

CALCULATION OF PARTITION FUNCTIONS OF TETRA-ATOMIC MOLECULES

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Abstract

A calculation of partition functions of tetra-atomic molecules performed on the basis of the data obtained by means of the ab initio quantum mechanical method is proposed. The symmetry coordinates are used for partitioning the vibrational secular problem. The results for N_2H_2 and C_2H_2 molecules are presented. The accuracy is found to be comparable with those of results obtained using the experimentally derived structural parameters.

1. Introduction

In a former paper [1], the calculation of the partition functions of triatomic molecules using the data obtained by the ab initio calculations was considered. Special attention was paid to properly taking into account the consequences of the vibronic interaction in spatially degenerate ground electronic states. Furthermore, various approximative approaches for the computation of the rotational partition functions were analysed. It was shown that ab initio calculated partition functions were of approximately the same accuracy as those computed employing experimental (spectroscopic) data. In the present study, we extend these investigations to the class of tetra-atomic molecules. The conclusions made in [1] concerning the evaluation of the rotational partition functions are valid also for tetra-atomic molecules. On the other hand, the electronic–vibration interaction plays a much less important role in tetra-atomic molecules than in triatomic molecules because it is rarely significant, especially in the ground electronic states contributing predominantly to the total partition function. Instead, the calculation of the vibrational partition function is a much more difficult problem because of the fact that the number of vibrational degrees of freedom is six (seven for linear molecules). Therefore, even if we are satisfied with the harmonic approximation, the calculation of the fundamental frequencies, requiring as a first step a knowledge of a six-dimensional potential surface, can be connected with prohibitive computer time expenses. For example, if the number of points in one dimension is $n = 3-5$ (which represents a minimal requirement), the total number of potential energy points is roughly n^6 , i.e. at least a few hundred. Thus, it is imperative to find ways to substantially reduce computational requirements.

The most radical way to save computer time would consist of replacing the calculation of the six-dimensional potential surface by a computation of six one-dimensional potential curves.* If a vibrational frequency were calculated on the basis of the corresponding potential curve determined by 3–5 points, the total number of electronic energy calculations would be only about twenty. The problem is, however, that the various vibrational modes are generally coupled to each other, and that neglecting the coupling can cause serious errors in the computation of the vibrational frequencies and consequently of the partition function. It is well known that there exist so-called normal coordinates, in terms of which the vibrational Hamiltonian is represented in the harmonic approximation by a sum of mutually independent parts. Unfortunately, these coordinates are only exceptionally known in advance and normally a knowledge of the complete potential surface (at least in the vicinity of the energy minimum) is required for the determination. Thus, the normal coordinates cannot be used to avoid the calculation of this surface. However, another type of coordinates, the symmetry coordinates, may be used to achieve this aim. The symmetry coordinates transform according to particular irreducible representations of the molecular point group, as the normal coordinates do, but in contrast to the latter, their construction does not require any knowledge about the potential surface. Unfortunately, the symmetry coordinates do not enable a complete separation of the corresponding vibrational modes from each other, but instead they bring the vibrational secular equation into a quasi-diagonal form, the modes belonging to the same symmetry remaining interacting.

Let us illustrate the use of the vibrational symmetry coordinates by calculating the partition functions for the $A-B-B-A$ class of tetra-atomic molecules. As examples, we consider the diimide N_2H_2 and the acetylene C_2H_2 . We restrict ourselves to planar nuclear arrangements, sufficient for the discussion that follows. In fig. 1, a set of vibrational symmetry coordinates is presented for each of the three point groups of particular interest, $D_{\infty h}$, C_{2v} , and C_{2h} , and the correlation [3] between the corresponding species. Therefore, the six- (seven-)dimensional reducible representation of the molecular point group spanned by Cartesian nuclear displacement coordinates (after removing six (five) species corresponding to the translational and rotational motions) decomposes into $3A_1 + A_2 + 2B_2$ in the C_{2v} group, into $3A_g + A_u + 2B_u$ in C_{2h} , and into $2\Sigma_g^+ + \Sigma_u^+ + \Pi_g + \Pi_u$ for the linear equilibrium geometry. In this way, in the lower symmetries (C_{2v} , C_{2h}) we have to solve a 3×3 , a 1×1 and a 2×2 secular problem to calculate the harmonic vibrational frequencies; in $D_{\infty h}$ symmetry, various vibrational modes are almost completely decoupled from each other. The two bending modes, each one doubly degenerate in the linear geometry, correlate in the lower

