

THE SPECTROSCOPIC CONSTANTS AND THE PARTITION FUNCTIONS OF THE ELECTRONIC AND INTERNAL ENERGIES OF THE TiO MOLECULE

BY W. ŻYRNICKI AND A. CZERNICHOWSKI

Institute of Inorganic Chemistry and Rare Elements Metallurgy, Wrocław Technical University*

(Received July 7, 1970)

This work gives the values of the partition functions of the electronic and internal energies of the TiO molecule in the temperature range from 4,000 to 10,000°K. The TiO molecule is treated as a nonrigid rotator and anharmonic oscillator. The calculations took account of all the known electronic states (from spectroscopic observations and theoretical deliberations). Some of the spectroscopic constants of the TiO molecule are compared and analysed.

Introduction

In recent years more and more efforts have been expended on technological and physico-chemical research conducted at high temperatures with utilization of thermal plasma.

When determining the temperature of the plasma, the concentration of plasma components and the oscillator power, it is necessary to know a quantity known as the sum over states or partition function (of internal, electronic, vibrational and rotational energies). Knowledge of the internal partition function and its derivatives enables calculation of the thermodynamic functions.

The error made in determinations of the physico-chemical quantities just mentioned depends to a large extent on the accuracy with the spectroscopic constants (electronic energy vibration and rotation constants), used in calculations, are determined. Information on the spectroscopic constants of a very many molecules, including TiO, is still highly unsatisfactory. A number of constants are unknown, while some of those which are, in the light of new research, require correction.

The internal partition functions of heteronuclear diatomic molecule

Assuming that energy levels of electronic, vibrational and rotational states are independent of one another, we can write the partition function of the internal energy of a diatomic molecule, Q_{int} , in the form

$$Q_{int} = Q_{sym} Q_{nuc} Q_{el} Q_{vib} Q_{rot} \quad (1)$$

* Address: Politechnika Wroclawska, Wrocław, Wybrzeże Wyspiańskiego 27, Poland.

Q_{sym} denotes the symmetry number (for heteronuclear molecules $Q_{\text{sym}} = 1$). Q_{nuc} is the nuclear spin statistical weight or partition function related to the rotational motion of the nuclei, and is expressed as:

$$Q_{\text{nuc}} = g_{j1}g_{j2} = (2I_1+1) \cdot (2I_2+1) \quad (2)$$

where g_{j1} , g_{j2} and I_1 , I_2 are the respective statistical weights and spin quantum numbers of the nuclei 1 and 2. Q_{el} is the electronic partition function, which is expressed by the formula

$$Q_{\text{el}} = \sum_i g_e^{(i)} \cdot \exp \left[- \frac{hc}{kT} \cdot T_e^{(i)} \right] \quad (3)$$

where $g_e^{(i)}$ and $T_e^{(i)}$ are the statistical weight and energy of the i -th electronic state, h , c , k are universal constants, and T is temperature in degrees Kelvin. Q_{vib} is the vibrational partition function, described by the equation

$$Q_{\text{vib}} = \sum_v g_v \cdot \exp \left[- \frac{hc}{kT} \cdot G(v) \right] \quad (4)$$

where v is the vibrational quantum number, g_v is the statistical weight of the given vibrational level (in the case of diatomic molecules $g_v = 1$ for each of the vibrational levels), and $G(v)$ is the vibrational energy of the molecule. Q_{rot} is the rotational partition function, given by the formula

$$Q_{\text{rot}} = \sum_J g_{\text{rot}} \cdot \exp \left(- \frac{hc}{kT} \cdot F(J) \right) \quad (5)$$

where J is the rotational quantum number, $F(J)$ is rotational energy, and g_{rot} is the statistical weight of the rotational level, equal to

$$g_{\text{rot}} = 2J+1. \quad (6)$$

Some spectroscopic researchers lump the rotational motion of the nuclei together with molecular rotation. In this case

$$g_{\text{rot}} = (2J+1) \cdot (2I_1+1) \cdot (2I_2+1). \quad (7)$$

Since the vibrational energy depends on electronic state, and the rotational energy on the electron-vibrational state, we cannot use formula (1) in more precise calculations, but

$$Q_{\text{int}} = Q_{\text{sym}} \cdot Q_j \cdot \sum_i \sum_v \sum_J g_e^{(i)} \cdot 2J+1 \exp \left\{ - \frac{hc}{kT} [T_e^{(i)} + G^{(i)}(v) + F^{(i,v)}(J)] \right\}. \quad (8)$$

