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Internal rotation in molecular complexes: some problems concerning the evaluation of equilibrium and rate constants*,**

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The conventional one-term partition function of free internal rotation (so far the only means used in the literature for evaluation of the thermodynamics of this motion) shows incorrect limit behavior for low temperatures and/or small values of reduced moments of inertia. This situation is particularly pertinent to van der Waals molecules and hydrogen bonded systems. Consequences of the application of the newly suggested improved formulae for the heat content function, entropy, and heat capacity have been analyzed for $(H_2)_2$, $(N_2)_2$, ClF.HF, HF.ClF, HCN.HCl, HCN.DCl, $(H_2O)_2$, $CF_3H.OH_2$, $CCl_3H.OH_2$, and cyclopropane.H_2O. Considerable changes in the values of thermodynamic or kinetic characteristics of the systems have been found when applying the new formulae. Relations to the results available with the exact partition function of the free internal rotation have been analyzed. Consequences of the new approach for the recently performed theoretical evaluation of anesthetic activity based on the conventional formula are briefly discussed.

Key words: Free internal rotation in molecular complexes — Thermodynamics thereof — Rigorous and approximative partition functions of free internal rotation — Application of ϑ_3 functions — van der Waals and hydrogen-bonded dimers

1. Introduction

Recently there has been a considerable progress in theoretical and conceptual studies of molecular complexes, namely of van der Waals molecules [1-3] and

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* Dedicated to Professor Camille Sandorfy on the occasion of his 65th birthday

** Part XXVII in the series Multi-Molecular Clusters and Their Isomerism; Part XXVI, see [52] hydrogen bonded systems [4-6]. A gradual transition from the traditional treatment in terms of structure-potential energy to descriptions considering all types of motions possible in the given system represents one of the advances in this field. Thus an ever increasing number of papers dealing with theoretical studies of weak intermolecular interactions include and evaluate such terms as entropy, temperature or time effects. For various molecular complexes equilibrium [7-12] as well as rate characteristics [12-14] are extracted from potential energy hypersurface(s). Studies of this type are focusing their interest on the construction of partition functions themselves. Recently, the quality of existing formulae for the partition functions of various quantum models [15-24] has been examined and improved. In fact, even in the case of the usual simple textbook models a rigorous (but still manageable) formula exists quite rarely [25], for instance for the partition function of the harmonic oscillator. Unusual applications or special requirements with respect to accuracy can frequently necessitate the development of formulae with a higher degree of sophistication than that of the conventional ones. This was, e.g., the case of the partition function of the rigid overall rotation of a linear [26] or nonlinear [27-29] molecule.

It can be supposed, and it was proved [30-34] in several cases by theoretical as well as experimental techniques, that in weak molecular complexes there are frequently one or even several internal degrees of freedom which may be described (at least at some temperatures) as free internal rotation. It was, moreover, pointed out [35, 36] that for such systems the conventional formula [37, 38] for the partition function of free internal rotation cannot be applied. Thus, a new approach has to be developed. The present paper deals with such an improved partition function of the free internal rotation and its application to the evaluation of thermochemical characteristics of weak molecular complexes: heat content function, entropy, heat capacity, and equilibrium and rate constants.

2. Outline of methodology

The conventional formula [37, 38] $q_0^{(\mathrm{fir})}$ for the partition function of free internal rotation of a single top against a rigid frame is given by:

$$q_0^{(\mathrm{fir})} = \frac{1}{n}\left(\frac{8\pi^3 IkT}{h^2}\right)^{1/2} = \left(\frac{\pi}{\sigma}\right)^{1/2}, (\sigma > 0), \tag{1}$$

where I is the reduced moment of inertia; n is the internal rotation symmetry number; the other symbols have their usual significance. However, this approximation, $q_0^{(\mathrm{fir})}$, is not quite satisfactory as it gives the value 0, instead of the correct 1, when $\sigma \to \infty$ (i.e., low temperatures and/or low reduced moments of inertia). It was shown [35, 36] that this breakdown of the $q_0^{(\mathrm{fir})}$ approximation is a result of the impossibility to approximate the summation through integration when deriving Eq. (1) under these limit conditions in the conventional textbook manner. Two improved approximations (which may be used in practice) can be introduced [35, 36], namely:

$$q_1^{(\mathrm{fir})} = \left(\frac{\pi}{\sigma}\right)^{1/2} + 1, \tag{2}$$

$$q_2^{(\mathrm{fir})} = \left(\frac{\pi}{\sigma}\right)^{1/2} + 1 + e^{-\sigma} - \left(\frac{\pi}{\sigma}\right)^{1/2} \Phi(\sigma^{1/2}), \tag{3}$$

where Φ denotes the well-known error function. Clearly enough, the approximations (2), (3) exhibit the physically correct limit behavior for $\sigma \to \infty$.

