Evaluation of Partition Functions of Triatomic Molecules Using Data Obtained by ab initio Calculations – Sums of States of Molecules with Spatially Degenerate Lowest Electronic States

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The evaluation of partition functions of triatomic molecules based on data obtained by means of the ab initio method is discussed. Special attention is paid to molecules exhibiting the Renner-Teller effect. Various approximate approaches for the calculations of partition functions are explicitly considered. The results are shown for HNF, NCO and BH_2.

1. Introduction

Molecular spectroscopy has for a long time been the only source of data needed for the calculation of partition functions of molecules. However difficulties in the preparation of the investigated species, spectra in inconvenient wave length regions, unresolved rotation structure, forbidden transitions etc. have restricted the number of molecules for which the partition functions have been determined. Special problems did arise for short-living radicals and hypothetical species (e.g. activated complexes) appearing in the theoretical treatment of chemical reactions.

One of the most promissing alternative ways for evaluation of molecular structural parameters represent ab initio calculations which have become in the last years, at least for small molecules, accurate enough to ensure a quite reliable reproduction and prediction of experimental findings. In this paper we present the results of calculation of partition functions for triatomic molecules, particularly those exhibiting the Renner-Teller effect [1]. Various approximations used in the application of the ab initio method are discussed and numerical data for three characteristic species are given.

2. Calculation of Partition Functions of Triatomic Molecules

Calculation of partition functions of polyatomic molecules encounters a number of difficulties reflecting the complexity of their structure. In many cases various degrees of freedom are strongly coupled with each other and it is necessary to examine carefully which simplifying assumptions may be applied. On the other hand, it is almost imperative to find a means of reducing the number of degrees of freedom which have to be treated simultaneously because of the multidimensional potential surfaces involved and the gigantic secular equations (if a variational approach is applied) which have to be solved for computing the vibration-rotation energy levels.

The most important simplification is based on the Born-Oppenheimer approximation which enables a separation of electronic motions from the nuclear problem. However, in some cases the Born-Oppenheimer approximation breaks down. The most common example occuring in triatomic molecules (also in larger linear and quasilinear molecules) is the Renner-Teller effect [1] appearing in electronic states spatially degenerate in linear nuclear arrangements – in course of the bending vibrations this degeneracy is lifted and two component electronic states, strongly interacting with one another, can not be treated separately.

Another peculiarity of triatomic molecules is the interplay between the rotations and the bending vibrations having as a consequence the characteristic vibration-rotation structure of quasilinear molecules. During the bending vibrations a gradual transformation of one of the rotational degrees of freedom (of the bent molecule) into the second component of the bending mode (at the linear geometry) takes place, and consequently both of these degrees of freedom have to be treated simul-

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taneously. Quasilinear molecules are also characterized by highly anharmonic bending vibrations which makes the separation of bending and stretching vibrations from one another rather problematic and the calculation of vibrational partition functions by means of analytical expressions (derived in harmonic approximation) impossible – instead a direct counting of vibrational energy levels has to be performed. An accurate calculation of the rotational partition function is in the general case (asymmetric top) not trivial because there do not exist any analytical expression for the energy levels, and consequently, the corresponding partition function can only be obtained by direct summing. The spin-orbit coupling causes in some cases large and irregular splittings of vibration levels.

For the mentioned reasons it is not possible to develop a general, optimal routine for the evaluation of partition functions of triatomic molecules. Therefore we consider separately 1) nonlinear and 2) linear and quasilinear triatomics, and in each case i) spatially nondegenerate (Σ at the linear geometry) and ii) degenerate (Π, Δ...) electronic species.

2.1. Nonlinear Molecules

2.1.i Σ-Electronic States

In the case of a triatomic molecule having nonlinear equilibrium geometry with the barrier to linearity being large compared to kT the approximation of mutual independence of electronic, vibrational and rotational motions works normally well, and a calculation of the total partition function is relatively simple. Some difficulties may arise only in the evaluation of the rotational part of the partition function because these molecules are asymmetric tops for which the rotation energy levels can not be calculated analytically. In the present paper three types of calculation of the rotation partition function are discussed:

a) The rotation energy levels are calculated by diagonalizing the exact Hamiltonian of the rigid asymmetric top

$$H_\mathrm{r} = \frac{J_x^2}{2I_x} + \frac{J_y^2}{2I_y} + \frac{J_z^2}{2I_z} \tag{1}$$

in the basis consisting of the eigenfunctions of the closest symmetric top [2]. The rotation partition function is then obtained by direct summing, taking into account that the degeneracy of each level characterized by the value of the unique good quantum number J is $2J+1$.

b) If the molecule possesses a hydrogen atom it is nearly a symmetric top ($I_z \equiv I_a \ll I_x \cong I_y \equiv I_b$) with the rotation Hamiltonian

$$H_\mathrm{r} = \frac{J^2 - J_z^2}{2I_b} + \frac{J_z^2}{2I_a} \tag{2}$$

whose eigenvalues are

$$E_\mathrm{r} = \frac{\hbar^2}{2I_b} J(J+1) + \frac{\hbar^2}{2}\left(\frac{1}{I_a} - \frac{1}{I_b}\right) K^2. \tag{3}$$