The electronic energy levels of a molecule are usually known with satisfactory accuracy. The vibrational and rotational energies, mathematically described by means of series, are functions of the quantum numbers v and J , respectively. For metal oxides the vibrational

constants ω_e and $\omega_e x_e$ and rotational constants B_e , α_e and D_e (or D_0) are usually attainable. The values of other coefficients in the expressions for the vibrational and rotational energies are known sporadically, but even then in most cases they are just estimates.

In statistical calculations the energies of electronic, vibrational and rotational states are taken relative to the lowest energy value, conventionally assumed to be equal zero. In calculations of the internal partition function the authors used the following formulae for the vibrational and rotational energies

$$G_0(v) = \omega_0 v - \omega_0 x_0 v^2 \quad (9)$$

$$\omega_0 = \omega_e - \omega_e x_e \quad (9a)$$

$$\omega_0 x_0 = \omega_e x_e \quad (9b)$$

where ω_e and ω_0 are the frequencies of the oscillator in the equilibrium and zero point and x_e and x_0 are the first anharmonicity constants in the equilibrium and zero point, and

$$F_v(J) = B_v \cdot J(J+1) - D \cdot J^2(J+1)^2 \quad (10)$$

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2} \right). \quad (10a)$$

Calculations made here make use of the assumption that the constant D is independent of v (Eq. (10)), for in practice this does not affect the results of calculations. The values of D_e were used when those of D_0 were unknown. In actual fact, there is a dependence, namely,

$$D_v = D_e - \beta_e \left(v + \frac{1}{2} \right). \quad (10b)$$

Equation (10) describes the rotational energy of the $d^1 \sum$ state ($A=0$), A being the quantum number of the component of the electronic orbital angular momentum along the internuclear axis. For singlet states with $A \neq 0$ the equation for the rotational energy has the form

$$F(J) = B_v J(J+1) - D_v J^2(J+1)^2 + \dots + (A - B_v) A^2. \quad (10c)$$

The rotation constant A is

$$A = \frac{h}{8\pi^2 c I_A} \quad (10d)$$

where I_A is the moment of inertia of the electrons along the internuclear axis. The expression $(A - B_v) A^2$ is usually included in the electronic energy of the molecule.

The energy of rotation of the triplet state, being an intermediate case between Hund's a and b cases, is described by the formulae given by Budó [1]

$$F_v^{(1)}(J) = B_v J(J+1) - D_v J^2(J+1)^2 - B_v \left\{ [y_1 + 4J(J+1)]^{1/2} + \frac{2}{3} \frac{y_2 - 2J(J+1)}{y_1 + 4J(J+1)} \right\}$$

$$F_v^{(2)}(J) = B_v J(J+1) - D_v J^2(J+1)^2 + B_v \frac{4}{3} \frac{y_2 - 2J(J+1)}{y_1 + 4J(J+1)} \quad (11)$$

$$F_v^{(3)}(J) = B_v J(J+1) - D_v J^2(J+1)^2 + B_v \left\{ [y_1 + 4J(J+1)]^{1/2} - \frac{2}{3} \frac{y_2 - 2J(J+1)}{y_1 + 4J(J+1)} \right\}$$

$$y_1 = A^2 Y(Y-4) + \frac{4}{3}$$

$$y_2 = A^2 Y(Y-1) - \frac{4}{9} \quad (11a)$$

$$Y = A/B_v \quad (11b)$$

where A is the so called interaction (splitting or coupling) constant. The product associated with the rotational constant D may have a somewhat different form. This has no practical significance, for the contribution of this expression in the value of energy is minute and energy, comes to light only at high J values for which

