

# High-Temperature Thermodynamic Properties of Mars-Atmosphere Components

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**Methods of calculation of high-temperature thermodynamic properties for some selected Mars-atmosphere components in the temperature range from 200 to 50,000 K and results are discussed and compared with previous works. Aspects such as quasi-bound rotational states, cutoff criteria, and autoionizing states are considered.**

## Nomenclature

$a_{ij}$	= stoichiometric coefficient for the formation reaction of the $i$ th species
$C_{\text{int},p}$	= internal specific heat
$C_p$	= total specific heat
$c$	= speed of light
$D_e$	= dissociation energy
$E_i$	= ionization energy
$E_{\text{int}}$	= internal energy
$E_n$	= energy of the $n$ th quantum level
$F_v$	= rotational energy (polyatomic molecules)
$G$	= Gibbs free energy
$G_0(v_1, \dots)$	= vibrational energy of the state $(v_1, v_2, \dots, v_m)$
$g_n$	= statistical weight of the $n$ th quantum level
$H_i$	= molar enthalpy of the $i$ th species
$h$	= Planck constant
$I_A, I_B, I_C$	= moments of inertia
$J$	= rotational quantum number
$k_B$	= Boltzmann constant
$m_i$	= mass of the $i$ th species
$n$	= principal quantum number
$p_i$	= statistical weight of the $i$ th electronic states (polyatomic molecules)
$p_v$	= statistical weight of the state $(v_1, v_2, \dots, v_m)$
$Q_{\text{h.o.}}$	= partition function for the harmonic oscillator (polyatomic molecules)
$Q_i$	= total partition function of the $i$ th species
$Q_{\text{int},i}$	= internal partition function of the $i$ th species
$Q_{\text{r.r.}}$	= partition function for the rigid rotator (polyatomic molecules)
$Q_{\text{tr},i}$	= translational partition function of the $i$ th species

$R$	= universal gas constant
$R_y$	= Rydberg constant
$R_y^*$	= modified Rydberg constant
$r_e$	= equilibrium distance
$S$	= entropy
$T$	= temperature
$T_0^{(i)}$	= excitation energy of the $i$ th electronic states (polyatomic molecules)
$V$	= volume
$v$	= vibrational quantum number
$\Delta E_i$	= lowering of the ionization potential
$\Delta H_{f,i}$	= variation of the enthalpy for the formation of the $i$ th species
$\mu$	= reduced mass
$\sigma$	= symmetry factor
$\omega_n$	= frequency of the $n$ th vibrational mode (polyatomic molecules)

## I. Introduction

**F**UTURE missions to Mars foresee hypersonic entries into and aerobraking maneuvers through the atmosphere of that planet. Heatshield design will require the high-speed aerodynamics analysis of spacecraft configurations. In this regard, the availability of accurate thermodynamic properties of the chemical constituents that may exist in the flow field during hypersonic flight is mandatory. The literature offers basically a few main sources: the JANAF tables,<sup>1</sup> the table series from NASA,<sup>2,3</sup> and the impressive tabulation edited by Gurvich et al.<sup>4</sup> The JANAF tables are limited to 6000 K; Gurvich et al.'s tables and the recent tables from NASA reach 20,000 K. Concerning molecular components, all tabulations can be considered in satisfactory agreement up to 6000 K. However, atomic components and their ions are not dealt with the same accuracy because the number of energy levels included in the calculation of electronic partition functions is not sufficient. Even the old tables produced by Browne<sup>5</sup> qualify for better accuracy with regard to this aspect, although this author included only the observed energy levels as published by Moore.<sup>6</sup> Moreover, the problems connected with the divergence of internal partition functions and related to the completion of the energy-level set were not dealt with adequately.

In this paper, we present a new calculation of the thermodynamic properties of Mars-atmosphere components from 200 to 50,000 K, carried out with the purpose of dealing with the aforementioned problem in an accurate as possible manner. In particular, the problem of the energy-level completion will be confronted by avoiding the hydrogenic approximation recently used by Wang and Rhodes<sup>7</sup> for the calculation of air-component thermodynamic properties. In addition, the thermodynamic properties produced in this work are

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meant to constitute the platform to support the development of a high-temperature gas-mixture thermodynamic model of Mars atmosphere suitable for implementation in hypersonic flowfield solvers.

