APPLICABILITY OF SEMIEMPIRICAL METHODS IN CALCULATIONS OF EQUILIBRIUM CONSTANTS OF GAS-PHASE CHEMICAL REACTIONS*

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Semiempirical methods of quantum chemistry (CNDO/2, INDO, MINDO/2) have been tested as a source of molecular constants needed for calculations of equilibrium constants of gas-phase chemical reactions. Equilibrium constants have been expressed in terms of partition functions, and ideal gas, rigid rotator, and harmonic oscillator approximations have been adopted. The set investigated consists of twelve molecules (NH_3, H_2CO, CH_4, CH_3OH, CH_3NH_2, CH_3CN, CH_2CH_2, C_2H_4O, C_2H_4NH, CH_3CH_3, C_3H_6, $CH_3CH_2CH_3$). It has been found that at temperatures below 2000 K with systems related to the ones investigated the error in the logarithm of the calculated equilibrium constant is smaller than 0·5. The MINDO/2 method has failed with all compounds containing σ-double-bonded oxygen or pyramidal nitrogen. Special attention has been paid to the position of the rigid rotator, harmonic oscillator approximation in modern-day numerical quantum chemistry, and to its validity for calculating equilibrium and rate constants.

Semiempirical methods of quantum chemistry[1] represent a widely used tool for studying the electronic structure of molecules. During recent years extensive information has been accumulated on their applicability to most types of physical characteristics and classes of compounds. Regrettably enough, the scope of calculations of absolute values of equilibrium and rate constants by means of semiempirical method has remained limited[2-4]. This is evidently due to the fact that, until recently, the semiempirical treatment of rotational-vibrational behaviour in the simplest approximation (rigid rotator and harmonic oscillator — RRHO) was possible only with molecules consisting of a few atoms. Rapid progress was made possible upon the introduction of methods for efficient automatic optimization[5] of molecular geometry. These methods are based on the use of the potential energy gradient, followed by calculation of the force-constant matrix by the finite difference method[6]. Similar progress has also been made with the *ab initio* methods[7]. The methods of the first group are prefered with polyatomic systems because of the computational time economy and because of the absence of correlation energy problem. Another reason which makes the use of semiempirical method expedient is that they were adopted for calculations of heats of formation and heats of atomizations of molecules. The Dewar's MINDO method[8,9] has proved especially useful for these purposes; also the bicentric rescaling[10] of

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CNDO/2 seems to be valuable. Regardless of the nature of the method used, the cubic and quartic terms in the potential are beyond present computational possibilities, except for biatomic molecules[11].

Calculations of equilibrium and rate constants within the framework of the RRHO approximation require knowledge of molecular geometries, frequencies of the harmonic vibrational modes, and zero-point energies of all components of the reaction under study. Very extensive attention has been paid to calculations of all these characteristics during recent years (*cf.* for example refs[1,9]). However, only zero-point energies permit comparisons between calculated and observed data sufficiently sophisticated to lead to conclusions useful for calculating K_p values. We still need a critical evaluation of semiempirical methods as a source of molecular constants necessary for generation of rotational and vibrational partition functions and for calculations of equilibrium and rate constants, standard entropy and activation entropy changes. Moreover, comparisons between calculated and observed values for molecular geometries and force field are often defective.

For example, calculated geometry is frequently evaluated by means of data which were optimized only with respect to a few selected bond lengths and/or angles. Such a procedure can, however, lead to qualitatively incorrect results. This was shown recently in case of glyoxal[12]. The problem has been solved only recently by introduction of fully automated molecular geometry optimizations[5,13,14] at the semiempirical level. Direct comparison between calculated and observed geometry characteristics is of limited values for estimates of the quality of K_p and k calculations. The relationship between errors in calculated geometrical parameters and the consequences of these errors in partition and thermodynamic functions based on them is far from linear. This is true for both the rotational and vibrational parts of the total partition function. For describing rotational movement (the RRHO approximation), the critical term is represented by the product of the main moments of inertia. Therefore, isolated information on bond length errors is not sufficient for estimating the error affecting the rotational partition function: in this the key role is played by the distance between the terminal atoms and their mass in the system under study.