Within these three approximations of the partition function of the free internal rotation the contributions of this motion to the molar heat content function, $H_{T,i}^{(\mathrm{fir})}$, read:

$$H_{T,0}^{(\mathrm{fir})}/(RT) = \tfrac{1}{2}, \tag{4}$$

$$H_{T,1}^{(\mathrm{fir})}/(RT) = \frac{q_0^{(\mathrm{fir})}}{2q_1^{(\mathrm{fir})}}, \tag{5}$$

$$H_{T,2}^{(\mathrm{fir})}/(RT) = \frac{1}{q_2^{(\mathrm{fir})}} \left[\frac{1}{2}\left(\frac{\pi}{\sigma}\right)^{1/2} + e^{-\sigma} + \sigma e^{-\sigma} - \frac{1}{2}\left(\frac{\pi}{\sigma}\right)^{1/2} \Phi(\sigma^{1/2})\right], \tag{6}$$

while for the contribution $S_{T,i}^{(\mathrm{fir})}$ to the molar entropy term holds generally:

$$S_{T,i}^{(\mathrm{fir})}/R = \ln q_i^{(\mathrm{fir})} + H_{T,i}^{(\mathrm{fir})}/(RT), \quad (i = 0, 1 \text{ or } 2). \tag{7}$$

Finally, the contributions of the free internal rotation to the molar heat capacity at, e.g., constant pressure, $C_{p,T,i}^{(\mathrm{fir})}$, are in the three approximations given by:

$$C_{p,T,0}^{(\mathrm{fir})}/R = \tfrac{1}{2}, \tag{8}$$

$$C_{p,T,1}^{(\mathrm{fir})}/R = \frac{q_0^{(\mathrm{fir})}}{q_1^{(\mathrm{fir})}} - \frac{q_0^{(\mathrm{fir})}(q_0^{(\mathrm{fir})} + q_1^{(\mathrm{fir})})}{4q_1^{(\mathrm{fir})2}}, \tag{9}$$

$$\begin{aligned} C_{p,T,2}^{(\mathrm{fir})}/R &= H_{T,2}^{(\mathrm{fir})}/(RT) - [H_{T,2}^{(\mathrm{fir})}/(RT)]^2 + \frac{1}{q_2^{(\mathrm{fir})}} \\ &\quad \times \left[\frac{1}{4}\left(\frac{\pi}{\sigma}\right)^{1/2} + \frac{1}{2}e^{-\sigma} + \sigma^2 e^{-\sigma} - \frac{1}{4}\left(\frac{\pi}{\sigma}\right)^{1/2} \Phi(\sigma^{1/2})\right]. \end{aligned} \tag{10}$$

Clearly enough, Eqs. (8)-(10) can equally well be applied to the contributions of the free internal rotation to the molar heat capacity at constant volume. Moreover, the contributions (4)-(10) are independent of the choice of a standard state with the standard overall thermodynamic terms.

The results (1)-(10) allow the evaluation of any important equilibrium or rate characteristic of a species with a free-internal-rotation degree of freedom or of a process including such a species. Remarkably enough, all the above formulae are expressed in a (reduced) form in terms of the dimensionless quantity σ.

3. Systems studied

To thoroughly study the approximations $q_i^{(\mathrm{fir})}$ and their applicability to evaluation of thermodynamic or kinetic characteristics, ten molecular complexes, either van der Waals molecules or hydrogen bonded systems, were chosen (Table 1). Each of these species was studied earlier in a theoretical and/or experimental way and its structural features were described. Mostly, a very low or negligible barrier to

Table 1. Examples of contributions $H_{T,i}^{(\mathrm{fir})}$ of free internal rotation to the heat content function evaluated within the studied q_i approximations for the selected molecular complexes