Taking into account that the degeneracy of each energy level is $g_J = (2J+1)\, g_K$ ($g_K = 1$ for $K = 0$ and 2 for $K \neq 0$) and that the second good quantum number K (if now assumed to be signed) has the values $-J \leqq K \leqq J$, one obtains for the partition function

$$\sum_{J=0}^{\infty} \sum_{K-J}^{J} (2J+1) \exp\{-[bJ(J+1) + aK^2]\}, \tag{4}$$

where $b \equiv \hbar^2/2I_b kT$ and $a \equiv \hbar^2(1/I_a - 1/I_b)/2kT$. If the rotation levels lie close to one another ($\hbar^2/2I \ll kT$) the sum (4) can be replaced by the integral (high-temperature, classical approximation)

$$\begin{aligned} Z_\mathrm{r} &\cong \int_{K=-\infty}^{\infty} \int_{J=|K|}^{\infty} (2J+1) \\ &\quad \cdot \exp\{-[bJ(J+1) + aK^2]\}\, \mathrm{d}K\, \mathrm{d}J \\ &\cong \frac{1}{b} \int_{-\infty}^{\infty} \exp\{-[bK(K+1) + aK^2]\}\, \mathrm{d}K \\ &\cong \frac{1}{b} \int_{-\infty}^{\infty} \exp[-(b+a)K^2]\, \mathrm{d}K \\ &= 8\pi^2 (8\pi^3)^{1/2} I_b I_a^{1/2} (kT)^{3/2} h^{-3}. \end{aligned} \tag{5}$$

The final form of (5) is derived by neglecting the linear term in K in the expression $bK(K+1) + aK^2$, i.e. assuming an appreciable population of higher rotation levels.

c) It has been shown [3] that a symmetric top can in a good approximation be treated as a combination of an one-dimensional and a two-dimensional rotator being independent from one another. The eigenvalues of the Hamiltonian for the one-dimensional rotator, $H_1 = J_z^2/2I_1$, are given by

$$E_{\mathrm{r}_1} = \frac{K^2 \hbar^2}{2I_1} \tag{6}$$

with the degeneracy $g_K = 1$ for $K = 0$ and 2 for $K \neq 0$. The corresponding partition function in the classical approximation is

$$Z_{r_1} = (8\pi^3 I_1 kT)^{1/2} h^{-1} . \tag{7}$$

The eigenvalues of a rigid two-dimensional rotator with the two moments of inertia being equal are

$$E_{r_2} = \frac{J(J+1)\hbar^2}{2I_2} \tag{8}$$

and are $2J+1$ degenerate. The corresponding partition function is

$$Z_{r_2} = \sum_{J=0}^{\infty} (2J+1) \exp[-bJ(J+1)] \tag{9}$$

with $b \equiv \hbar^2/2I_2 kT$. In the high temperature approximation, replacing the sum in (9) with the integral, one obtains

$$Z_{r_2} \cong 8\pi^2 I_2 kT h^{-2} . \tag{10}$$

By multiplying (10) with (7), (5) is recovered.

Therefore, if higher rotation levels are appreciably populated it is quite possible to treat a hydrogen containing molecule as being composed of a one-dimensional and a two-dimensional rotator which may be a very useful approximation in quasilinear molecules when one of the rotational degrees of freedom has to be separated from the other two in order to be handled together with the bending vibration. However, is should be kept in mind that the treatments b) and c) give the same results only for the sum of states (in classical approximation) but somewhat different densities of states which are needed e.g. if an isomerization reaction on a more sophisticated level is studied [3]. If, furthermore, I_b in (5) is replaced by $(I_b I_c)^{1/2}$, one obtains the formula usually given for calculations of the rotational partition of polyatomic molecules [4][*].

In calculations of the vibration partition functions the harmonic approximation is usually quite satisfactory in the case considered because at not very high temperatures only the lowest vibration levels are appreciably populated and therefore contribute considerably to the sum of states. In this case the vibration partition function is given by the well known formula

$$\begin{aligned} Z_v &= \sum_{v_1=0}^{\infty} \sum_{v_2=0}^{\infty} \sum_{v_3=0}^{\infty} \exp\{-[(v_1+\tfrac{1}{2})\hbar\omega_1 + (v_2+\tfrac{1}{2})\hbar\omega_2 + (v_3+\tfrac{1}{2})\hbar\omega_3]/kT\} \\ &= \exp[-\hbar(\omega_1+\omega_2+\omega_3)/2kT] \prod_{i=1}^{3} [1-\exp(-\hbar\omega_i/kT)]^{-1}, \end{aligned} \tag{11}$$

where ω_1, ω_2 and ω_3 represent the frequencies of the normal vibrations. If the vibrations are highly anharmonic, the vibrational levels can be calculated as indicated in part 3., and the vibration partition function is obtained then by a direct summation.