The situation is even worse with regard to vibrational movement. Usually the calculation is only carried as far as the (frequently incomplete) matrix of the second derivatives of the potential energy is concerned and, moreover, force constants are determined for a molecular geometry which is not the optimal one within the framework of the method used. Only rarely are harmonic vibrational frequencies obtained by means of the **FG** vibrational analysis[15,16]. The quality of the force constants obtained by molecular spectroscopy is usually overestimated in spite of the fact that, in a general case, the ambiguity of the solution of the inverse secular problem is well known (*cf.*, for example, ref.[17]). This ambiguity cannot be removed even with simple molecules by using symmetry, by means of data for isotopically labeled parent molecule, or by extension of available vibrational data by use of Coriolis coupling constants or centrifugal stretching constants. A valuable warning is provided by the case where a given set of experimental data for molecules of XY_3 and XY_3Z types is equally well fitted by several different force fields[18,19]. It is worth mentioning that these alternative fields lead with certain force constants to values which differ by an order of magnitude and/or in signs. Testing MO methods by means of force fields of this quality can be misleading. It is desirable in such cases to exclude, by means of a properly organized MO calculation, sets of force constants which are unphysical but compatible with the experimental data[20]. Unfortunately it is very rare[21-23] for semiempirically calculated values to be compared with observed values at the level of frequencies of harmonic vibrational modes in spite of the fact that such a comparison is fundamental for quantum-chemical simulation of vibrational spectra[24]. It seems that authors at present pay more attention to another important problem for simulation of spectra, to the calculation of band intensities in infrared[25-27] and Raman[28] spectra. The situation with regard to *ab initio* calculations is similar[29].

For testing the applicability of the CNDO/2, INDO and MINDO/2 methods for the evaluation of the rotational and vibrational contributions to equilibrium and rate constants, we selected a set of twelve molecules. We performed a full geometry optimization and calculated harmonic vibrational frequencies for all members of the set. The aim of this work was to compare the partition functions and entropies calculated by means of theoretical and experimental rotational and vibrational molecular constants within the framework of the RRHO approximation.

CALCULATION

Compounds studied. The members of the set investigated satisfy the following requirements: *a*) they must be sufficiently representative and contain important groupings of atoms, *b*) their experimental rotational and vibrational characteristics must be known, *c*) for atoms constituting the molecules, the semiempirical parameters must be available. Some fundamental information for the members of our set is summarized in Table I. Experimental geometrical parameters for CH_3OH, C_2H_4NH, C_3H_6 and C_3H_8 were taken from refs[30-33], for other members from Herzberg[34]. All experimental vibrational characteristics originate from tables by Shimanouchi[35].

TABLE I

Basic Information about Compounds Studied

Molecule	Molecular point group[a]	Symmetry number σ[a]	Source of exp. mol. geometry (ref.)
NH_3	C_{3v} (D_{3h})	3 (6)	34
H_2CO	C_{2v}	2	34
CH_4	T_d	12	34
CH_3OH	C_s (C_{3v})	1 (3)	30
CH_3NH_2	C_s	1	34
CH_3CN	C_{3v}	3	34
CH_2CH_2	D_{2h}	4	34
C_2H_4O	C_{2v}	2	34
C_2H_4NH	C_s (C_{2v})	1 (2)	31
CH_3CH_3	D_{3d}	6	34
C_3H_6	D_{3h}	6	32
$CH_3CH_2CH_3$	C_{2v}	2	33

[a] CNDO and INDO calculations agree fully with experimental findings; three erroneous prediction based on MINDO/2 are presented in brackets.

Coordinate system. All calculations were performed in a Cartesian coordinate system. This is rather unusual in molecular spectroscopy, but permits the use of convenient automatic procedures for geometry optimization. It is true that symmetry coordinates used by Pulay[7,14] guarantee minimal dimension of the vibrational problem, they require, however, a special individual generation of coordinates for each studied molecule which is rather involved for routine calculations. Moreover, the symmetry group of the system must be known in advance. Finally, the reduction of the order of the problem by means of symmetry coordinates is negligible with more extensive systems.