				$H_{T,i}^{(\mathrm{fir})}$ (J mol^{-1})				
Complex[a]	$10^{48}I$ (kgm^2)	n	$q_i^{(\mathrm{fir})}$	50 K	100 K	200 K	298.15 K	500 K
			$q_0^{(\mathrm{fir})}$	208[b]	416[b]	831[b]	1240[b]	2079[b]
$(H_2)_2$ [39]	2.30	2	$q_2^{(\mathrm{fir})}$	0.005	6	224	740	1985
			$q_1^{(\mathrm{fir})}$	67	167	405	665	1247
$(N_2)_2$ [40]	70.1	2	$q_2^{(\mathrm{fir})}$	225	434	847	1253	2089
			$q_1^{(\mathrm{fir})}$	150	327	698	1072	1854
ClF.HF [30, 41]	0.282	1	$q_2^{(\mathrm{fir})}$	5×10^{-9}	0.008	11	120	892
			$q_1^{(\mathrm{fir})}$	52	133	332	555	1064
HF.ClF [30, 41]	0.662	1	$q_2^{(\mathrm{fir})}$	0.03	14	314	884	2103
			$q_1^{(\mathrm{fir})}$	70	174	419	686	1281
HCN.HCl [42]	0.607	1	$q_2^{(\mathrm{fir})}$	0.01	8	257	796	2034
			$q_1^{(\mathrm{fir})}$	68	169	410	673	1260
HCN.DCl [42]	1.04	1	$q_2^{(\mathrm{fir})}$	2	84	625	1222	2271
			$q_1^{(\mathrm{fir})}$	81	197	466	754	1388
$(H_2O)_2$ [43]	8.23	1	$q_2^{(\mathrm{fir})}$	222	452	871	1276	2110
			$q_1^{(\mathrm{fir})}$	133	298	650	1009	1767
$CF_3H.OH_2$ [31, 36]	18.9	6	$q_2^{(\mathrm{fir})}$	0.002	3	174	644	1889
			$q_1^{(\mathrm{fir})}$	65	162	395	651	1224
$CCl_3H.OH_2$ [31, 36]	19.1	6	$q_2^{(\mathrm{fir})}$	0.002	4	179	654	1899
			$q_1^{(\mathrm{fir})}$	65	163	396	652	1226
$C_3H_6.OH_2$ [31, 36][c]	18.6	6	$q_2^{(\mathrm{fir})}$	0.001	3	166	628	1871
			$q_1^{(\mathrm{fir})}$	64	162	394	649	1220

[a] The reference indicates source of structural data

[b] Results in the $q_0^{(\mathrm{fir})}$ approximation are independent of the substance nature

[c] C_3H_6-cyclopropane (throughout the article)

internal rotation was indicated with these systems so that free internal rotation can be postulated. The water dimer is an exception - here a barrier of about 1 kJ mol^{-1} was found [13]. The latter system was added to include the simplified Pitzer-Gwinn approach to restricted internal rotation [44]. Moreover, thermodynamics of some of the members of the set was already evaluated within the $q_0^{(\mathrm{fir})}$ approach [30, 31]. Reduced moments of inertia I and internal rotation symmetry numbers n are available from the structural intermediates using the standard general treatment suggested for an unsymmetrical top attached to a rigid frame by Pitzer [45] - see Table 1. Within our set the I values as well as the (decisive) ratio I/n^2 vary within three orders of magnitude. Nevertheless, there are also systems in the set the high symmetry number of which leads to the lowest included I/n^2 values in spite of the relatively high I values themselves, namely the associates $CF_3H.OH_2$, $CCl_3H.OH_2$, and $C_3H_6.OH_2$. The symmetry number (i.e., 6) of the latter species deserves a comment. The three-fold symmetry of the larger component of the associates is apparently slightly distorted during the associate formation. However, n is introduced [38] in such a way that the term of $2\pi/n$ would be a period of the potential function in the hindered rotation case. With respect to geometry relaxation in the course of internal rotation it is thus more appropriate to consider 6 as the symmetry number in the case.