$$D_v \left(J - \frac{1}{2} \right)^4 \approx D_v J^2(J+1)^2$$

$$D_v \left(J + \frac{1}{2} \right)^4 \approx D_v J^2(J+1)^2$$

$$D_v \left(J + \frac{3}{2} \right)^4 \approx D_v J^2(J+1)^2. \quad (11c)$$

Summation limits

The values of the internal partition function depend on the limits of summation. In approximate calculations summation is over the limits $v = 0$ to ∞ and $J = 0$ to ∞ . In some simplified methods of calculating Q_{int} (Gordon-Barnes), summation takes place from $J = 0$ to $J = \infty$ and from $v = 0$ to $v = v_{\text{max}}$, where v_{max} is the actual maximum vibrational quantum number for the given electronic state. If Eq. (9) describes the vibrational energy, v_{max} may be determined from the formula

$$v_{\text{max}} = \frac{\omega_e^2}{2\omega_e x_e} - \frac{1}{2}. \quad (12)$$

In actual molecules the maximum rotational quantum number J_{max} is also finite. It is a function of the quantum number v . In the first approximation we can assume that the sum of rotational and vibrational energies is constant and equal to the dissociation energy D_{dis} (for a given electronic state) of the molecule,

$$F(J) + G(v) = D_{\text{dis}}. \quad (13)$$

From this relation it is possible to determine J_{max} for the individual values of v . To determine J_{max} as a function of v accurately an analysis must be made of the vibration-rotation potential curves, which may be defined, following [2], as

$$V(r, J) = D_{\text{dis}} \cdot \left\{ 1 - \exp \left[- \frac{\omega_e}{2\sqrt{B_e \cdot D_{\text{dis}}}} \left(\frac{r}{r_e} - 1 \right) \right] \right\}^2 + \frac{B_e J^2(J+1)}{r^2} - \frac{D_e r^6 J^2(J+1)^2}{r^6}. \quad (14)$$

Here, r denotes the internuclear distance (r_e is the equilibrium internuclear distance). The J_{\max} defined in this way is for small v higher than that calculated from relation (13) by 30 to 40 per cent.

When calculating the internal partition function the authors summed over v from $v = 0$ to $v = v_{\max}$ (determined from Eq. (12)) and over J from $J = 0$ to $J = J_{\max}$ (determined by vibration-rotation potential curves analysis). In principle, summation should begin from $J = \Lambda$ for singlet states and $J = \Omega$ for degenerate states, but the error caused by summation from $J = 0$ bears no practical effect on the calculated value.

Spectroscopic constants of the TiO molecule

In TiO there are singlet and triplet electronic states. In the energy range up to 20,000 cm^{-1} experiments have revealed the existence four singlet and four triplet electronic states. No forbidden transitions between the singlet and triplet states have been observed. Three systems of singlet bands and three systems of triplet bands resulting from the transitions between the appropriate electron-vibration-rotation states have been identified. These are:

orange	$c^1\Phi - a^1\Delta$	blue-green	$C^3\Phi - X^3\Delta$
infrared	$b^1\pi - a^1\Delta$	orange-red	$B^3\pi - X^3\Delta$
infrared	$b^1\pi - d^1\Sigma^+$	red	$A^3\Phi - X^3\Delta$

Phillips [3] has shown that the triplet state is the ground state of the TiO molecule, and he found the energy of the $a^1\Delta$ state relative to the $X^3\Delta$ state to be equal to 581 cm^{-1} .

The $b^1\pi - d^1\Sigma^+$ system was investigated by Petterson and Lindgren [4] and Petterson [5], who determined the electronic transition energy $\nu_e = 9106.4 \text{ cm}^{-1}$ and the constants ω_e , $\omega_e x_e$, B_e , D_e , α_e of these states. They determined $\omega_e - 2\omega_e x_e$ experimentally and calculated the values of $\omega_e x_e$ from Pekeris' formula [6].