Molecular geometry. The Pancíř procedure[36] was used for optimization of molecular geometry. It is based on the minimization of the total energy and uses explicit formulas for the first derivatives of the total energy according Cartesian coordinates of atoms. The actual optimization is an iterative process performed by a generally applicable minimization due to Murtagh and Sargent[37] (variable metric method).

Vibrational frequencies. The force constant matrix has been set up numerically from differences of the first derivatives of the total energy corresponding to equidistant shifts of all coordinates[36]. These shifts amounted to $\pm 10^{-12}$ m in all cases, which means that for a molecule consisting of n atoms (assuming the knowledge of its minimum) $(6n + 1)$ SCF calculation were necessary for setting up the corresponding force constant matrix. The order of the **FG** characteristic problem is higher in our procedure than with symmetry coordinates, but this is partly compensated by the ease of setting up the matrix of the kinetic energy[16]. Six Eckart conditions[38] among Cartesian coordinates manifest themselves in the solution of the characteristic problem by six vanishing eigenvalues, the eigenvectors of which correspond to translation and rotation of a molecule.

Statistical thermodynamic approach. A simple model reaction has been used to evaluate the results obtained. The molecule under study occurs in this reaction with a stochiometric coefficient equal to unity. The differences in selected thermodynamic characteristics were investigated with this model reaction in the following cases: *a*) Partition functions of all components were calculated by means of molecular constants taken from experiment; *b*) In contrast to the case *a*) the rotational partition function was based on semiempirical calculations; *c*) This case is analogous to the case *b*) but concerns the vibrational partition function.

The passage from *a*) to *b*) or to *c*) introduces into the logarithm of the equilibrium constant of our reaction an error $\delta \log K_\mathrm{p}$ defined by

$$\delta \log K_\mathrm{p} = \log Q^{(\mathrm{exp.})} - \log Q^{(\mathrm{theor.})}\,, \qquad (1)$$

where Q stands for the partition function of the molecule under investigation, the index exp. means that molecular constants were obtained according to *a*), the index theor. means that they were obtained according to *b*) or *c*). The error $\delta\,\Delta S^0$, which concerns the standard entropy change of our hypothetical reaction, is defined analogously:

$$\delta\,\Delta S^0 = S^{(\text{exp.})} - S^{(\text{theor.})}\,. \qquad (2)$$

For errors (*1*) and (*2*), within the framework of the RRHO approximation[39], the following expressions are valid in case of the rotational contribution:

$$\log\left(Q^{(\text{exp.})}/Q^{(\text{theor.})}\right)_{\text{rot.}} = \log\left(\sigma^{(\text{theor.})}/\sigma^{(\text{exp.})}\right) + $$
$$+ 1/2\log\left(I_A I_B I_C{}^{(\text{exp.})}/I_A I_B I_C{}^{(\text{theor.})}\right. \qquad (3)$$

$$\left(S^{(\text{exp.})} - S^{(\text{theor.})}\right)_{\text{rot.}} = \frac{R}{0{\cdot}43429\ldots}\log\left(Q^{(\text{exp.})}/Q^{(\text{theor.})}\right)_{\text{rot.}}, \qquad (4)$$

where R is the gas constant, $I_A I_B I_C$ is the product of the main moments of inertia[40], and σ is the symmetry number[39] given by the symmetry point group to which the molecule under study belongs.