2.1.ii Spatially Degenerate Electronic States

Even in the case when the ground electronic state is a component of a spatially degenerate electronic state at the linear molecular geometry, no complications arise if the upper component is energetically well separated from the lower one at the ground state equilibrium geometry. The opposite case, in which the existence of the upper component state can not be neglected, has to be treated as described in part 2.2.ii.

2.2. Linear and Quasilinear Molecules

2.2.i Σ Electronic States

The calculation of the partition functions is again very simple if the excited electronic states are well separated from the ground state and if the harmonic approximation is applicable. Since one of the moments of inertia becomes zero at the linear nuclear arrangement, in linear molecules there are only two rotational degrees of freedom and the rotation energies and the corresponding partition functions are given by formulas (8 – 10).

Two of four vibrational degrees of freedom belong now to the two-dimensional bending representing one of the normal vibrational modes. The corresponding partition function can be obtained as the

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[*] Finally, one can try to treat a three-dimensional rotator as being composed of three mutually independent one-dimensional rotators. However, in this way the high-temperature expression $Z_{r_3} = 8\pi^3 (8\pi^3 I_a I_b I_c)^{1/2} (kT)^{3/2} h^{-3}$ is obtained, differing by the factor π from that derived from (5).

product of two expressions for the one-dimensional oscillators with the same frequency or using the formula for the eigenvalues $E_{v_2} = (v+1)\hbar\omega$ and the degeneracy $g_v = v+1$ of the two-dimensional harmonic oscillator:

$$Q_{v_2} = \sum_{v=0}^{\infty} (v+1)\exp[-(v+1)\hbar\omega/kT] = \exp(-\hbar\omega/kT)[1-\exp(-\hbar\omega/kT)]^{-2}. \quad (12)$$

If the bending vibrations can not be considered as being harmonic, e.g. in quasilinear molecules*, the situation becomes more complicated. The degeneracy of bending energy levels is partly lifted – a level having the vibrational quantum number v is split into $v/2+1$ for even v, and $(v+1)/2$ levels for odd v-values, each one corresponding to a particular value of the (unsigned) vibrational quantum number $l = v, v-2, \ldots, 0$ or 1. All of these levels are twofold degenerate except those with $l = 0$. Molecules having linear or nearly linear equilibrium geometry, especially those containing hydrogen atoms, are nearly symmetric tops, and both of the approximations b) and c) from part 2.1.i can be applied in this case provided the rotations corresponding to the smallest moment of inertia (vanishing at linear geometry) are treated as the second component of the bending vibrations. However, in some cases (as e.g. in a treatment of the isomerization, when the conservation of the total angular momentum has to be taken into account) it is desirable to have the possibility to classify the states according to the values of the quantum number J – a basis for such a treatment ensures a (formal) separation of the symmetric top Hamiltonian into

$$H_r = \frac{J^2 - J_z^2}{2I_b} + \frac{J_z^2}{2I_a}, \quad (13)$$

whereby $I_a = 0$ at the linear geometry. The second term on the right-hand side of (13) can be comprehended as part of the bending Hamiltonian. The eigenvalues of the first term are

$$E_r = \frac{[J(J+1) - l^2]\hbar^2}{2I_b} \quad (14)$$

and are $(2J+1)\,g_l$ degenerate ($g_l = 1$ for $l = 0$, 2 for $l \neq 0$ and $|J| \geqq l$). Therefore, the bending-rotation energies are given by

$$E_{br} = E_b + \frac{[J(J+1) - l^2]\hbar^2}{2I_b}. \quad (15)$$

The calculation of the bending energies E_b is described elsewhere (see Part 3). If the bending vibrations are assumed to be harmonic and if $\hbar\omega \gg \hbar^2/2I_b$, the high-temperature approximation ($\hbar^2/2I_b \ll kT$) for the bending-rotation partition function is, as shown in the appendix,

$$Z_{br} \cong \frac{2I_b kT\exp(-\hbar\omega/kT)}{\hbar^2[1-\exp(-\hbar\omega/kT)]^2}, \quad (16)$$

i.e. it is equal to the product of the partition function of a two-dimensional harmonic oscillator (12) with the rotation partition function of a linear molecule (9).

2.2.ii Spatially Degenerate Electronic States

The most complicated case arises when the lowest electronic state is spatially degenerate, with both correlating species remaining during bending relatively close to one another. The Born-Oppenheimer approximation is then completely unapplicable because both component electronic states are strongly coupled with each other through the bending mode and the rotations around the a-axis. In case of a weak Renner-Teller effect, when both components retain linear equilibrium geometries, it is possible to calculate the position of the vibronic levels employing the formulas derived by Renner [1] by a perturbation approach. However, in general one or both electronic states in question may have nonlinear equilibrium geometry, and the vibronic energies have to be computed by a numerical [5] or a variational [6] solution of the Schrödinger equation. Accurate values of the corresponding partition function can (especially because of irregularities in the vicinity of the barrier towards linearity) generally be evaluated only by direct summing. The rotational contribution to the total partition function can be included employing the approach described in part 2.2.i) (15) but with the quantum number l replaced by $K = |l \pm \Lambda|$.