The authors of the present work, analyzing the $b^1\pi - a^1\Delta$ system on the basis of data in Refs [7], [8], [9], [10] and [11], determined the electronic transition energy $\nu_e = 11,322.4 \text{ cm}^{-1}$ and vibrational constants for the $b^1\pi$ and $a^1\Delta$ states, which are $\omega'_e = 918.8 \text{ cm}^{-1}$, $\omega'_e x'_e = 3.8 \text{ cm}^{-1}$ and $\omega''_e = 1018.4 \text{ cm}^{-1}$, $\omega''_e x''_e = 4.5 \text{ cm}^{-1}$, respectively. From an analysis of the positions of the R and Q heads of the orange β system, quoted in Refs [9] and [11], we obtained:

$$\nu_e(c^1\Phi - a^1\Delta) = 17,890.5 \text{ cm}^{-1}, \quad \omega''_e - \omega'_e = 99.5 \text{ cm}^{-1}, \quad \omega'_e x'_e - \omega''_e x''_e = 0.36 \text{ cm}^{-1}.$$

The energy of the $c^1\Phi$ state is

$$T_e(c^1\Phi) = T_e(a^1\Delta) + \nu_e(c^1\Phi - a^1\Delta) = 18,471.5 \text{ cm}^{-1}. \quad (15)$$

On the basis of the R heads determined for the identified vibration-rotation bands of the $b^1\pi - a^1\Delta$ system, Lockwood [10] proposed the acceptance, in first approximation, of the values $\nu_e = 11,332.4 \text{ cm}^{-1}$, $\omega''_e = 1015.8 \text{ cm}^{-1}$ and $\omega'_e x'_e = \omega''_e x''_e = 4 \text{ cm}^{-1}$. The value of electronic transition energy that Lockwood determined is lagerr than the actual value of ν_e by the distance between the R head and the center of the band (10 to 13 Å).

Linton and Nicholls [12] determined the positions of new bands of the $c^1\Phi - a^1\Delta$ system. Assuming that the R and Q heads for the $\Delta v = v' - v'' = 0$ and $\Delta v = 1$ sequences are separated by a constant value of 19 cm^{-1} , they obtained for $c^1\Phi$ and $a^1\Delta$ the values $\omega'_e = 916.7 \text{ cm}^{-1}$, $\omega'_e x'_e = 4.33 \text{ cm}^{-1}$ and $\omega''_e = 1016.3 \text{ cm}^{-1}$, $\omega''_e x''_e = 3.93 \text{ cm}^{-1}$, respectively, and $T_e(c^1\Phi) = 18,471.5 \text{ cm}^{-1}$.

In actual fact the distance between the positions of the R and Q heads (in practice, the band center) is different not only for every sequence of a given system of bands, but also varies (however slightly) within the sequence itself. For bands of the $\Delta v = 1$ sequence of the $c^1\Phi - a^1\Delta$ system this distance is about 15 cm^{-1} . If the position of the R heads are known, it is possible to calculate the position of the Q heads from

$$v_{vv}(Q) - v_{vv}(R) = -\frac{(B_{v''} + B_v)^2}{4(B_{v''} - B_v)}. \quad (16)$$

A difficulty in making an accurate determination of the Q head position on the basis of Eq. (16) is the ignorance of the quantity α_e for the $c^1\Phi$ and $a^1\Delta$ states. In the present work an estimated $\alpha_e = 0.003$ was accepted for these states.

Basing on Refs [6] to [11], the authors propose the following vibrational constants:

$c^1\Phi$	$\omega_e = 919.2 \text{ cm}^{-1}$	$\omega_e x_e = 4.6 \text{ cm}^{-1}$
$b^1\pi$	$\omega_e = 918.8 \text{ cm}^{-1}$	$\omega_e x_e = 3.7 \text{ cm}^{-1}$
$a^1\Delta$	$\omega_e = 1018.3 \text{ cm}^{-1}$	$\omega_e x_e = 4.3 \text{ cm}^{-1}$.

