(A)-(C)$ described[2] on the basis of the $I_{red}^{(c)}$ values. More essential quantitative changes are only encountered (in this correction) with some entropy terms.

The results given in Fig. 3 represent now the best assessment of thermodynamics of the processes $(A)-(C)$. With respect to experiment, particularly significant are the total characteristics of the process (C), because it can be expected that experimental investigation of thermodynamics of the association of HF and ClF will provide[37,38] total terms rather than partial values. Future investigations may bring

more precise theoretical values of thermodynamic characteristics of the processes $(A)–(C)$ especially in connection with increasing quality of the used basis sets (which will be manifested in changes of geometry, energy, and force fields of the isomers studied) and also in connection with reliable evaluation of correlation effects and respecting of apparent anharmonicity and non-rigidity of the individual structures in quality of the partition functions (for a more comprehensive discussion, see ref.[2]).

To maintain consistency, we used the conventional partition function of free internal rotation[12] in this paper. Let us mention, however, that there exist two reasons for preference of application (to analogous situations) of partition function of harmonic torsional vibrational motion, *viz.* incorrect limit behaviour of partition function of free rotation in the region of low temperatures and low I_{red} and, furthermore, the discontinuity in the partition function which appears on transition to strictly linear arrangement of quasi-linear triads of atoms in the complexes in question. As such linearization is possible[31], it would be very desirable to secure continuous behaviour of partition function during such transition[39]. None of the mentioned defects is found in the partition function of harmonic torsion motion. Its application, however, presumes reliable knowledge of the corresponding vibrational frequency, which can be connected (with respect to the fact that the required value is usually the smallest one in a set of intermolecular frequencies) with substantial demands for accuracy of numerical quantum-chemical calculations. Finally, let us mention that a qualitatively higher level of theoretical study of the HF–ClF system would be achieved by transition from its representation by means of two isolated frozen isomers to its treatment as a single system with fluxional behaviour (refs[2,40,41]).

In spite of exceeding somewhat the scope of this paper, let us state that the results of Table I indicate that in the case of Cl_2S_2 it would be necessary to define with more precision the partition function of internal rotation given in literature. Transition from the $I_{red}^{(c)}$ used in ref.[22] to $I_{red}^{(a)}$ will cause that the entropy value[22] must be lowered by about 2.72 J K^{-1} mol^{-1}. Similarly, contribution of internal rotation to the entropy of Cl_2S_2 given in ref.[42] should be lowered by about 1.17 J K^{-1} mol^{-1}.

CONCLUSIONS

Possibility was studied of approximation of reduced moment of inertia $I_{red}^{(a)}$ of a system consisting of an asymmetric top attached to a rigid frame by artificial treating the top as a symmetrical one or by artificial treating the system as two coaxial tops. Although these approximations often lead to close agreement, there exist cases of considerable differences. The van der Waals molecule HF.ClF (unlike its isomer ClF.HF) belongs to the cases. It was shown that failure of the both rougher approximations is due not only to value of off-balance factor[10]. According to the arguments gathered, calculation of $I_{red}^{(a)}$ (if it must be carried out at all by means

of a simpler model) should prefer the model of two coaxial tops to the approach of a symmetrical top.

In the two isomeric structures representing the HF—ClF system, the $I_{red}^{(a)}$ was found to be extremely sensitive to equilibrium magnitudes of deviation from linearity in the quasi-linear three-atomic chain in these isomers. It was shown that the error caused in $I_{red}^{(a)}$ of these isomers by using the approach of two coaxial tops is smaller than the error due to transition to the other of the two basis sets (4-31G and 4-31G*) recently used[12] for the study of structure and energetics of the system. Future application of basis sets of better quality can, therefore, bring profound changes in $I_{red}^{(a)}$ values of the two isomers in question. A reevaluation was carried out of thermodynamic characteristics of formation of the individual isomers and the whole association with the use of correct $I_{red}^{(a)}$ values. The former values[2] based on the model of two coaxial tops are practically unaffected by the reevaluation, as far as the enthalpy term is concerned. Changes were encountered with the entropy terms, out of which the most affected is the standard entropy of association to the HF.ClF isomer (the decrease is about $2 \cdot 7 \, \text{J K}^{-1} \, \text{mol}^{-1}$). All qualitative features of interplay between partial and total thermodynamic values of HF and ClF association reported in ref.[2] were, however, reproduced with application of the correct $I_{red}^{(a)}$ value. Also it was proved that application of the 4-31G* energetics leads to agreement with reality, *viz.* that only the non-hydrogen-bonded isomer has been observed experimentally so far. It was shown that, within the terms of 4-31G* energy data, the HF.ClF isomer represents a fully predominant component of the equilibrium mixture of the two isomers up to at least 40 K, whereas equimolar ratio is not reached until at the temperature of 90 K. The ClF.HF isomer becomes more abundant component of the equilibrium mixture above the temperature of this inversion, but it never becomes fully predominant component. Also it was shown that application of partition function of harmonic torsion motion instead that of internal free rotation can exhibit certain physical advantages in analogous situations.

Note added in proof: After submitting this article the problem of incorrect limit behaviour of partition function of free internal rotation (discussed on p. 3218) was solved[43]. In connection with the marginal problem of Cl_2S_2 it should be mentioned that there are also two[44,45] evaluations of its thermodynamic functions based on full (harmonic) vibrational partition function and a third, newer calculation[46] (the methodology of which is however not specified[47] enough).

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