*In this paper, we follow the classical way for computing the vibrational frequencies, based on differentiation of the potential energy surface/curves. It should be noted that it is possible to obtain the same quantities by direct analytical evaluation of the energy gradients on both the SCF and CI level of sophistication (see, for example, [2] and references therein).

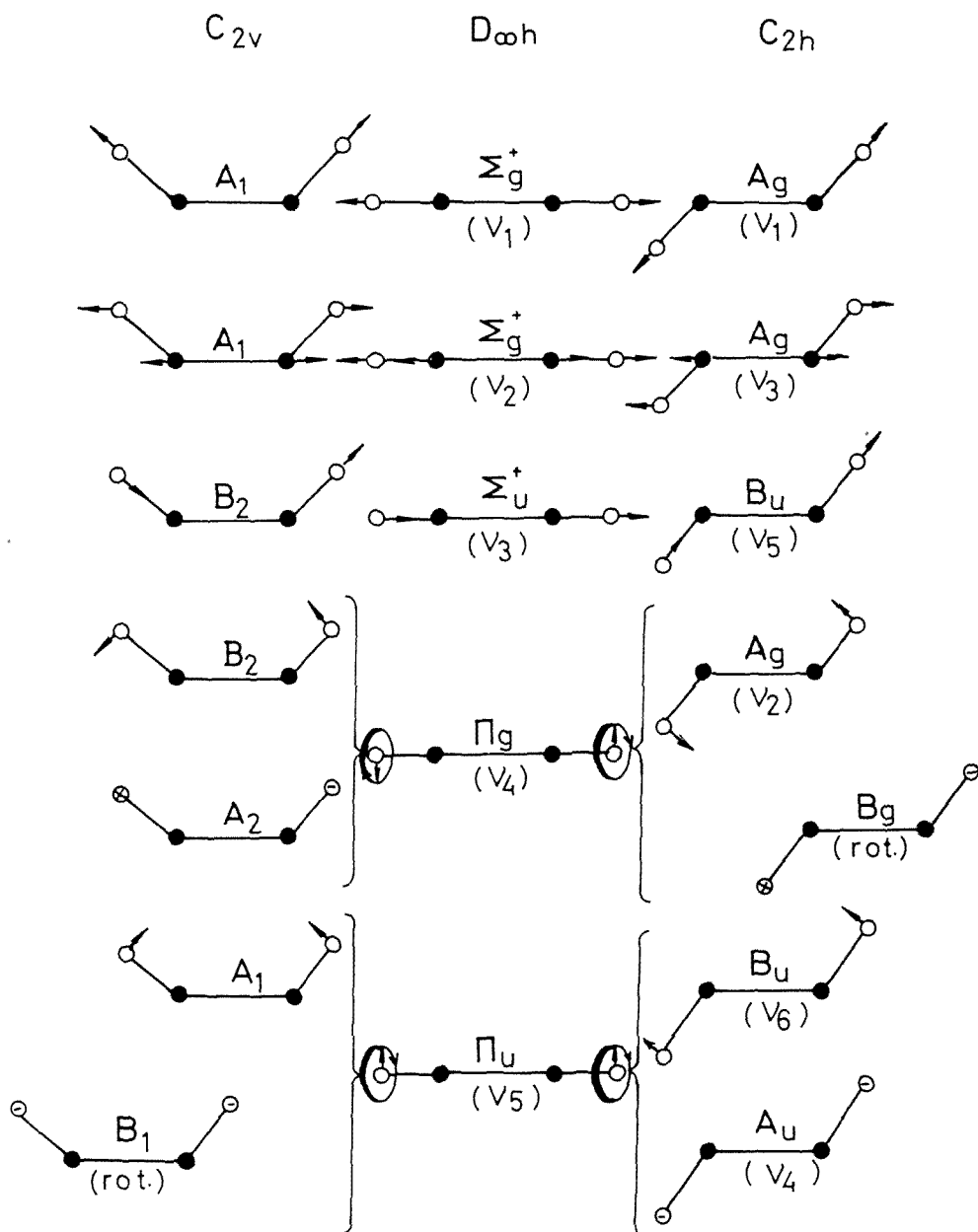


Fig. 1. Vibrational symmetry coordinates for $D_{\infty h}$, C_{2v} and C_{2h} point groups and the correlation between the corresponding species.

symmetries with two nondegenerate bending modes, a hindered rotational (torsional) motion and a free-rotational degree of freedom.

A general form of the vibration-rotation Hamiltonian for tetra-atomic molecules was published recently by Handy [4]. Restricting ourselves to the small amplitude vibrations of the $A-B-B-A$ molecules and introducing the symmetry coordinates:

$$\begin{array}{rcc}
 & C_{2v} & C_{2h} \\
 S_1 = \frac{r_1 + r_2}{2} & A_1 & A_g \\
 S_2 = \frac{\alpha_1 + \alpha_2}{2} & A_1 & A_g \\
 S_3 = R & A_1 & A_g \\
 S_4 = \frac{\phi}{2} & A_2 & A_u \\
 S_5 = \frac{r_1 - r_2}{2} & B_2 & B_u \\
 S_6 = \frac{\alpha_1 - \alpha_2}{2} & B_2 & B_u
 \end{array} \quad (1)$$