4. Results and discussion

Let us start to discuss the problem without reference to any particular species but in terms of the dimensionless parameter σ instead (Fig. 1). It is apparent that in all four cases studied (i.e. $q_i^{(\text{fir})}$, $H_{T,i}^{(\text{fir})}/(RT)$, $S_{T,i}^{(\text{fir})}/R$, and $C_{p,T,i}^{(\text{fir})}/R$) the differences for $\sigma \to \infty$ between $q_0^{(\text{fir})}$ and $q_2^{(\text{fir})}$ approaches are tremendous and increasing with increasing σ (while there is a convergency between $q_1^{(\text{fir})}$ and $q_2^{(\text{fir})}$ approximations). A quite fruitful illustration of these differences is supplied by the entropy term: the conventional term $S_{T,0}^{(\text{fir})}$ continuously decreases towards values of $-\infty$, i.e. for some σ values negative entropy contributions appear (this being, of course, a methodical artefact). On the other hand, there is a convergency between all the three approaches studied for $\sigma \to 0$. For the exact partition function of free internal rotation $Q^{(\text{fir})}$ the following inequality can be derived:

$$q_0^{(\text{fir})} - 1 < Q^{(\text{fir})} \leq q_1^{(\text{fir})}, \tag{11}$$

which is visualized in Fig. 1, too.

Values of the enthalpy $H_{T,i}^{(\text{fir})}$ term evaluated within the set of five selected temperatures are presented in Table 1. The largest deviation between $q_0^{(\text{fir})}$ and

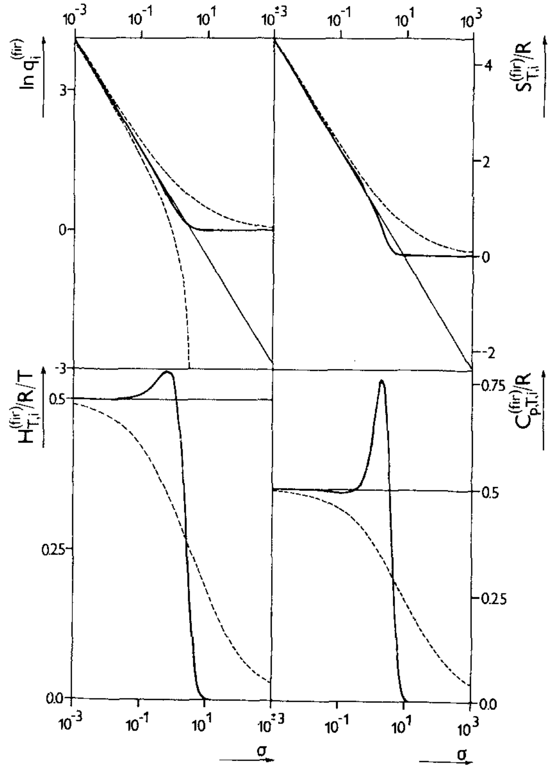

Fig. 1. The dependences of functions q_i, $H_{T,i}^{(\text{fir})}/(RT)$, $S_{T,i}^{(\text{fir})}/R$, and $C_{p,T,i}^{(\text{fir})}/R$ evaluated within the $q_0^{(\text{fir})}$ (Eq. (1), *straight line*), $q_1^{(\text{fir})}$ (Eq. (2), *dashed curve*), and $q_2^{(\text{fir})}$ (Eq. (3), *solid curve*) approaches on the dimensionless parameter σ (see Eq. (1)); with the q_i dependence the other dashed curve indicates the function $(q_0^{(\text{fir})} - 1)$ (cf. Eq. (11))

$q_2^{(\mathrm{fir})}$ approximations is exhibited with the ClF.HF complex at a temperature of 500 K, namely 1187 J mol^{-1}. In most cases the difference attains a value of hundreds of J mol^{-1}; its smallest value is found with $(N_2)_2$ at 500 K: 10 J mol^{-1}. In the area studied the results derived from $q_1^{(\mathrm{fir})}$ usually differ considerably from the other two approximations. Table 2 indicates comparable conditions for $S_{T,i}^{(\mathrm{fir})}$ terms, the largest deviation between $q_0^{(\mathrm{fir})}$ and $q_2^{(\mathrm{fir})}$ approaches being found again with ClF.HF at 500 K: 1080 J mol^{-1}. Remarkably enough, the negative entropy contribution in $q_0^{(\mathrm{fir})}$ approximation appears not only at 50 K but also at 100 K. Finally, differences in the heat capacity contribution caused by applying the different approaches are again far from being negligible (Table 3). Within the samples studied the largest differences in $C_{p,T,i}^{(\mathrm{fir})}$ terms evaluated in $q_0^{(\mathrm{fir})}$ and $q_2^{(\mathrm{fir})}$ approximations appear at the temperature of 50 K, for most substances being