## II. Method of Calculation

### A. Partition Function

The thermodynamic properties of high-temperature gas mixtures can be obtained if the partition functions of single components are known. In general, the partition function can be factorized as the product of the translational  $Q_{tr,i}$  and the internal  $Q_{int,i}$  contributions

$$Q_i = Q_{tr,i} Q_{int,i} \quad (1)$$

The translational partition function is available in analytical form

$$Q_{tr,i} = \left(2\pi m_i k_B T / h^2\right)^{3/2} V \quad (2)$$

The internal partition function can be written in general terms as

$$Q_{int,i} = \sum_n g_n \exp\left(-\frac{E_n}{k_B T}\right) \quad (3)$$

Equation (3) assumes different explicit forms for atoms and for molecules.

### B. Internal Partition Function of Atomic Components

For an isolated atom, an infinite number of bound states exists below the ionization limit. Then, the internal partition function is the sum over the infinite electronic levels

$$Q_{int} = \sum_n g_n \exp\left(-\frac{E_n}{k_B T}\right) \quad (4)$$

However, the sum in Eq. (4) diverges because the statistical weight is not bound when the principal quantum number increases ( $n \rightarrow \infty$ ) indefinitely. For example,  $g_n = 2n^2$  for atomic hydrogen. Thus, the summation in Eq. (4) must be adequately truncated. Unfortunately, there is no universal cutoff criterion. Reviews<sup>4,8</sup> of various cutoff methods can be found in the literature. The existing cutoff criteria yield partition functions and their derivatives that depend on either the electron density or the gas pressure. This means that the thermodynamic properties of the components depend not only on the temperature but also on the pressure. In particular we refer to Griem's criterion,<sup>9</sup> according to which the ionization energy of an atom in the presence of other components is lowered by a factor that, in general, depends on the number of charged particles. All the levels the energies of which are lower than the corrected ionization potential are accounted for in the sum (4); that is, we sum up to the last energy level that arises from the limitation

$$E_n \leq E_i - \Delta E_i \quad (5)$$

In our calculations  $\Delta E_i$  is set as a parameter, and results are reported for various  $\Delta E_i$  values. In addition to the divergence problem, there is also the issue of including only experimentally observed energy levels or also adding the theoretically predicted levels. Tabulations<sup>6,10</sup> are available that provide energies and statistical weights for many experimentally observed levels. Nonetheless, supplementing that information with semiempirical laws is a useful way to obtain the missing energy levels. Exact quantum-mechanical calculations for high-lying levels, that is, near the continuum limit, although possible, are still a prohibitive task.

### C. Thermodynamic Properties

From the partition functions and their first and second derivatives, we can calculate all the thermodynamic properties of the components according to the formulas of statistical thermodynamics.<sup>11</sup>

The Helmholtz potential, the internal contribution  $E_{int}$  to the thermodynamic energy, the entropy, and the internal constant-pressure specific heat  $C_{int,p}$  are obtained, respectively, from

$$F - H(0) = -RT \ln Q \quad (6)$$

$$E_{int} = RT^2 \left( \frac{\partial \ln Q_{int}}{\partial T} \right)_v \quad (7)$$

$$U - H(0) = E_{int} + \frac{3}{2} RT \quad (8)$$

$$S = R \ln Q + \frac{RT}{Q} \left( \frac{\partial Q}{\partial T} \right) \quad (9)$$

$$C_{int,p} = R \left[ 2T \left( \frac{\partial \ln Q_{int}}{\partial T} \right)_v + T^2 \left( \frac{\partial^2 \ln Q_{int}}{\partial T^2} \right)_v \right] \quad (10)$$

The total specific heat is obtained by adding the translational contribution

$$C_p = C_{int,p} + \frac{5}{2} R \quad (11)$$

The enthalpy is given by

$$H - H(0) = E_{int} + \frac{5}{2} RT \quad (12)$$

The Gibbs free energy is calculated from the entropy and the enthalpy as

$$G - H(0) = -RT \ln Q + RT \quad (13)$$

The Helmholtz potential, the internal contribution to the thermodynamic energy, and the internal constant-pressure specific heat strongly depend on the assumed sets of energy levels and adopted cut-off criterion.