where r_1 and r_2 are the $A-B$ bond lengths, R is the $B-B$ distance, α_1 and α_2 are the angles between the $B-B$ and $A-B$ directions ($\alpha = \pi - \theta$ of ref. [4]) and ϕ is the torsional coordinate defined as the angle between the two ABB planes, we obtain the following expression for the vibrational kinetic energy operator:

$$\begin{aligned}
 -2T/\hbar = & \frac{1}{2} \left(\frac{1}{m} + \frac{1}{M} \right) \frac{\partial^2}{\partial S_1^2} + \frac{1}{2r_0^2} \left(\frac{1}{m} + \frac{1}{M} \right) \frac{\partial^2}{\partial S_2^2} + \frac{2}{M} \frac{\partial^2}{\partial S_3^2} \\
 & - \frac{2 \cos \alpha_0}{M} \frac{\partial^2}{\partial S_1 \partial S_3} + \frac{2 \sin \alpha_0}{Mr_0} \frac{\partial^2}{\partial S_2 \partial S_3} \\
 & + \frac{1}{2 \sin^2 \alpha_0} \left[\left(\frac{1}{m} + \frac{1}{M} \right) \frac{1}{r_0^2} + \frac{4 \cos \alpha_0}{MR_0} \left(\frac{\cos \alpha_0}{R_0} + \frac{1}{r_0} \right) \right] \frac{\partial^2}{\partial S_4^2} \\
 & + \frac{1}{2} \left(\frac{1}{m} + \frac{1}{M} \right) \frac{\partial^2}{\partial S_5^2} + \left[\left(\frac{1}{m} + \frac{1}{M} \right) \frac{1}{2r_0^2} + \frac{2}{MR_0} \left(\frac{1}{R_0} + \frac{\cos \alpha_0}{r_0} \right) \right] \frac{\partial^2}{\partial S_6^2} \\
 & + \frac{2 \sin \alpha_0}{MR_0} \frac{\partial^2}{\partial S_5 \partial S_6}; \quad (C_{2v})
 \end{aligned} \quad (2a)$$