Table 2. Examples of contributions $S_{T,i}^{(\mathrm{fir})}$ of free internal rotation to the entropy term evaluated within the studied q_i approximations for the selected complexes

		$S_{T,i}^{(\mathrm{fir})}$ (J K^{-1} mol^{-1})				
Complex[a]	$q_i^{(\mathrm{fir})}$	50 K	100 K	200 K	298.15 K	500 K
$(H_2)_2$	$q_2^{(\mathrm{fir})}$	0.0001	0.07	1.43	3.50	6.69
	$q_1^{(\mathrm{fir})}$	4.56	5.93	7.56	8.62	10.11
	$q_0^{(\mathrm{fir})}$	−2.05	0.83	3.71	5.37	7.52
$(N_2)_2$	$q_2^{(\mathrm{fir})}$	12.17	15.07	17.93	19.58	21.73
	$q_1^{(\mathrm{fir})}$	13.69	16.13	18.70	20.22	22.22
	$q_0^{(\mathrm{fir})}$	12.15	15.03	17.91	19.57	21.72
ClF.HF	$q_2^{(\mathrm{fir})}$	1×10^{-10}	9×10^{-5}	0.06	0.49	2.39
	$q_1^{(\mathrm{fir})}$	3.42	4.53	5.89	6.79	8.09
	$q_0^{(\mathrm{fir})}$	−5.02	−2.14	0.75	2.41	4.55
HF.ClF	$q_2^{(\mathrm{fir})}$	0.0006	0.16	2.07	4.37	7.51
	$q_1^{(\mathrm{fir})}$	4.82	6.24	7.93	9.01	10.53
	$q_0^{(\mathrm{fir})}$	−1.47	1.41	4.29	5.95	8.10
HCN.HCl	$q_2^{(\mathrm{fir})}$	0.0002	0.10	1.66	3.83	7.01
	$q_1^{(\mathrm{fir})}$	4.66	6.05	7.70	8.77	10.27
	$q_0^{(\mathrm{fir})}$	−1.83	1.05	3.93	5.59	7.74
HCN.DCl	$q_2^{(\mathrm{fir})}$	0.04	1.04	4.68	7.12	9.82
	$q_1^{(\mathrm{fir})}$	5.71	7.30	9.15	10.32	11.94
	$q_0^{(\mathrm{fir})}$	0.40	3.28	6.16	7.82	9.97
$(H_2O)_2$	$q_2^{(\mathrm{fir})}$	8.67	11.90	14.81	16.46	18.59
	$q_1^{(\mathrm{fir})}$	11.20	13.47	15.91	17.36	19.30
	$q_0^{(\mathrm{fir})}$	9.00	11.88	14.77	16.43	18.58
$CF_3H.OH_2$	$q_2^{(\mathrm{fir})}$	3×10^{-5}	0.04	1.09	2.97	6.15
	$q_1^{(\mathrm{fir})}$	4.40	5.74	7.34	8.38	9.84
	$q_0^{(\mathrm{fir})}$	−2.43	0.45	3.34	4.99	7.14
$CCl_3H.OH_2$	$q_2^{(\mathrm{fir})}$	4×10^{-5}	0.04	1.12	3.02	6.21
	$q_1^{(\mathrm{fir})}$	4.42	5.76	7.36	8.40	9.86
	$q_0^{(\mathrm{fir})}$	−2.39	0.49	3.37	5.03	7.18
$C_3H_6.OH_2$	$q_2^{(\mathrm{fir})}$	3×10^{-5}	0.03	1.04	2.88	6.06
	$q_1^{(\mathrm{fir})}$	4.38	5.71	7.30	8.33	9.79
	$q_0^{(\mathrm{fir})}$	−2.49	0.39	3.27	4.93	7.08

[a] For the reduced moments of inertia and internal-rotation symmetry numbers – see Table 1

Table 3. Examples of contributions $C_{p,T,i}^{(\mathrm{fir})}$ of free internal rotation to the heat capacity at constant pressure evaluated within the studied q_i approximations for the selected molecular complexes