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* The anharmonicity of the stretching vibrations causes much less difficulties because the corresponding frequencies are normally relatively high, and consequently only the lowest-lying levels are populated – assuming separability of the stretching vibrations from others degrees of freedom, their contribution to the total partition function appears in form of a multiplicative factor.

3. Method for Calculation of Energy Levels

All the parameters used in the present paper for the evaluation of partition functions are obtained by employing the potential surfaces calculated by means of the ab initio MRD CI method developed by Buenker and Peyerimhoff [7]. Vibration energies are computed using the variational approach described in detail elsewhere [6, 8, 9]. In the treatment of the bending vibrations the large amplitude formalism developed by Bunker and coworkers [10, 11] is generally applied, but the corresponding Schrödinger equation is solved by diagonalization of the Hamiltonian in suitable bases, rather than numerically as proposed in [10, 11]. The treatment of the Renner-Teller effect is described extensively in papers [9] and [6].

4. Results

In this work we study in detail three molecules: HNF, NCO and BH_2, all of them having a ground electronic state of the $^2\Pi$ type, but characterized by different manifestations of the Renner-Teller effect. In the case of HNF both component electronic states are stabilized by bending and possess nonlinear equilibrium geometries; the upper potential surface for BH_2 and both surfaces for NCO have minima at the linear geometry.

4.1. HNF

An ab initio study of the two lowest lying electronic states of HNF ($\tilde{X}^2A''$, $\tilde{A}^2A'$) correlating at the linear nuclear arrangement with a $^2\Pi$ species has been reported in [12]. As a consequence of the large energy difference (of roughly 20 000 cm^{-1}) between the minima of the $\tilde{X}^2A''$ and A^2A' potential surfaces the existence of the upper electronic state can at all relevant temperatures be safely neglected in the evaluation of the partition function. Since the barrier to linearity for the ground state is even higher, the change of the vibrational structure in its vicinity does not influence the partition function. Since the spin-orbit splittings of the lowest vibrational levels are relatively small compared with the errors in the calculated vibrational frequencies* (which are generally of the order of 50 cm^{-1} for the bending and $100-200\ \mathrm{cm}^{-1}$ for the stretching vibrations – see Table 3 of [6]), and since furthermore the anharmonic effects at higher energies are effectively smothered by the factor $\exp(-E/kT)$, we find it quite justified to treat the vibrations in harmonic approximation, using the frequency values of $\omega_1 = 3200\ \mathrm{cm}^{-1}$, $\tilde{\omega}_2 = 1430\ \mathrm{cm}^{-1}$ and $\tilde{\omega}_3 = 1000\ \mathrm{cm}^{-1}$ obtained in [12].

HNF represents at its ground state equilibrium geometry, H–N = 1.95 au (1.03 Å), N–F 2.62 au (1.39 Å), ∢ HNF 101° [12, 6], an asymmetric top very close to a prolate symmetric top ($A = 17.92\ \mathrm{cm}^{-1}$, $B = 1.020\ \mathrm{cm}^{-1}$, $C = 0.965\ \mathrm{cm}^{-1}$). In this case we test the three ways of calculation of the rotation partition function described in 2.1.i. Fig. 1 shows the numbers of states up to a definite rotation energy as function of the rotation energy value. For convenience the energy region $0-500\ \mathrm{cm}^{-1}$ is divided into intervals of 10 cm^{-1}. No difference can be noted if the summation over the asymmetric top

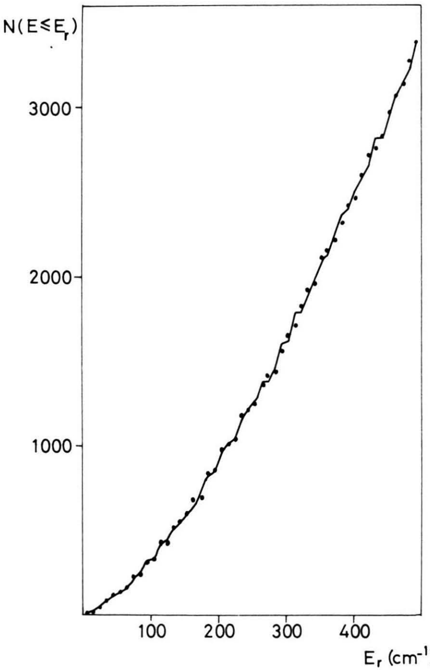

Fig. 1. Comparison of the results obtained for the rotation partition function of the HNF molecule using three approaches described in the text: i) by direct summing of exact asymmetric top energy levels (full lines) ii) in the symmetric top approximation (indistinguishable from i) at the scale of the picture) iii) in the two-dimensional plus one-dimensional rotator approximation (points).