Calculations made use of the positions of the Q heads found by means of Eq. (16). The authors believe the electronic energies of the $b^1\pi$ and $d^1\Sigma^+$ states quoted in the literature to be erroneous. The energy of the $b^1\pi$ electronic state is

$$T_e(b^1\pi) = T_e(a^1\Delta) + v_e(b^1\pi - a^1\Delta) = 11,903.4 \text{ cm}^{-1} \quad (17)$$

and the $d^1\Sigma^+$ state

$$T_e(d^1\Sigma^+) = T_e(a^1\Delta) + v_e(b^1\pi - a^1\Delta) - v_e(b^1\pi - d^1\Sigma) = 2.797 \text{ cm}^{-1}. \quad (18)$$

Phillips [13] analyzed the vibration states of the $\gamma'(B^3\pi - X^3\Delta)$ system of bands and the rotational states of the (0,0) band. He proposed the following formula for the position of R heads of the γ' system of vibration-rotation bands:

$$v_{vv}(R) = \frac{16,309}{16,162} + 862 \left(v' + \frac{1}{2} \right) - 1.0 \left(v' + \frac{1}{2} \right)^2 - 1014 \left(v'' + \frac{1}{2} \right) + 2.5 \left(v'' + \frac{1}{2} \right)^3. \quad (19)$$

The present authors believe that a critical view must be taken of Phillips formula. The γ' system is formed as a result of transitions to the ground state (this is corroborated by the determined rotational constants, though the vibrational constants for the lower state contradict this). For given v' and v'' the equation (19) is not satisfied by all three heads of the band under consideration. Some of the bands probably come from other systems (this is also considered by Phillips). Making a selection from among the bands given

by Phillips (the criterion was the distance between the individual R heads at fixed v' and v''), the authors propose in first approximation for the $B^3\pi$ state $T_e = 16,220 \text{ cm}^{-1}$, $\omega_e = 873 \text{ cm}^{-1}$ and $\omega_e x_e = 4.5 \text{ cm}^{-1}$.

The value of the rotational constant $D(D_0)$ for the $c^1\Phi$ state, proposed by Phillips [9], seems to be too low, and the authors submit the value of $D(D_e)$ as calculated from the formula

$$D_e = \frac{4B_e^3}{\omega_e^2}. \quad (20)$$

In this way $D(D_e)$ can be determined relatively accurately, for this formula expresses the relation between D_e , B_e and ω_e well, and the error of B_e and ω_e determination is small. The conformity between the experimental values of D with those calculated from Eq. (20) for other states of TiO is very good.

In calculating the partition function the largest contribution to the calculated value is given by the ground state. The ground state of the TiO molecule is the triplet $X^3\Delta$. It becomes split into $^3\Delta_3$, $^3\Delta_2$ and $^3\Delta_1$. Taking the energy of the lowest sublevel, $^3\Delta_1$, to be zero, the authors calculated the energies of the higher sublevels from the equation for the triplet state. They are 102.5 cm^{-1} and 204.0 cm^{-1} , respectively. These values are different than those given by Herzberg [14].

The spectroscopic constants for eight states of the TiO molecule are arranged in Table I. The authors preferred the experimental values of $\omega_e x_e$ to values calculated from Pekeris' formula.