		$C_{p,T,i}^{(\mathrm{fir})}$ (J K^{-1} mol^{-1})				
Complex[a]	$q_i^{(\mathrm{fir})}$	50 K	100 K	200 K	298.15 K	500 K
	$q_0^{(\mathrm{fir})}$	4.16[b]	4.16[b]	4.16[b]	4.16[b]	4.16[b]
$(H_2)_2$	$q_2^{(\mathrm{fir})}$	0.001	0.44	4.07	6.03	5.92
	$q_1^{(\mathrm{fir})}$	1.79	2.17	2.54	2.75	2.99
$(N_2)_2$	$q_2^{(\mathrm{fir})}$	4.28	4.13	4.13	4.14	4.15
	$q_1^{(\mathrm{fir})}$	3.42	3.62	3.77	3.84	3.91
ClF.HF	$q_2^{(\mathrm{fir})}$	3×10^{-9}	0.001	0.39	1.99	5.29
	$q_1^{(\mathrm{fir})}$	1.42	1.78	2.16	2.37	2.65
HF.ClF	$q_2^{(\mathrm{fir})}$	0.007	0.84	4.95	6.26	5.62
	$q_1^{(\mathrm{fir})}$	1.87	2.24	2.62	2.82	3.05
HCN.HCl	$q_2^{(\mathrm{fir})}$	0.003	0.57	4.42	6.15	5.81
	$q_1^{(\mathrm{fir})}$	1.82	2.20	2.57	2.77	3.02
HCN.DCl	$q_2^{(\mathrm{fir})}$	0.25	3.36	6.28	5.77	4.77
	$q_1^{(\mathrm{fir})}$	2.11	2.49	2.84	3.02	3.24
$(H_2O)_2$	$q_2^{(\mathrm{fir})}$	5.17	4.31	4.14	4.13	4.14
	$q_1^{(\mathrm{fir})}$	3.15	3.40	3.60	3.70	3.80
$CF_3H.OH_2$	$q_2^{(\mathrm{fir})}$	0.0005	0.27	3.46	5.75	6.08
	$q_1^{(\mathrm{fir})}$	1.74	2.12	2.49	2.70	2.95
$CCl_3H.OH_2$	$q_2^{(\mathrm{fir})}$	0.0005	0.28	3.52	5.78	6.07
	$q_1^{(\mathrm{fir})}$	1.75	2.12	2.50	2.71	2.96
$C_3H_6.OH_2$	$q_2^{(\mathrm{fir})}$	0.0004	0.24	3.35	5.69	6.11
	$q_1^{(\mathrm{fir})}$	1.73	2.11	2.49	2.69	2.94

[a] For the reduced moments of inertia and internal-rotation symmetry numbers - see Table 1

[b] Results in the $q_0^{(\mathrm{fir})}$ approximation are independent of the substance nature and temperature

close to the value of 4.16 J K^{-1} mol^{-1}. For all the three thermodynamic functions two common conclusions can be drawn from the results in Tables 1-3. First, the replacement of the conventional, still frequently used approximation $q_0^{(\mathrm{fir})}$ by the approximation $q_2^{(\mathrm{fir})}$ affects the values of the thermodynamic functions, at least at low and moderate temperatures, in a way which is comparable or even more significant than the anticipated values of the corrections for the deviations from the rigid rotator and harmonic oscillator model [46], i.e. the model on which at present most thermodynamic and kinetic evaluations in the field are based. Second, at very low temperatures, the $q_0^{(\mathrm{fir})}$ approach yields results which are principally wrong within the Boltzmann framework: $H_{T,0}^{(\mathrm{fir})}/T$ equals $R/2$ instead of zero, $S_{T,0}^{(\mathrm{fir})}$ approaches $-\infty$ instead of zero, and $C_{p,T,0}^{(\mathrm{fir})}$ equals to $R/2$ instead of zero.

While the $q_0^{(\mathrm{fir})}$ approximation is apparently handicapped when compared to $q_2^{(\mathrm{fir})}$ and $q_1^{(\mathrm{fir})}$, it is still not clear which one of the latter approximations should be preferred. From the framework [35, 36] of the $q_2^{(\mathrm{fir})}$ derivation is is clear that this approximation works well in the regions of large and low σ values, however for $\sigma \approx 1$ its quality may be questionable; this is connected with the structure of the Laplace method [47] used in the derivation [35, 36]. The exact partition function of free internal rotation $Q^{(\mathrm{fir})}$ can be correlated with one class of elliptic functions, namely with a special case of theta functions [48], viz. ϑ_3 functions of the zero argument $\vartheta_3(0, q)$:

$$Q^{(\mathrm{fir})} = \vartheta_3(0, q), \tag{12}$$

where the parameter q is related to σ by:

$$q = e^{-\sigma}. \tag{13}$$

The function $\vartheta_3(0, q)$ is related to the complete elliptic integrals of the first kind $K(k)$ with the modulus k [48]:

$$\vartheta_3(0, q) = \left(\frac{2K(k)}{\pi}\right)^{1/2}, \tag{14}$$

where the interrelation between q and k reads:

$$\ln q = -\frac{\pi K((1-k^2)^{1/2})}{K(k)}. \tag{15}$$

Numerical techniques for the evaluation of the complete elliptic integrals of the first kind are available [48]. Moreover, methods for the evaluation of $Q^{(\mathrm{fir})}$ (and its σ-derivatives) through direct summation with a reliable residuum estimation are under study [49]. It should give a possibility, inter alia, to study local extrema found on $H^{(\mathrm{fir})}_{T,2}/(RT)$ and $C^{(\mathrm{fir})}_{p,T,2}/R$ curves (Fig. 1). Such local extrema cannot a priori be excluded on the temperature dependences of thermodynamic functions (cf., e.g., [50]); they are however rather rare.

From our point of view, the cases with a relatively low I/n^2 term are most interesting. Such conditions can be established either by relatively medium I values combined with a higher symmetry or by relatively low values themselves. The latter situation can frequently occur together with quasi-linearity in the arrangement of the complex. The precision of theoretical calculations of the deviation from linearity can hardly be better than units of the angle degree. Table 4 illustrates that such a small variation of the equilibrium value of a characteristic

Table 4. Dependence of the entropy contribution $S^{(\mathrm{fir})}_{T,2}$ of free internal rotation evaluted in the q_2 approximation on the deviation from linearity[a] in ClF.HF and HF.ClF van der Waals complexes

ClF.HF				HF.ClF			
∡HFF (°)	$S^{(\mathrm{fir})}_{T,2}$ (J K^{-1} mol^{-1})			∡ ClFF (°)	$S^{(\mathrm{fir})}_{T,2}$ (J K^{-1} mol^{-1})		
	100 K	298.15 K	500 K		100 K	298.15 K	500 K
5.2	1×10^{-13}	0.0008	0.07	0.7	4×10^{-12}	0.002	0.12
7.2	2×10^{-6}	0.14	1.22	1.2	0.001	1.08	3.66
8.2[b]	9×10^{-5}	0.49	2.39	1.7[b]	0.16	4.37	7.51
9.2	0.001	1.11	3.70	2.7	2.42	8.82	11.26
11.2	0.04	2.93	6.11	3.7	5.06	10.92	13.15

[a] Deviation from linearity of quasilinear triad of atoms in the complexes: ∡HFF and ∡ClFF for ClF.HF and HF.ClF isomer, resp.; see schemes in [30]

[b] Equilibrium value [30]

angle can cause dramatic variations in the corresponding values of the thermodynamic functions. Consequently, different quantum-chemical methods used for the evaluation of equilibrium structures can produce a quite pronounced variation in the contributions of free internal rotation to thermodynamic functions. However, this effect might be partly compensated using a proper treatment of the correlation between internal and overall rotation (essentially neglected here).

Let us finish this article with an example of practical nature. To study anaesthetic activity Sandorfy et al. [31] described thermodynamics of three equilibrium processes (Table 5) of the type:

$$(H_2O)_2 + A \rightleftharpoons A.OH_2 + H_2O, \tag{16}$$

using $q_0^{(\mathrm{fir})}$ approximation for the evaluation of free internal rotation found in $A.OH_2$ complexes. One can ask whether the application of more sophisticated $q_2^{(\mathrm{fir})}$ approximation will influence the values [31] of the equilibrium constants K of the processes (16) and the reasoning [31] based on them. The results in Table 5 can give an answer. For the evaluation of anesthetic activity of various species, a reduced extent α of reaction (16) can be employed:

$$\alpha = \frac{c_{A.OH_2}}{c_A^0} = \frac{1+z-[(1-z)^2+4z/K]^{1/2}}{2(1-1/K)}, \tag{17}$$

where $c_{A.OH_2}$ denotes the equilibrium concentration of the $A.OH_2$ associate, $z = c_A^0/c_{(H_2O)_2}^0$, and c_A^0 and $c_{(H_2O)_2}^0$ denotes the starting [31] concentrations of