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* In the present work we use the term "vibrational frequency" for both $\omega \sim E/\hbar$ (dimensional sec^{-1}) and $\tilde{\omega} \sim E/hc$ (dimension cm^{-1}).

eigenvalues is replaced by counting of the levels corresponding to the symmetric top with the moments of inertia I_a and $I_{bc} \equiv (I_b + I_c)/2$. The approximation of a two-dimensional plus a one-dimensional rotator with the moments of inertia I_a and I_{bc}, respectively, gives results which are only slightly different from those of the first two sets. Therefore, both of the mentioned approximations generate in the case of the hydrogen atom containing molecules excellent results. The speed of convergence towards the exact results depends, of course, on the temperature: at 273 K the values for Z_r of 1094.87, 1105.111 and 1105.114 are obtained for sums including all rotation levels up to $J = 30$, 50 and 60, respectively, (symmetric top approximation). At 1000 K full convergence is reached much more slowly (for $J = 30$, 50, 60, 80, 90, 100, $Z_r = 5534.86$, 7513.43, 7691.17, 7736.99, 7737.77 and 7737.84, respectively). The application of the high-temperature approximation is examined explicitly too. The results are in the whole temperature range considered (273 – 6000 K) very close to those obtained by direct summing. So e.g. at $T = 273$ K the classical approximation gives the value $Z_r = 1103$.

The partial sums of states for various degrees of freedom as well as the total partition function of HNF for temperatures between 273 and 6000 K are presented in Table 1.

4.2. NCO

NCO is in a sense oposite to HNF: both of its potential surfaces correlating with the lowest $^2\Pi$ electronic state have minima at the linear geometry. Because of that, not only both component electronic states must be included into the partition function, but also an explicit consideration of the vibronic coupling, as well as the interplay between the bending vibrations and the a-axis rotations has to be taken into consideration. Furthermore, the spin-orbit coupling causes in such a case dramatic effects: the splitting of the lowest levels for each $K \neq 0$ value ("unique levels" [5]) is exceptionally large, the spin-orbit pattern is generally very irregular for other vibronic levels and the effect dies away far above the minimum of the potential surfaces [13, 14].

In calculations of the partition function we assume that two of the rotational degrees of freedom can be separated from other motion modes. The corresponding sum of states is then calculated employing the formula for a two-dimensional rotator with equal moments of inertia assumed to remain constant during the vibrations. The bond lengths N–C = 1.25 Å, C–O = 1.18 Å, obtained in paper [14], are used. The stretching vibrations are also treated independently from other degrees of freedom. Their partition function is calculated in the harmonic approximation using the values of $\tilde{\omega}_1 = 1250\ \text{cm}^{-1}$ and $\tilde{\omega}_3 = 2000\ \text{cm}^{-1}$ [14].

The calculated vibronic energy scheme [14] is presented in Figure 2. It reflects the effects of the mentioned vibronic and spin-orbit couplings and differs from the more familiar picture which would

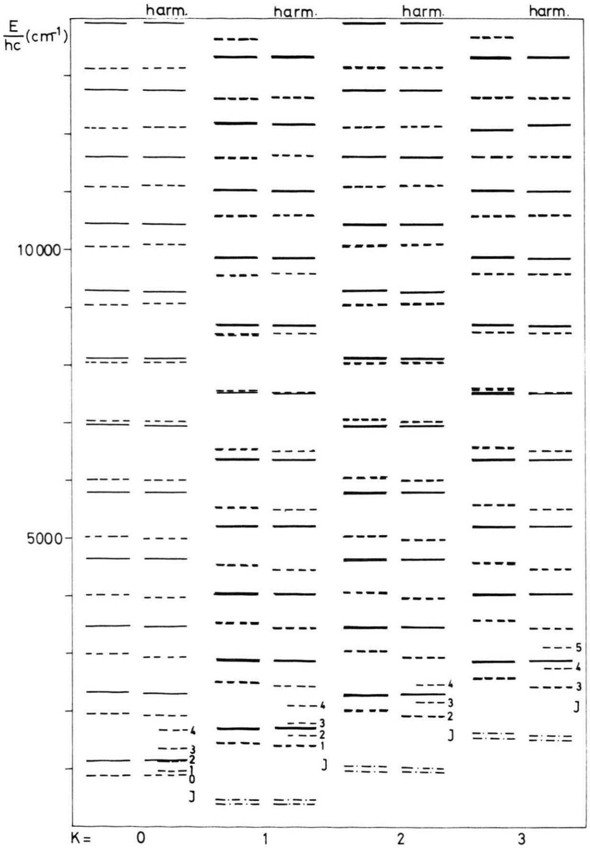

Fig. 2. Vibronic energy levels of the NCO molecule obtained by ab initio calculations [14]. - - - levels belonging predominantly to the lower electronic component; —— levels of the upper electronic state; –·–·– "unique levels". Spin-orbit splittings cannot be noted at the scale of the picture except for the lowest vibronic levels. Right columns: vibronic levels obtained in the harmonic approximation as described in the text. For the lowest lying vibronic species some rotational levels are also indicated, but with the spacing augmented by a factor of 100.