$$\begin{aligned}
 -2T/\hbar = & \frac{1}{2} \left(\frac{1}{m} + \frac{1}{M} \right) \frac{\partial^2}{\partial S_1^2} + \left[\left(\frac{1}{m} + \frac{1}{M} \right) \frac{1}{2r_0^2} + \frac{2}{MR_0} \left(\frac{1}{R_0} + \frac{\cos \alpha_0}{r_0} \right) \right] \frac{\partial^2}{\partial S_2^2} \\
 & + \frac{2}{M} \frac{\partial^2}{\partial S_3^2} + \frac{2 \sin \alpha_0}{MR_0} \frac{\partial^2}{\partial S_1 \partial S_2} - \frac{2 \cos \alpha_0}{M} \frac{\partial^2}{\partial S_1 \partial S_3} + \frac{2 \sin \alpha_0}{Mr_0} \frac{\partial^2}{\partial S_2 \partial S_3} \\
 & + \frac{1}{2 \sin^2 \alpha_0} \left(\frac{1}{m} + \frac{1}{M} \right) \frac{1}{r_0^2} \frac{\partial^2}{\partial S_4^2} \\
 & + \frac{1}{2} \left(\frac{1}{m} + \frac{1}{M} \right) \frac{\partial^2}{\partial S_5^2} + \left(\frac{1}{m} + \frac{1}{M} \right) \frac{1}{2r_0^2} \frac{\partial^2}{\partial S_6^2}. \quad (C_{2h}) \quad (2b)
 \end{aligned}$$

In these equations, r_0 ($= r_{10} = r_{20}$), α_0 ($= \alpha_{10} = \alpha_{20}$) and R_0 represent the equilibrium values for the $A-B$ distance, the $A-B-B$ bond angles, and the $B-B$ bond length, respectively. The equilibrium value of the torsional coordinate is set equal to zero (planar geometry). The mass of nucleus A is denoted by m , and that of nucleus B by M . The terms (2a,b) represent the elements of the commonly used G -matrix [5]. For a linear geometry $\alpha_0 = 0$, and the single cross term is $(-2/M)\partial^2/\partial S_1 \partial S_3$, representing the coupling of the two Σ_g^+ species. The classical expressions for T in the velocity form T_c , which we use for the calculation of the harmonic vibrational frequencies, are obtained by inverting the matrices (2a,b). For the C_{2h} case, one obtains:

$$\begin{aligned}
 2T_c = & \left(2m - \frac{m^2 R_0^2 \sin^2 \alpha_0}{2a} \right) \dot{S}_1^2 + \frac{m r_0^2 R_0^2 (M + m \sin^2 \alpha_0)}{2a} \dot{S}_2^2 \\
 & + \left(\frac{m + M}{2} - \frac{m^2 r_0^2 \sin^2 \alpha_0}{2a} \right) \dot{S}_3^2 - \frac{m^2 r_0 R_0 \sin \alpha_0 (2r_0 + R_0 \cos \alpha_0)}{a} \dot{S}_1 \dot{S}_2 \\
 & + \left(2m \cos \alpha_0 + \frac{m^2 r_0 R_0 \sin^2 \alpha_0}{a} \right) \dot{S}_1 \dot{S}_3 \\
 & + \left[\frac{m^2 r_0^2 \sin \alpha_0 (2r_0 + R_0 \cos \alpha_0)}{a} - 2m r_0 \sin \alpha_0 \right] \dot{S}_2 \dot{S}_3 \\
 & + \frac{2m M r_0^2 \sin^2 \alpha_0}{m + M} \dot{S}_4^2 + \frac{2m M}{m + M} \dot{S}_5^2 + \frac{2m M r_0^2}{m + M} \dot{S}_6^2, \quad (3)
 \end{aligned}$$

where $a \equiv 1/4(m + M)R_0^2 + mr_0^2 + mr_0 R_0 \cos \alpha_0$. The vibrational frequencies are computed by solving the equation $|V_{ij} - \omega^2 T_{ij}| = 0$, where V_{ij} are the coefficients in the expression for the harmonic potential

$$V = \frac{1}{2} \sum_i \sum_j V_{ij} S_i S_j \quad (4)$$

and are assumed to be obtained by fitting of potential surfaces calculated by means of the ab initio approach.