Table 5. Reevaluated equilibrium data for model anaesthetic processes

	$\log K^{a}$			
	100 K		298 K	
Process	$q_0^{(\mathrm{fir})c}$	$q_2^{(\mathrm{fir})}$	$q_0^{(\mathrm{fir})c}$	$q_2^{(\mathrm{fir})}$
$(H_2O)_2 + CF_3H \rightleftharpoons CF_3H.OH_2 + H_2O$	−2.92 (−3.13)	−2.93	−1.33 (−1.51)	−1.51
$(H_2O)_2 + CCl_3H \rightleftharpoons CCl_3H.OH_2 + H_2O$	0.79 (0.47)	0.66	−0.39 (−0.62)	−0.62
$(H_2O)_2 + C_3H_6 \rightleftharpoons C_3H_6.OH_2 + H_2O$	−8.77 (−8.67)	−8.47	−1.01 (−0.90)	−0.90

	α^{b}			
	100 K		298 K	
Process	$q_0^{(\mathrm{fir})c}$	$q_2^{(\mathrm{fir})}$	$q_0^{(\mathrm{fir})c}$	$q_2^{(\mathrm{fir})}$
$(H_2O)_2 + CF_3H \rightleftharpoons CF_3H.OH_2 + H_2O$	3.4 (2.7)	3.3	17.8 (14.9)	14.9
$(H_2O)_2 + CCl_3H \rightleftharpoons CCl_3H.OH_2 + H_2O$	71.3 (63.2)	68.2	39.0 (32.9)	32.9
$(H_2O)_2 + C_3H_6 \rightleftharpoons C_3H_6.OH_2 + H_2O$	0.004 (0.005)	0.006	23.8 (26.2)	26.2

[a] $K = p_{A.OH_2} p_{H_2O} / (p_{(H_2O)_2} p_A)$, where p_X denotes equilibrium pressure (or concentration) of species X; standard state choice is the same for all the components (e.g. an ideal gas at 101325 Pa pressure)

[b] α - reduced extent of reaction related to the starting amount of species $(H_2O)_2$ (in %) for $z = 1$

[c] In the first column the values according to [31] are given, in parentheses the data derived within the same approximation in this work (see Table 1 and 2) are presented

species A and $(H_2O)_2$, resp. For the purposes of Table 5, the value $z = 1$ was straightforwardly used, though it does not necessarily correspond to conditions in vivo. It is apparent from Table 5 that the transition from $q_0^{(\mathrm{fir})}$ to $q_2^{(\mathrm{fir})}$ approximation moderately changes the α values at 100 K, but it is unimportant at room temperature. Consequently, the qualitative conclusions of [31] would not have been changed by the application of the more sophisticated $q_2^{(\mathrm{fir})}$ approach. It is not important in our connections that our I values may slightly differ from the values originally used [31] (I and n values are not specified in [31]). Remarkably enough, within the cases studied application of the $q_2^{(\mathrm{fir})}$ approach has a non-uniform effect on the stability of $A.OH_2$ associate when compared with $q_0^{(\mathrm{fir})}$ data: both an increase as well as decrease of stability follows (however, the decrease is so small that in Table 5 it is swamped by rounding off).

5. Concluding remarks

The present study points out considerable errors in thermodynamic functions of species with free internal rotation(s) caused by the application of the simple conventional formula (1) in the region of low temperatures and/or low I/n^2 values. The conclusions are important for a further study of molecular complexes not only in the equilibrium but also in kinetic situations [13, 51]. As it is, of course, hard to believe that any system has a zero barrier height with regard to a very low temperature, connections of our problem with hindered internal rotation should be explored. The usefulness of the results for a simplified approximation[1] of the partition function of hindered internal rotation suggested by Pitzer and Gwinn [44] is apparent. The correction terms connected with the transition from $q_0^{(\mathrm{fir})}$ to $q_2^{(\mathrm{fir})}$ approximation should also be added to thermodynamic functions derived in the Pitzer-Gwinn approach[1] to hindered internal rotation. This is the case of systems $(H_2)_2$, $(N_2)_2$, and $(H_2O)_2$ from our set and the recently derived data [39, 40, 43]. Finally, all our reasoning is limited to Boltzmann statistics. With low temperatures we should, however, use the Fermi-Dirac or Bose-Einstein statistics (whichever is appropriate).

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[1] Viz. Eq. (28) of [44].

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