Table 1. Calculated internal partition functions (without the nuclear spin contribution) for the HNF molecule. Values for the rotation partition function are obtained in the high-temperature approximation, and the vibrations are assumed to be harmonic.

T	Z_r	Z_v	Z_{evr}
273	$1.103 \cdot 10^3$	1.006	$2.219 \cdot 10^3$
300	$1.271 \cdot 10^3$	1.006	$2.566 \cdot 10^3$
400	$1.957 \cdot 10^3$	1.034	$4.047 \cdot 10^3$
600	$3.595 \cdot 10^3$	1.137	$8.177 \cdot 10^3$
800	$5.534 \cdot 10^3$	1.302	$1.441 \cdot 10^4$
1000	$7.734 \cdot 10^3$	1.518	$2.347 \cdot 10^4$
2000	$2.188 \cdot 10^4$	3.371	$1.475 \cdot 10^5$
3000	$4.019 \cdot 10^4$	6.742	$5.419 \cdot 10^5$
4000	$6.187 \cdot 10^4$	12.040	$1.490 \cdot 10^6$
5000	$8.647 \cdot 10^4$	19.700	$3.407 \cdot 10^6$
6000	$1.137 \cdot 10^5$	30.156	$6.856 \cdot 10^6$

Table 2. Internal partition functions (Z_{evr}) for the NCO molecule calculated employing the ab initio results [14]. Sums of states for the rotations around the axes perpendicular to the molecular axis (Z_r^{bc}) are calculated in the high-temperature approximation and for the stretching vibrations (Z_{str}) assuming their harmonicity. The part of the partition function corresponding to the bending vibrations including the rotations around the a-axis, R^a_{rb}, is obtained using the approach described in the text. The total internal partition function calculated by employing the simplified approach, in which the splitting of the potential surfaces during the bending vibrations as well as the spin-orbit splitting is neglected, is also given (Z_{evr}^{harm}). The last colums represents the results of Rossi et al. [15] obtained using the experimentally derived data.

T	Z_r^{bc}	Z^a_{rb}	Z_{str}	Z_{evr}	Z_{evr}^{harm}	Z_{evr} [15]
273	496	3.718	1.001	$1.847 \cdot 10^3$	$2.233 \cdot 10^3$	
300	546	3.909	1.002	$2.137 \cdot 10^3$	$2.546 \cdot 10^3$	
400	727	4.718	1.011	$3.469 \cdot 10^3$	$3.984 \cdot 10^3$	
600	1091	6.804	1.061	$7.867 \cdot 10^3$	$8.704 \cdot 10^3$	
800	1455	9.469	1.150	$1.584 \cdot 10^4$	$1.714 \cdot 10^4$	
1000	1818	12.686	1.270	$2.930 \cdot 10^4$	$3.127 \cdot 10^4$	$3.137 \cdot 10^4$
2000	3637	36.806	2.210	$2.958 \cdot 10^5$	$3.056 \cdot 10^5$	$3.101 \cdot 10^5$
3000	5455	74.159	3.596	$1.455 \cdot 10^6$	$1.483 \cdot 10^6$	$1.513 \cdot 10^6$
4000	7273	124.700	5.383	$4.882 \cdot 10^6$	$4.942 \cdot 10^6$	$5.059 \cdot 10^6$
5000	9092	188.422	7.564	$1.296 \cdot 10^7$	$1.306 \cdot 10^7$	$1.339 \cdot 10^7$
6000	10910	265.319	10.135	$2.934 \cdot 10^7$	$2.947 \cdot 10^7$	$3.023 \cdot 10^7$

be obtained if the two potential surfaces were not interacting with one another. However, this scheme can in a good approximation be considered as being composed of three parts: i) "unique levels" (the lowest $K \neq 0$) ii) all other levels belonging predominantly to the lower potential surface (dashed lines) and iii) levels belonging to the upper surface (full lines). The situation is considerably simplified by the fact that both of these potential energy surfaces are very nearly harmonic – due to that the energy level schemes ii) and iii) are very similar to those of two two-dimensional harmonic oscillators with the frequencies found to be 510 cm^{-1} and 580 cm^{-1}, respectively (Fig. 2, right columns). Since the spin-orbit splittings for these vibronic levels do not exceed a few cm^{-1} the effect of the spin-orbit coupling can be taken into account simply by multiplying the sums of states with two. Therefore, the contribution of the levels ii) and iii) to the total partition function is

$$Z_b^{1,2} = 2 \exp(-E_0^{1,2}/kT)\,[1 - \exp(-\hbar\,\omega^{1,2}/kT)]^{-2} \tag{17}$$

with the $\omega^{1,2}$ values given above and $E_0^{1,2}$ representing the energies of the lowest members of both vibronic series with respect to the absolutely lowest vibronic level ($K = 1_{3/2}$) "unique level" taken as the zero-energy ($E_0^1/hc = 500$ cm^{-1}, $E_0^2/hc = 750$ cm^{-1}).