2. N₂H₂

As the first example, we consider the diimide molecule N₂H₂. It is now well established that it possesses in the ground electronic state ¹A_g a planar equilibrium geometry with a trans position of the hydrogen nuclei. The energy minimum of the corresponding cis structure lies, according to SCF calculations [6], roughly 0.5 eV above the absolute minimum of the trans configuration and might contribute to the molecular partition at high temperatures; however, since the potential barrier to the isomerization via torsion is high (several eV), in (thermo-)dynamical problems trans- and cis-diimide should be considered as two distinct molecular species. On the other hand, the lowest excited electronic state ¹B_g lies roughly 2.5 eV above the ground state, and its contribution to the partition function can safely be ignored.

The equilibrium geometry parameters and the harmonic force field for the electronic ground state of N₂H₂ calculated by means of the ab initio MRDCI method [7,8] are presented in table 1. On the basis of these data and using the formulae (3), the vibrational frequencies given in table 2 are obtained by solution of a 3 × 3, a 1 × 1 and a 2 × 2 secular equation corresponding to the A_g, A_u and B_u symmetries [8]. A comparison with the corresponding experimental data shows that the calculation error (except in the case of torsional vibration, where the experimental result is not quite reliable) is generally below 5%. Presented in the same table are also the results obtained by means of the rather rough approximation of mutually independent vibrations corresponding to the adopted internal coordinates [7]; in that case, the discrepancies between the calculated and experimentally determined vibrational frequencies are much larger (up to 20%). It should be noted that the force constants of the corresponding one-dimensional potential curves generally do not have the same values as the diagonal terms in table 1.

The vibrational partition functions for different temperatures (500–6000 K), calculated employing the three sets of vibrational frequencies given in table 2, are presented in table 3. The contribution due to the torsional mode is omitted. Validity of the harmonic approximation is assumed, and the partition function is thus calculated by means of the formula

$$Z_v = \prod_i [1 - \exp(-h\nu_i/kT)]^{-1}.$$

Agreement between the ab initio results and those obtained by means of the experimentally derived data is better than 5% at 2000 K and better than 10% at very

Table 1

The equilibrium geometry parameters and the harmonic force field for the electronic ground state of N_2H_2 , calculated by means of the ab initio MRDCI method [7, 8]

r_0 [bohr]	1.897
R_0 [bohr]	2.506
a_0 [degree]	71.36
V_{11} [hartree bohr ⁻²]	0.6895
V_{22} [hartree radian ⁻²]	0.5738
V_{33} [hartree bohr ⁻²]	0.7019
V_{12} [hartree bohr ⁻¹ radian ⁻¹]	-0.0018
V_{13} [hartree bohr ⁻²]	0.1944
V_{23} [hartree bohr ⁻¹ radian ⁻¹]	-0.1907
V_{44} [hartree radian ⁻²]	0.50
V_{55} [hartree bohr ⁻²]	0.7210
V_{66} [hartree radian ⁻²]	0.3501
V_{56} [hartree bohr ⁻¹ radian ⁻¹]	0.00

Table 2

Vibrational frequencies of the ground state of N_2H_2 . Presented are the results of the ab initio calculations in which the coupling between the modes corresponding to various internal coordinates is completely neglected, third column [7]; in the next column are given the results of a calculation where the complete vibrational space is partitioned into its symmetry subspaces [8]; the last column [9, 10] represents experimentally derived data

Vibrational modes	Symmetry	$\tilde{\nu}$ [cm ⁻¹]		
		[7]	[8]	exp, [9, 10]
S_1 (NH_s)	A_g	3467	3115	3128
S_2 (α_s)	A_g	1465	1630	1583
S_3 (NN)	A_g	1566	1452	1529
S_4 (torsion)	A_u	1476	1476	1286 [11]
S_5 (NH_a)	B_u	3086	3183	3131
S_6 (α_a)	B_u	1039	1169	1286

high temperature, 5000 K. The discrepancies are larger by roughly a factor of two if the coupling between the various internal coordinates is neglected in the theoretical treatment.