TABLE I

Spectroscopic constants of TiO molecule

i	State	g_e	T_e [cm^{-1}]	Ref.	ω_e [cm^{-1}]	$\omega_e x_e$ [cm^{-1}]	Ref.	B_e [cm^{-1}]	Ref.	α_e [cm^{-1}]	Ref.	D_e [cm^{-1}]	Ref.
1	$X^3\Delta$	6	0		1008.6	4.61	[14]	0.5355	[17]	0.00303	[15]	$0.61 \cdot 10^{-6}$	[18]
	$^3\Delta_1$	2	0										
	$^3\Delta_2$	2	102.5	A									
	$^3\Delta_3$	2	204.0	A									
2	$a^1\Delta$	2	581	[3]	1018.3	4.3	A	0.5377 0.5362(o)	A [8]	0.003	A	$0.63 \cdot 10^{-6}(o)$	[9]
3	$d^1\Sigma^+$	1	2797	A	1023.8	4.64	[4]	0.5490	[4]	0.00337	[4]	$0.62 \cdot 10^{-6}(o)$	[4]
4	$b^1\pi$	2	11903.4	A	918.8	3.7	[4]	0.5134(c)	[4]	0.00293(c)	[4]	$0.70 \cdot 10^{-6}(o)$	[4]
								0.5132(d)	[4]	0.0028(d)	[4]		
5	$A^3\Phi$	6	14163.1	[17]	866.3	3.83	[14]	0.5074	[17]	0.00318	[17]	$0.70 \cdot 10^{-6}$	[17]
6	$B^3\pi$	6	16220	A	873	4.5	A	0.5080	A	0.003	A	$0.70 \cdot 10^{-6}(o)$	[13]
								0.5065(o)	[13]				
7	$c^1\Phi$	2	18471.5	[12]	919.2	4.6	A	0.5227	A	0.003	A	$0.67 \cdot 10^{-6}$	A
								0.5212(o)	[9]				
8	$C^3\Delta$	6	19430.4	[19]	837.9	4.55	[18]	0.4889	[14]	0.0029	[14]	$0.67 \cdot 10^{-6}$	[18]

The reference (Ref.) denotes the source of the quoted value A — these authors' proposal, (o) — experimental value of constant at $v = 0$, (c) and (d) — for $^1\pi c$ and $^1\pi d$ states, respectively

A number of new states are to be expected in addition to those whose existence has been confirmed by spectroscopic observations. At higher temperatures they contribute considerably to the partition function. These states, and their presumptive energies are quoted from Ref. [15] in Table II.

TABLE II
Unobserved electronic states of TiO molecule and their energies

i	State	g_e	T_e cm ⁻¹
9	³ π	6	9 000
10	³ Σ^+	3	13 000
11	¹ Σ^+	1	15 000
12	¹ π	2	19 000
13	¹ Δ	2	22 000
14	³ π	6	22 000
15	¹ π	2	25 000
16	³ Φ	6	25 000
17	³ π	6	29 000
18	¹ Φ	2	30 000
19	¹ π	2	33 000

Lately, Pathak and Palmer [16] observed the emission spectrum of TiO in the UV range. This spectrum consists of systems of bands due to transitions from the high-energy states (of electronic energies over 30,000 cm⁻¹). The share of these states in the electronic or internal energy partition functions at temperatures up to 10,000°K is very small.

Partition functions

In order to simplify the complicated computations, the electronic energies of the sublevels of the $X^3\Delta$ state were determined by means of Eqs (11), (11a) and (11b). Calculations of the internal partition function employed the expressions (10) and (10a) for the rotational energy. The error caused by this simplification is insignificant.

The electronic energy of the excited electronic states was increased (because of the splitting structure of the $X^3\Delta$ state) by the difference in energy of the ³ Δ_1 and ³ Δ levels. Since the excited triplet states of the TiO molecule lie high, their splitting was neglected in the calculations.

The vibration and rotation constants for the states given in Table II are unknown. Therefore, to each of these states the authors of this paper assigned values of vibration-rotation partition function which are the arithmetic mean of these functions known for the eight states. The vibration-rotation partition function for a given electronic state was defined by the equation

$$Q_{\text{vib. rot.}}^{(i)} = \sum_n \sum_J (2J+1) \cdot \exp \left\{ - \frac{hc}{kT} [G_0^{(i)}(v) + F^{(i,v)}(J)] \right\} \quad (21)$$