The "unique levels" themselves represent two series of levels ($\Sigma = \pm 1/2$) separated by ~ 80 cm^{-1}. The corresponding sums of states are those of two one-dimensional oscillators, multiplied with two because of the twofold spatial degeneracy of all $K \neq 0$ levels:

$$Z_b^{3,4} = 2 \exp(-E_0^{3,4}/kT)\,[1 - \exp(-\hbar\,\omega^{3,4}/kT)]^{-1} \tag{18}$$

with $E_0^3 = 0$ ($\Sigma = 1/2$) and $E_0^4/hc = 80$ cm^{-1} ($\Sigma = -1/2$ series) and $\tilde{\omega}^{3,4} = 545$ cm^{-1}. The total bending partition function is equal to the sum of four expressions (17) and (18).

The calculated partition functions for NCO are presented in Table 2. For comparison are also given the results obtained by a more simplified approach according to which both component potential surfaces of the $\tilde{X}^2\Pi$ state are assumed to coincide, having the common value for $\tilde{\omega}_2 = 545$ cm^{-1} ($= (510 + 580)/2$). The spin-orbit splitting is neglected in these calculations and the effects of both the spin-orbit and the spatial degeneracy are taken into account simply as multiplying factors. It can be seen that the disagreement between the two sets of results is ranging between 20% (at $T = 273$ K) and 0.5% (at $T = 6000$ K). On the other hand, the partition functions computed in this less sophisticated way are in very good agreement with those obtained by Rossi et al. [15] employing the same approach but using the experimentally derived data (Table 2, last column). This is not surprising since the agreement between the ab initio and the experimentally derived values for relevant molecular parameters is quite satisfactory in the case of NCO [14] – so e.g. the calculated value for $\tilde{\omega}_2$ is very close to that (539 cm^{-1} [16]) obtained by fitting of the observed band positions. Therefore it can be concluded that the mentioned not very large but significant discrepancies between the ab initio results for partition functions and those reported in [15] are caused by the oversimplified treatment of the Renner-Teller effect and the spin-orbit coupling in the latter work.

4.3. BH_2

In the BH_2 radical we have the third example of a manifestation of the Renner-Teller effect. In this case the lower component electronic state is moderately bent (131 ° [17]) with the barrier to linearity calculated from its lowest vibrational level of ~ 2000 cm^{-1}, whereas the upper potential surface has the minimum at the linear nuclear arrangement. Figure 3 shows the vibronic energy levels of $^{11}BH_2$ calculated employing the potential surfaces obtained by the MRD CI method with a large AO basis including *f*-functions [17, 18]. The observed band positions are also indicated [19]. The very scarce experimental data made a reproduction of the vibronic energy schema rather problematic, as shown in [17].

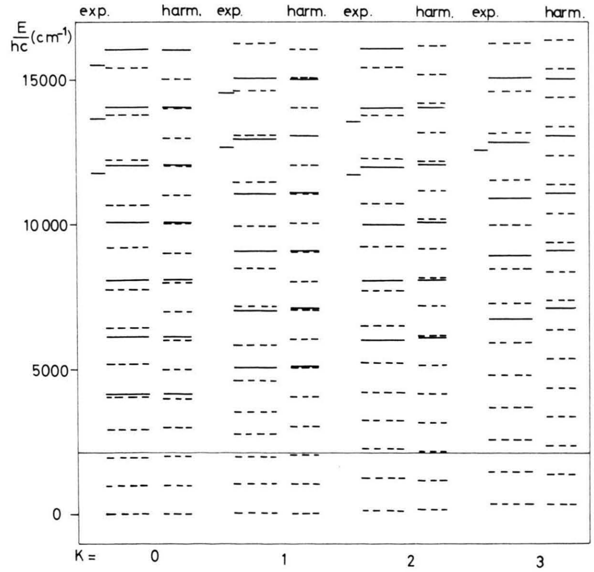

Fig. 3. Vibronic energy levels of BH_2 calculated by means of the MRD CI method [18]. Experimental results as well as the vibronic energy scheme obtained assuming harmonical vibrations are presented too. Dashed lines denote the levels belonging to the lower surface, full lines these of the upper electronic state.