The computation of the rotational partition functions does not pose any serious problem. Since on the one hand the ab initio calculations give accurate geometry parameters and on the other hand the coupling between the rotations and the vibrational

Table 3

Vibrational partition functions of N_2H_2 molecules at different temperatures calculated by means of three sets of vibrational frequencies given in table 2. The contribution due to torsional mode is omitted

T [K]	Ab initio without coupling	Ab initio	Exp.
500	1.08	1.06	1.05
1000	1.67	1.55	1.52
2000	5.28	4.89	4.56
3000	15.27	14.11	13.01
4000	38.05	35.14	32.22
5000	83.47	77.10	70.44
6000	165.63	155.08	139.50

and/or electronic motions is not significant in the present case, the agreement of the results for Z_{rot} generated by the ab initio calculations and by the experimentally derived data must be very good, provided the same level of sophistication has been applied in both cases by calculation of the rotation energy levels and by summing over them [1].

3. C_2H_2

The acetylene molecule is linear in its ground electronic state $^1\Sigma_g^+$. All other electronic states are well separated from the ground state and thus can be ignored in calculating the partition function. Because the ground state is nondegenerate, there are no complications due to the vibronic interaction. However, one of the principal moments of inertia vanishes at the equilibrium (linear) geometry so that there remain only two rotational degrees of freedom, while the number of vibrational modes becomes seven. If the symmetry vibrational coordinates are employed, only two species belonging to the Σ_g^+ irreducible representation remain coupled. Two bending species Π_g and Π_u are doubly degenerated (fig. 1).

The Hamiltonian derived by Handy [4] can be used also for the description of molecules having linear equilibrium geometries. However, because of the fact that one of the rotational degrees of freedom (rotation around the axis corresponding to the smallest moment of inertia, becoming in the linear geometry the molecular axis) becomes the second component of a doubly degenerate bending mode, the corresponding part of the kinetic energy operator has to be included in the vibration Hamiltonian. The other degenerate mode is built by the other bending distortion and the torsion, transforming gradually into free rotation as the molecule approaches the linear geometry. Thus, the Hamiltonian for small amplitude vibrations around a linear geometry has the form:

$$\begin{aligned}
 -2T/\hbar = & \frac{1}{2} \left(\frac{1}{m} + \frac{1}{M} \right) \frac{\partial^2}{\partial S_1^2} + \frac{2}{M} \frac{\partial^2}{\partial S_2^2} - \frac{2}{M} \frac{\partial^2}{\partial S_1 \partial S_2} + \frac{1}{2} \left(\frac{1}{m} + \frac{1}{M} \right) \frac{\partial^2}{\partial S_3^2} \\
 & + \frac{MR_0^2 + m(R_0 + 2r_0)^2}{2mMr_0^2R_0^2} \left(\frac{\partial^2}{\partial S_4^2} + \frac{1}{S_4} \frac{\partial}{\partial S_4} + \frac{1}{S_4^2} \frac{\partial^2}{\partial \chi_1^2} \right) \\
 & + \frac{1}{2r_0^2} \left(\frac{1}{m} + \frac{1}{M} \right) \left(\frac{\partial^2}{\partial S_5^2} + \frac{1}{S_5} \frac{\partial}{\partial S_5} + \frac{1}{S_5^2} \frac{\partial^2}{\partial \chi_2^2} \right). \tag{5}
 \end{aligned}$$

The symmetry coordinates are those indicated in the middle of fig. 1. χ_1 and χ_2 are the coordinates correlating with the a -axis rotation and the torsion in nonlinear geometries, respectively. The integration volume element is assumed to be $dV = S_4 S_5 dS_1 dS_2 dS_3 dS_4 d\chi_1 d\chi_2$.