Analogously, for errors connected with the vibrational contribution, we can write:

$$\log\left(Q^{(\text{exp.})}/Q^{(\text{theor.})}\right)_{\text{vibr.}} = \log\prod_i\left(1 - \exp\left(-h\omega_i{}^{(\text{exp.})}/kT\right)\right)^{-1} -$$
$$- \log\prod_i\left(1 - \exp\left(-h\omega_i^{(\text{theor.})}/kT\right)\right)^{-1} \qquad (5)$$

$$\left(S^{(\text{exp.})} - S^{(\text{theor.})}\right)_{\text{vibr.}} = R\sum_i\left(h\omega_i{}^{(\text{exp.})}/kT\right)\left(\exp\left(h\omega_i{}^{(\text{exp.})}/kT\right) - 1\right)^{-1} -$$
$$- R\sum_i\left(h\omega_i{}^{(\text{theor.})}/kT\right)\left(\exp\left(h\omega_i{}^{(\text{theor.})}/kT\right) - 1\right)^{-1} -$$
$$- \frac{R}{0{\cdot}43429\ldots}\log\left(Q^{(\text{exp.})}/Q^{(\text{theor.})}\right)_{\text{vibr.}}, \qquad (6)$$

where ω_i is the frequency of the normal vibrational modes of the molecule studied and the other symbols possess their usual meaning.

The results obtained by means of Eqs (*3*)–(*6*) for the individual members of the set were treated by applying standard methods of the mathematical statistics[41].

RESULTS

Optimal molecular geometry has been obtained for all members of the set by means of the three semiempirical methods investigated. The experimental symmetry point group has been reproduced except for three molecules in the MINDO/2 method (Table I). That method failed in the following cases (theoretical and experimental data): NH_3 (D_{3h}, C_{3v}(ref.[34]), CH_3OH (linear and bent[30] arrangement of the grouping C—O—H), C_2H_4NH (coplanar and nonplanar[31] arrangement of the H atom on N atom in the CCN plane). All those failures of the MINDO/2 method manifest themselves also by the change of symmetry numbers (Table I). Moreover, the MINDO/2 method was unable to reproduce the pyramidal arrangement of atoms attached to the nitrogen atom in methylamine which, of course, was not connected with an error in determining the symmetry point group.

The results concerning some important geometrical characteristics obtained by the three methods used are compared in Table II.

The main results of the work are summarized in Tables III–V. Table III contains information on the quality of the semiempirical approach to the rotational contribution to the partition function. Results concern both the values obtained from Eqs (*1*) and (*2*) and their absolute values. A similar comparison for vibrational terms is made in Table IV. In this case there is no reason to include absolute values also, because magnitudes defined by Eqs (*1*) and (*2*) have the same sign for all members of the set within the framework of each method used. Table V indicates the quality of the estimates of the vibrational contribution to the entropy.

TABLE II

A Comparison of Selected Geometrical Characteristics Obtained Experimentally and by Semiempirical Calculations for Twelve Members of the Set Studied

Structural parameter ξ	Independent values	$\xi^{(\text{exp.})} - \xi^{(\text{theor.})}$, 10^{-10} m[a]		
		CNDO/2	INDO	MINDO/2
C—H bonds	16	−0·027 ± 0·0002	−0·029 ± 0·0007	−0·019 ± 0·0007[b]
C—C bonds	7	0·050 ± 0·001	0·046 ± 0·001	0·035 ± 0·001
N—H bonds	3	−0·054 ± 0·002	−0·056 ± 0·002	0·009 ± 0·002[b]
HCH bond angles[c]	15	2·5 ± 0·3	2·7 ± 0·3	4·6 ± 0·4
CNH and HNH bond angles[c]	4	1·7 ± 0·5	− 0·3 ± 0·6	− 18·2 ± 3·3

[a] Results averaged over all members of the set and presented as arithmetic mean ± probable error. [b] C—H and N—H equilibrium bond lengths were shortened by 10^{-11} m in accordance with the Dewar recommendation[9]. [c] Values in degrees.

TABLE III

Comparison of Partition Functions Q and Entropies S Based on Experimental and Calculated Molecular Geometries for All Members of the Set[a]