Since the barrier to linearity is relatively low, the vibronic levels belonging to the lower surface can not be fitted successfully with the harmonic oscillator formula (Fig. 3, right columns, $\tilde{\omega}_2'' = 992\ cm^{-1}$) – above the barrier the spacing of the vibrational levels corresponding to the same *K*-value is significantly larger than below it. It is also impossible to reproduce by a simple formula the irregularities of the pattern of the vibronic energy levels in the vicinity of the barrier. The behaviour of the levels which can be attributed to the upper surface is quite regular and they can be fitted satisfactorily with the harmonic frequency of $2\tilde{\omega}_2' = 1984\ cm^{-1}$. However, it should be noted that the position of the lowest vibronic level ($K = 0$) of the upper electronic states lies at an energy corresponding to $\sim 2\tilde{\omega}_2'$ above the minimum of that surface.

The mentioned irregularities of the vibronic energy scheme reflect themselves in the calculated partition functions, especially at higher temperatures. So, e.g., the parts of the bending partition function corresponding to the $K = 0$ vibronic species at $T = 5000$ K calculated by direct summing are 3.747 for the lower component state and 0.698 for the upper state (without taking into account the spin degeneracy) – the corresponding values obtained in the harmonic approximation are 4.027 and 0.698, respectively. As expected the harmonic approximation does not work well for the lower electronic state, and the contribution of the upper state to the partition function is appreciable. The rotational contribution to the total sum states can in this case be evaluated for each state separately. The partial sums of states for the $K = 1$ bending levels calculated by explicite summing are 3.926 and 0.534 (without spin and *K* degeneracy) for the lower and the upper states, respectively, and 4.027 and 0.525 in harmonic approximation. It is interesting to note that the value corresponding to the lower component is for $K = 1$ somewhat larger than for $K = 0$ in spite of the fact that the lowest $K = 1$ level lies by 45 cm^{-1} above its $K = 0$ counterpart. This is the consequence of the rearranging of the vibronic energy scheme in the vicinity of the barrier to linearity, characteristic for the Renner-Teller effect [5]. On the other hand, the part of the partition function corresponding to the $K=1$ levels of the upper electronic state is smaller than for $K=0$ levels because the vibronic pattern is that of a linear molecule with the $K=1$ series beginning at an energy by $\hbar\omega_2'$ above the $K=0$ one. At lower temperatures the harmonic approximation works well – so e.g. at $T-1000$ K the values 1.318 and 0.00274 are obtained for the $K=0$ levels of the lower and the upper electronic states, respectively, by direct summing and 1.316 and 0.00274 in the harmonic approximation. The slightly smaller value for the sum of states of the lower surface obtained in the harmonic approximation is caused by the gradually decreasing spacing of the vibration levels in approaching the barrier to linearity. For $K=1$ the values of 1.242 and 0.000713 are obtained for the lower and the upper state, respectively. In this case the sum of the $K=1$ vibronic states for the lower electronic component is somewhat smaller than for $K=0$ as a consequence of the fact that the lowest lying levels contribute predominantly to the partition function.

5. Conclusion

It has been shown that ab initio calculations can be used for the evaluation of partition functions of small molecules. By this method

a) the required data for every molecule can in principle be obtained;

b) one gets a complete insight into the structure of the molecule in question which enables an estimation of the reliability of various approximations which can be performed in order to simplify the calculations.

Appendix

If the bending vibrations are harmonic, E_b in (15) is equal to $(v+1)\,\hbar\,\omega = (2\,n + l + 1)\,\hbar\,\omega$ with $n = 0, 1, 2, \ldots$. In this case the bending-rotation partition function is

$$Z_{b\mathrm{r}} = \sum_{l=0}^{\infty} \sum_{n=0}^{\infty} \sum_{|J|=l}^{\infty} g_l\,(2J+1)\exp\{-(2\,n+l+1)\,\hbar\,\omega + [J\,(J+1) - l^2]\,\hbar^2/2\,I_b\}/k\,T$$

$$\cong \sum_{l=0}^{\infty} g_l \exp[-(l\,\hbar\,\omega - l^2\,\hbar^2/2\,I_b)/k\,T] \sum_{n=0}^{\infty} \exp[-(2\,n+1)\,\hbar\,\omega/k\,T]$$

$$\cdot \int_{|J|=l}^{\infty} (2J+1)\exp[-J\,(J+1)\,\hbar^2/2\,I_b\,k\,T]\,\mathrm{d}J$$

$$= \frac{2\,k\,T\,I_b \exp(-\hbar\,\omega/k\,T)}{\hbar^2[1-\exp(-2\,\hbar\,\omega/k\,T)]}\,\frac{1+\exp[-(\hbar\,\omega + \hbar^2/2\,I_b)/k\,T]}{1-\exp[-(\hbar\,\omega + \hbar^2/2\,I_b)/k\,T]},$$

where the integration indicates that the high-temperature approximation is assumed. For the normal case when $\hbar\omega \gg \hbar^2/2\,I_b$ this expression becomes

$$Z_{br} \cong 2\,I_b k T \exp(-\hbar\,\omega/kT)/\hbar^2[1-\exp(-\hbar\,\omega/kT)]^2\,.$$

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