The frequencies for all the vibrational modes except for the antisymmetric stretching Σ_u^+ , were calculated by means of the ab initio MRDCI method by Perić et al. [12]. The results are presented in table 4, together with the corresponding

Table 4

Equilibrium bond lengths and vibrational frequencies for the ground state of C_2H_2 . Ab initio results are given in the third column [12]. The last column [13] represents experimentally derived data

Structural parameter	Symmetry	[12]	[13] exp.
C-H [bohr]		2.041	1.999
C-C [bohr]		2.321	2.283
$\tilde{\nu}_1$ [cm^{-1}]	Σ_g^+	3400	3372.5
$\tilde{\nu}_2$ [cm^{-1}]	Σ_g^+	2000	1973.5
$\tilde{\nu}_3$ [cm^{-1}]	Σ_u^+	–	3294.85
$\tilde{\nu}_4$ [cm^{-1}]	Π_g	590	611.70
$\tilde{\nu}_5$ [cm^{-1}]	Π_u	700	729.15

experimental findings. The vibrational part of the partition function is given in the harmonic approximation by the formula:

$$\begin{aligned}
 Z_v = & \prod_{i=1}^3 [1 - \exp(-h\nu_i/kT)]^{-1} \times [1 - \exp(-h\nu_4/kT)]^{-2} \\
 & \times [1 - \exp(-h\nu_5/kT)]^{-2}, \tag{6}
 \end{aligned}$$

the last two terms representing the sums of states for the two doubly degenerate bending-type vibrations. The rotational partition function in the classical high-temperature approximation is

$$Z_r = \frac{2IkT}{h^2}, \quad (7)$$

where $I = 1/2[MR_0^2 + m(R_0 + 2r_0)^2]$.

The results of the calculation of the partition functions for acetylene obtained by means of the ab initio and the experimentally derived data from table 4 are given in table 5. Since the vibrational frequency ν_3 has not been calculated in [12], in the evaluation of Z (ab initio) $\tilde{\nu}_3 = 3295 \text{ cm}^{-1}$ (experimental value) is used. In the case

Table 5

Vibrational partition functions of C_2H_2 at different temperatures calculated by means of the ab initio and the experimentally derived data given in table 4

T [K]	Ab initio	Exp.
500	2.00	1.90
1000	8.17	7.47
2000	84.60	75.60
3000	514.00	456.10
4000	2196.59	1942.39
5000	7368	6502
6000	20742	18281

of this molecule, the discrepancies in the vibrational partition functions are 12–13%. The moment of inertia calculated using the ab initio values for the internuclear distances from table 4 is 96577 a.u. The corresponding experimentally derived value is 93242 a.u. The rotational partition functions calculated by means of these values show the same discrepancy (3.5%) because of the linear dependence on I .

4. Conclusion

In this paper, we discuss two ways of calculating the vibrational partition functions of tetra-atomic molecules by means of the ab initio quantum mechanical method. The first approach is based on the use of symmetry coordinates, while in the second, appropriate internal coordinates are used whereby the coupling between various vibrational modes is entirely neglected. Both approaches are motivated by the need to reduce computational requirements, especially those caused by the calculation of multidimensional potential surfaces. Molecules of the type

$A-B-B-A$ in $D_{\infty h}$, C_{2h} and C_{2v} symmetry arrangements are considered, and the results for N_2H_2 and C_2H_2 are presented. It is shown that the maximal discrepancies between the ab initio results generated by the first approach and their counterparts in which the experimentally derived data (vibrational frequencies) are employed are roughly 10% in the temperature range up to 5000 K. Thus, it can be concluded that the ab initio calculated partition functions are of satisfactory reliability for all practical purposes. It should be stressed that in the more complicated example (N_2H_2 , C_{2h} geometry), only about twenty-five potential surface points have been computed. On the other hand, neglecting the coupling between various vibrational modes, as in the second approach, represents a rather rough approximation. The main advantage of using the results of theoretical ab initio calculations for the computation of partition functions is that experimental values for all the structural parameters needed are known very rarely.

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