Term	CNDO/2	INDO	MINDO/2	
			corrected[b]	optimized[c]
$\log Q^{(\mathrm{exp.})} - \log Q^{(\mathrm{theor.})}$	$0{\cdot}002 \pm 0{\cdot}004$	$-0{\cdot}008 \pm 0{\cdot}008$	$0{\cdot}108 \pm 0{\cdot}037$ $(0{\cdot}010 \pm 0{\cdot}002)^d$	$0{\cdot}051 \pm 0{\cdot}035$ $(-0{\cdot}042 \pm 0{\cdot}006)^d$
$\lvert \log Q^{(\mathrm{exp.})} - \log Q^{(\mathrm{theor.})} \rvert$	$0{\cdot}018 \pm 0{\cdot}002$	$0{\cdot}026 \pm 0{\cdot}005$	$0{\cdot}109 \pm 0{\cdot}036$ $(0{\cdot}011 \pm 0{\cdot}001)^d$	$0{\cdot}113 \pm 0{\cdot}027$ $(0{\cdot}042 \pm 0{\cdot}007)^d$
$S^{(\mathrm{exp.})} - S^{(\mathrm{theor.})}$ $(\mathrm{J\,mol^{-1}\,K^{-1}})$	$0{\cdot}04 \pm 0{\cdot}07$	$-0{\cdot}16 \pm 0{\cdot}15$	$2{\cdot}06 \pm 0{\cdot}70$ $(0{\cdot}18 \pm 0{\cdot}03)^d$	$0{\cdot}98 \pm 0{\cdot}67$ $(-0{\cdot}80 \pm 0{\cdot}12)^d$
$\lvert S^{(\mathrm{exp.})} - S^{(\mathrm{theor.})} \rvert$ $(\mathrm{J\,mol^{-1}\,K^{-1}})$	$0{\cdot}35 \pm 0{\cdot}04$	$0{\cdot}50 \pm 0{\cdot}10$	$2{\cdot}08 \pm 0{\cdot}70$ $(0{\cdot}21 \pm 0{\cdot}02)^d$	$2{\cdot}16 \pm 0{\cdot}52$ $(0{\cdot}80 \pm 0{\cdot}12)^d$

[a] Arithmetic means for all molecules of the set ± probable error. [b] The C—H, N—H and O—H bond lengths of the optimized molecular geometries corrected according to the ref.[9]. [c] Values based on optimized geometries. [d] Molecules for which the MINDO/2 method failed in reproducing their conformation (NH_3, CH_3OH, CH_3NH_2 and C_2H_4NH) were excluded from the set.

TABLE IV

Comparison of Partition Functions Q Based on Experimental[35] and Calculated Vibrational Modes for all Members of the Set[a]

T, K	$\log Q^{(\mathrm{exp.})} - \log Q^{(\mathrm{theor.})}$			
	CNDO/2	INDO	MINDO/2	
			12 molecules	8 molecules[b]
100	0·001 ± 0·0004	0·0007 ± 0·0005	−0·024 ± 0·011	−0·005 ± 0·003
298·15	0·024 ± 0·005	0·023 ± 0·005	−0·102 ± 0·026	−0·045 ± 0·011
500	0·089 ± 0·011	0·086 ± 0·011	−0·207 ± 0·036	−0·130 ± 0·022
1 000	0·297 ± 0·032	0·294 ± 0·032	−0·408 ± 0·052	−0·315 ± 0·047
1 500	0·489 ± 0·048	0·487 ± 0·049	−0·514 ± 0·061	−0·416 ± 0·062
2 000	0·650 ± 0·060	0·647 ± 0·062	−0·574 ± 0·066	−0·475 ± 0·070
2 500	0·779 ± 0·070	0·776 ± 0·072	−0·611 ± 0·070	−0·512 ± 0·075

[a] Arithmetic means for all molecules of the set ± probable error. [b] Molecules for which the MINDO/2 method failed in reproducing their conformation (NH_3, CH_3OH, CH_3NH_2 and C_2H_4NH) were excluded from the set.