TABLE III

Electronic partition function

<i>i</i>	State	$T(^{\circ}\text{K})$	4 000	4 500	5 000	5 500	6 000	6 500	7 000	7 500	8 000	8 500	9 000	9 500	10 000
1	$X^3\Delta$		5.786	5.809	5.828	5.843	5.856	5.868	5.878	5.885	5.893	5.900	5.906	5.911	5.916
2	$a^1\Delta$		1.564	1.607	1.643	1.673	1.698	1.720	1.739	1.755	1.769	1.782	1.794	1.804	1.813
3	$d^1\Sigma^+$		0.353	0.396	0.435	0.469	0.499	0.527	0.551	0.574	0.594	0.612	0.629	0.645	0.659
4	$b^1\pi$		0.027	0.043	0.063	0.087	0.112	0.140	0.170	0.200	0.231	0.262	0.294	0.325	0.356
5	$A^3\Phi$		0.036	0.063	0.099	0.144	0.196	0.255	0.320	0.389	0.462	0.537	0.614	0.692	0.771
6	$B^3\pi$		0.017	0.032	0.054	0.083	0.119	0.160	0.208	0.260	0.316	0.376	0.438	0.503	0.570
7	$c^1\Phi$		0.003	0.005	0.010	0.016	0.023	0.033	0.044	0.057	0.071	0.086	0.103	0.120	0.138
8	$C^3\Delta$		0.005	0.012	0.022	0.036	0.056	0.080	0.108	0.142	0.179	0.220	0.264	0.312	0.361
$\sum_{i=1}^8 g_e^{(i)} \cdot \exp\left(-\frac{hc}{KT} T_e^{(i)}\right)$			7.791	7.967	8.154	8.351	8.559	8.783	9.018	9.262	9.515	9.775	10.042	10.312	10.584
9	$^3\pi$		0.227	0.327	0.437	0.556	0.677	0.801	0.925	1.048	1.169	1.286	1.400	1.513	1.621
10	$^3\Sigma^+$		0.027	0.045	0.069	0.098	0.130	0.165	0.203	0.243	0.284	0.327	0.370	0.413	0.455
11	$^1\Sigma^+$		0.004	0.008	0.013	0.019	0.027	0.035	0.045	0.055	0.066	0.078	0.090	0.102	0.114
12	$^1\pi$		0.002	0.004	0.008	0.013	0.021	0.029	0.039	0.051	0.064	0.079	0.094	0.111	0.128
13	$^1\Delta$		0.001	0.002	0.003	0.006	0.010	0.015	0.021	0.029	0.038	0.048	0.058	0.071	0.083
14	$^3\pi$		0.002	0.005	0.010	0.019	0.030	0.045	0.064	0.086	0.113	0.143	0.175	0.212	0.250
15	$^1\pi$		0.000	0.001	0.001	0.003	0.005	0.008	0.011	0.016	0.022	0.029	0.036	0.044	0.054
16	$^3\Phi$		0.001	0.002	0.004	0.008	0.014	0.023	0.034	0.049	0.066	0.086	0.109	0.133	0.162
17	$^3\pi$		0.000	0.001	0.001	0.003	0.005	0.010	0.015	0.023	0.032	0.043	0.057	0.073	0.091
18	$^1\Phi$		0.000	0.000	0.000	0.001	0.001	0.003	0.004	0.006	0.009	0.012	0.016	0.021	0.026
19	$^1\pi$		0.000	0.000	0.000	0.000	0.004	0.001	0.002	0.003	0.005	0.007	0.010	0.013	0.017
$\sum_{i=9}^{19} g_e^{(i)} \exp\left(-\frac{hc}{KT} T_e^{(i)}\right)$			0.264	0.395	0.546	0.726	0.924	1.135	1.363	1.609	1.868	2.138	2.415	2.706	3.001
Q_{e1}			8.055	8.362	8.700	9.077	9.483	9.918	10.381	10.871	11.383	11.913	12.457	13.018	13.585