TABLE V

Comparison of Entropies Based on Experimental[35] and Calculated Vibrational Modes for All Members of the Set[a]

T, K	$S^{(\mathrm{exp.})} - S^{(\mathrm{theor.})}$, J mol^{-1} K^{-1}			
	CNDO/2	INDO	MINDO/2	
			12 molecules	8 molecules[b]
100	0·10 ± 0·04	0·08 ± 0·04	− 1·13 ± 0·46	− 0·31 ± 0·15
298·15	1·73 ± 0·24	1·66 ± 0·24	− 4·67 ± 0·83	− 2·80 ± 0·49
500	5·43 ± 0·63	5·35 ± 0·64	− 8·93 ± 1·1	− 6·87 ± 1·0
1 000	13·5 ± 1·3	13·5 ± 1·4	−13·3 ± 1·5	−11·2 ± 1·6
1 500	19·5 ± 1·8	19·5 ± 1·8	−14·3 ± 1·6	−12·2 ± 1·8
2 000	23·5 ± 2·0	23·4 ± 2·0	−14·5 ± 1·6	−12·6 ± 1·8
2 500	25·9 ± 2·2	25·8 ± 2·2	−14·6 ± 1·6	−12·7 ± 1·9

[a] Arithmetic means for all molecules of the set ± probable error. [b] Molecules for which the MINDO/2 method failed in reproducing their conformation (NH_3, CH_3OH, CH_3NH_2 and C_2H_4NH) were excluded from the set.

DISCUSSION AND CONCLUSIONS

Results summarized in Tables III–V permit an evaluation of the applicability of the individual semiempirical methods for calculating equilibrium constants of chemical reactions in the ideal gas phase for components which are structurally related to the molecules tested. Moreover, it seems reasonable to believe that the characteristics of the saddle points will be described with a comparable accuracy as the characteristics of local minima. Therefore, conclusions can be drawn concerning calculations of rate constants of processes adequately described by the transition state (activated complex) theory.

The rotational and vibrational contributions can be analyzed separately within the RRHO approximation. Meanwhile the error of the rotational part of the partition function is temperature independent, the vibrational part increases with increasing temperature (Eqs (*3*) and (*5*)). Due to this fact the accuracy of the vibrational partition function becomes critical for the accuracy of the complete partition function at about 500 K.

The results summarized in Table II confirm the well known capabilities[1,42] of semiempirical methods for calculating bond lengths and angles. Moreover, values based on completely optimized molecular geometries support the earlier finding[9] based on partly optimized geometries and concerning the overestimation of the C—H and N—H bond lengths by the MINDO/2 method. The CNDO/2 and INDO methods as sources of molecular geometries introduce into the logarithms of equilibrium constants errors which amount to hundreds and into the entropy term tenths of *J*/mol/K. The CNDO/2 results seem to be a little better than the INDO results. As already mentioned, some rather serious failures in estimates of molecular geometry are connected with the MINDO/2 method (see also ref.[23]). If we exclude molecules containing O—H and N—H bonds from the set and consider the Dewar proposal on C—H bond lengths shortening the MINDO/2 rotational partition functions are similar in quality to those based on CNDO/2 and INDO methods.

While the good quality of rotational partition functions with regard to semiempirical molecular geometries has been expected, it was hardly possible to make a reasonable estimate concerning vibrational partition function, especially at higher temperatures. Without going into details, let us note that the frequencies of the stretching vibrations, belonging to 170 vibrational modes of the molecules forming our set, are drastically overestimated. This fact has been known for a long time and was established in connection with calculations of force constants[1]. In spite of the poor quality of the calculated stretching modes, the values of vibrational partition functions are rather accurate. This is due to two fortunate circumstances. Firstly, the estimates of frequencies of the deformation modes are more accurate by orders of magnitude than those of stretching modes. Low frequencies of deformation vibrations are critical as far as the numerical value of $Q_{\text{vib.}}$ is concerned. In Fig. 1 the error of the logarithm of the $Q_{vib.}$ is plotted against the error in ω_i for important regions of frequencies and temperatures. The second fortunate circumstance is that the failure with stretching vibrations leads to their overestimation. The vibrational partition function, due to its form, in the region of ordinary values of stretching vibrations (Fig. 1) is not sensitive to the overestimation of frequencies. It is worth mentioning that if the semiempirical stretching frequencies were underestimated (instead of overestimated) to the same extent, the corresponding vibrational partition function would be completely useless. For temperatures up to 2000 K, the use of semiempirical vibrational frequencies introduces (in comparison with experimental fundamental frequencies) into the logarithm of equilibrium constants an error which is smaller than half of an order of magnitude, into the entropy term an error smaller than 20 J/mol/K. The observed deviations were systematically positive with the CNDO/2 and INDO methods, negative with the MINDO/2 method. These results suggest that, on the average, the lowest frequencies are overestimated with the former methods (which appear to be equivalent) and underestimated with the latter method.