TABLE IV

Internal partition function $Q_{\text{int}} \cdot 10^4$

<i>i</i>	State	<i>T</i> (°K)												
		4 000	4 500	5 000	5 500	6 000	6 500	7 000	7 500	8 000	8 500	9 000	9 500	10 000
1	X^3A	10.45	13.14	16.15	19.52	23.23	27.31	31.76	36.59	41.81	47.44	53.47	59.91	66.77
2	a^1A	2.78	3.58	4.48	5.49	6.61	7.84	9.20	10.68	12.28	14.01	15.87	17.85	19.97
3	$d^1\Sigma^+$	0.61	0.86	1.16	1.51	1.91	2.36	2.87	3.43	4.06	4.74	5.49	6.30	7.17
4	$b^1\Pi$	0.05	0.11	0.20	0.33	0.51	0.74	1.04	1.42	1.87	2.40	3.03	3.75	4.58
5	$A^3\Phi$	0.08	0.17	0.33	0.59	0.96	1.47	2.15	3.01	4.09	5.41	6.98	8.83	10.96
6	$B^3\Pi$	0.04	0.09	0.18	0.34	0.58	0.92	1.39	2.01	2.80	3.78	4.97	6.39	8.05
7	$c^1\Phi$	0.00	0.01	0.03	0.06	0.10	0.17	0.27	0.40	0.58	0.80	1.07	1.40	1.79
8	C^3A	0.01	0.03	0.08	0.16	0.30	0.50	0.79	1.20	1.73	2.42	3.28	4.32	5.58
$\sum_{i=1}^8 \mathcal{E}_e^{(i)} \exp\left(-\frac{hc}{KT} \cdot T_e^{(i)}\right) \cdot Q_{\text{vib, rot}}^{(i)}$		14.02	17.99	22.61	28.00	34.20	41.31	49.47	58.74	69.22	81.00	94.16	108.75	124.87
$\sum_{i=9}^{19} \mathcal{E}_e^{(i)} \exp\left(-\frac{hc}{KT} \cdot T_e^{(i)}\right) \cdot Q_{\text{vib, rot}}^{(i)}$		0.53	1.00	1.70	2.73	4.14	5.97	8.34	11.35	15.06	19.55	24.87	31.22	38.55
Q_{int}		14.55	18.99	24.31	30.73	38.34	47.28	57.81	70.09	84.28	100.55	119.03	139.97	163.42

The results of calculations of the electronic and internal partition functions are assembled in Tables III and IV.

The error with which these values are determined is rather difficult to establish. According to the authors, it should not exceed 3 per cent for the electronic partition function and 5 per cent for the internal partition function (this was found on the basis of an estimate of the accuracy of spectroscopic constant determination).

The authors thank Docent A. Bartecki for discussions and critical comments.

REFERENCES

- [1] A. Budo, *Z. Phys.*, **96**, 219 (1935).
- [2] *Termodinamicheskie svoystva individualnykh veshchestv*, Izd. AN SSSR, Moscow 1962.
- [3] J. G. Phillips, *Astrophys. J.*, **115**, 567 (1952).
- [4] V. A. Petterson, B. Lindgren, *Ark. Fys.*, **22**, 491 (1962).
- [5] V. A. Petterson, *Ark. Fys.*, **16**, 185 (1959).
- [6] C. L. Pekeris, *Phys. Rev.*, **45**, 98 (1934).
- [7] K. Wurm, H. J. Meister, *Z. Astrophys.*, **13**, 199 (1937).
- [8] C. C. Kiess, information passed on to J. G. Phillips, who published it [9].
- [9] J. G. Phillips, *Astrophys. J.*, **111**, 314 (1950).
- [10] G. W. Lockwood, *Astrophys. J.*, **157**, 449 (1969).
- [11] F. Lowater, *Proc. Phys. Soc.*, **41**, 557 (1929).
- [12] C. Linton, R. W. Nicholls, *J. Phys.*, **B2**, 490 (1969).
- [13] J. G. Phillips, *Astrophys. J.*, **157**, 449 (1969).
- [14] G. Herzberg, *Molecular Spectra and Molecular Structure* (I), D. Van Nostrand, Princeton (New Jersey) 1950.
- [15] L. Brewer, D. W. Green, *High Temp. Sci.*, **1**, 26 (1969).
- [16] C. N. Pathak, H. B. Palmer, *J. Mol. Spectrosc.*, **33**, 137 (1970).
- [17] J. G. Phillips, *Astrophys. J.*, **114**, 151 (1951).
- [18] A. Christy, *Phys. Rev.*, **33**, 701 (1929).
- [19] K. D. Carlson, R. K. Nesbet, *J. Chem. Phys.*, **41**, 1051 (1964).