The error in $\log K_p$ when the calculation was based on semiempirical figures was essentially due to the partition function. On the whole, it can be stated that all the three semiempirical procedures provide partition functions causing an error in $\log K_p$ which is smaller than 0·5 at temperature up to 2000 K.

It seems that the errors (*1*) and (*2*) are almost invariant in systems under study. This fact, together with the finding that the signs of errors of the vibrational partition function remain unchanged with each of the methods used, suggest that errors compensate to a significant extent with specific types of equilibria. For the error

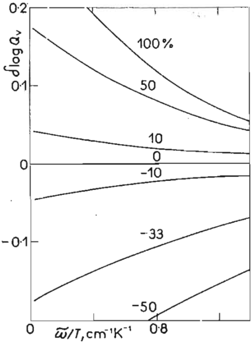

FIG. 1

Error in Determination of the Frequency of the Harmonic Vibrational Mode (Presented above Curves) and Its Consequence for Logarithm of the Vibrational Partition Function Q_v for Selected Region of Values of Harmonic Vibrational Wave-Numbers $\tilde{\omega}$ and Absolute Temperatures T

$\delta \log K_p$ of a reaction characterized by the change of the number of moles $\Delta\nu$, and with the above mentioned assumptions, the following unequality is valid at temperatures up to 2000 K:

$$\left|\delta \log K_p\right| \leqq 0{\cdot}5\left|\Delta\nu\right| . \tag{7}$$

Therefore reactions possessing $\Delta\nu = 0$ are especially suited for semiempirical treatment.

To test the quality of vibrational partition functions, we have used functions based on experimental fundamental frequencies[35]. The reason was twofold. Firstly, for the majority of molecules of our set, the experimental harmonic frequencies are not available. Secondly, it is well known[43] that with the RRHO approximation partition functions based on fundamental vibrational frequencies better reproduce experimentally determined thermodynamic functions. Moreover, in spite of the fact that we calculated the vibrational frequencies by means of the **FG** analysis[15,16] we cannot say with certainty that they correspond to the observed harmonic frequencies. This question can be settled only after solving the problem which force constants correspond to the semiempirically calculated values: the force constants obtained from harmonic or from fundamental experimental frequencies.

In this connection, at least a short comment on semiempirical calculations of the enthalpy term is desirable, MINDO/2 heats of formation of molecules belonging to our set are presented in Table VI. Obviously, ΔH^0_{f298} figures calculated by Dewar and coworkers[8,9,45] for partially optimized molecular geometries differs considerably from those based on fully optimized geometries. This supports the scepticism which followed the optimism at first generated by the MINDO/2 method. The average absolute deviation of the accurate MINDO/2 heats of formation from the experimental values[44] amounts to 61·6 kJ/mol. Clearly, this error greatly exceeds those reported in this paper for the entropy term evaluated by semiempirical methods.

The RRHO approximation corresponds to the contemporary possibilities of quantum chemical methods. For biatomics a more sophisticated description of the rotational-vibrational movement is widely used[46]. For triatomics, however, anharmonicity constants, for example, are only rarely evaluated[47]. For general polyatomic systems, it is at present impossible to obtain information on rotational-vibrational movement by means of MO calculations on a level better than the RRHO[11]. Therefore, it is desirable to know the error in thermodynamic functions evaluated by the RRHO approximation. Unfortunately the comparison of RRHO partition functions with those based on the approximation of the vibrating rotator (VR) is very limited, because of lack of polyatomic molecules for which the thermodynamic functions are available on the VR approximation[43,48] (this shortage is due to the fact that perfectly measured and analyzed rotational-vibrational spectra are available only for a few molecules). Nevertheless comparisons between the approximations

TABLE VI

Comparison of Experimental and MINDO/2 Calculated Heats of Formation (ΔH^0_{f298})

Molecule	ΔH^0_{f298}, kJ mol^{-1}		
	Exp.[44]	Calc. opt. geom.	
		partly	fully
NH_3 (g)	− 45·69	− 46·86[a]	− 76·04
H_2CO (g)	−115·90	− 94·14[a]	− 99·85
CH_4 (g)	− 74·85	− 67·78[a]	− 67·68
CH_3OH (g)	−201·17	−223·01[a]	−304·37
CH_3NH_2 (g)	− 23·01	− 40·17[a]	− 69·73
CH_3CN (g)	87·86	70·29[b]	311·83
CH_2CH_2 (g)	52·30	60·25[a]	55·93
C_2H_4O (g)	− 52·63	—	−161·82
C_2H_4NH (g)	123·43	115·90[a]	60·32
CH_3CH_3 (g)	− 84·68	− 95·40[a]	−103·78
C_3H_6 (g)	53·30	− 4·60[a]	− 41·80
$CH_3CH_2CH_3$ (g)	−103·85	−104·18[c]	−125·74

[a] Ref.[9]. [b] Ref.[45]. [c] Ref.[8].

TABLE VII

Comparison of Partition Functions Q and Entropies S for NH_3 (g) Calculated in the Vibrating Rotator[a] (VR) and the Rigid Rotator-Harmonic Oscillator (RRHO) Approximations Based on Molecular Constants Originating from Experiments (RRHO) and CNDO/2 Calculations (CNDO)

T, K	$\log Q^{(VR)} - \log Q^{(RRHO)}$	$\log Q^{(RRHO)} - \log Q^{(CNDO)}$	$S^{(VR)} - S^{(RRHO)}$ (J mol^{-1} K^{-1})	$S^{(RRHO)} - S^{(CNDO)}$ (J mol^{-1} K^{-1})
100	—	−0·062	—	−1·19
298·15	0·005	−0·058	0·06	−0·75
500	0·006	−0·038	0·23	0·48
1 000	0·015	0·030	0·66	3·19
1 500	0·025	0·099	1·03	5·89
2 000	0·035	0·166	1·45	8·03
2 500	0·046	0·225	2·02	9·50

[a] Ref.[48].

demonstrate the value of the RRHO partition functions. Godnev[49] has shown that the difference in entropy of water, $S^{0(VR)} - S^{0(RRHO)}$, at 1000 K amounts to 0·33 J/mol/K. Some results on similar comparison for NH_3 are presented in Table VII. Clearly, the correction corresponding to the VR approximation (as against the RRHO approximation) form just a small fraction of the (usually small) error caused by the use of molecular constants originating from a semiempirical calculation instead of an experiment. It has been pointed out[50] that corrections on anharmonicity of vibrations, rotation-vibration interactions and centrifugal stretching are not significant with hydrogen-deuterium exchange equilibria involving ammonia molecules. The unimportance of neglect of vibration anharmonicities is also apparent from papers by Bron[51,52]. The use of the Born–Oppenheimer approximation has a negligible importance for the analysis of the isotopic exchange equilibria[53].

Recently the nonharmonic force fields determined from spectral data were subject to criticizm. Simons[54] published examples of drastic failures of the conventional cubic and quartic fields with diatomic and triatomic molecules for non-equilibrium positions of nuclei. In our particular case his finding concerns limited possibilities of accurately calculated higher unobserved energy levels and overestimation of dissociation energies deduced from these potentials by nearly two orders of magnitude. A recently suggested[55] new type of a nonharmonic potential seems to be promising for exploitation by available quantum chemical methods. In contrast to traditional expansions it could make it possible to consider some effect of the vibrational anharmonicity without any serious extension of SCF calculations required for the description of the harmonic field.

The comparisons[42] between the INDO and *ab initio* (STO-3G and 4-31G basis sets) methods suggest that these *ab initio* procedures would lead to a slightly better partition functions than semiempirical methods on the RRHO level.

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