Finally, we calculate the formation enthalpy of the component under consideration from

$$\Delta H_{f,i} = H_i - \sum_j a_{ij} H_j \quad (14)$$

where  $H_i$ ,  $H_j$  are given in Eq. (12) and the sum runs on all the forming reactants. For example, for  $N$  formation

$$\frac{1}{2} N_2 \rightarrow N \quad (15)$$

the formation enthalpy is given by

$$\Delta H_{f,N}(T) = D/2 + [H(T) - H(0)]_N - \frac{1}{2} [H(T) - H(0)]_{N_2} \quad (16)$$

### D. Internal Partition Function of Molecular Components

The starting point for calculating the internal partition function of molecular components is to solve the Schrödinger equation of a representative molecule to obtain the energy levels corresponding to the independent molecular degree of freedom. The Schrödinger equation is solved in the Born–Oppenheimer approximation, which separates the motion of the electrons from that of the nuclei. The solution of the Schrödinger equation for the electrons yields the approximate wave functions of the infinite electronic states as well as their degeneracies. The energy corresponding to the  $n$ th electronic state is expressed as a function of the internuclear distance  $r$  and constitutes the potential energy  $V_n(r)$  seen by the internal motion of the nuclei, governed by the nuclear Schrödinger equation.

#### 1. Diatomic Molecules

The treatment of the diatomic molecules follows the method developed by Drellishak et al.<sup>12,13</sup> and by Stupochenko et al.<sup>14</sup> In this method the energy of a particular state in the molecule  $E_{nJv}$  is split into three contributions: the electronic excitation energy  $E_{el}(n)$ , the

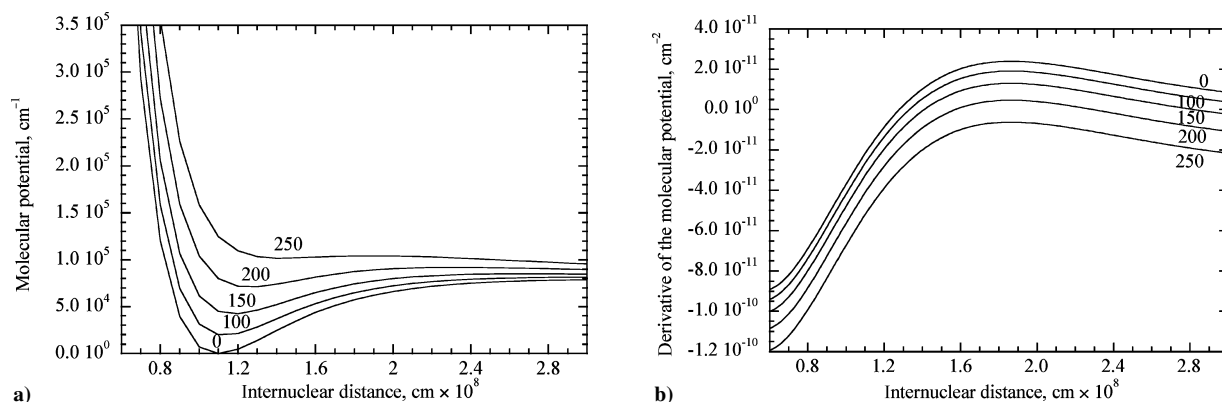


Fig. 1  $N_2$  ground state for different centrifugal distortions (numbers indicate the  $J$ s values): a) potential curves and b) their derivative.

vibrational energy  $E_{\text{vib}}(n, v)$  and the rotational energy  $E_{\text{rot}}(n, v, J)$ . Thus

$$E_{nJv} = E_{\text{el}}(n) + E_{\text{vib}}(n, v) + E_{\text{rot}}(n, v, J) \quad (17)$$

The vibrational energy associated with the  $v$ th vibrational level of the  $n$ th electronic state of a diatomic molecule is expressed in analytical form as<sup>11</sup>

$$\begin{aligned} \frac{E_{\text{vib}}(n, v)}{hc} &= \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2 \\ &+ \omega_e y_e \left( v + \frac{1}{2} \right)^3 + \omega_e z_e \left( v + \frac{1}{2} \right)^4 \end{aligned} \quad (18)$$

where  $\omega_e$ ,  $\omega_e x_e$ ,  $\omega_e y_e$ , and  $\omega_e z_e$  are spectroscopic constants for each electronic state. Expression (18) can be rewritten with the energy referenced to the first vibrational level, which reads

$$E_{\text{vib}}(n, 0) = (1/2)\omega_e + (1/4)\omega_e x_e + (1/8)\omega_e y_e + (1/16)\omega_e z_e \quad (19)$$

Assuming that expression (18) is valid for all vibrational states up to dissociation, we can determine the maximum permissible value  $v_{\text{max}}$  of the vibrational quantum number for each rotationless ( $J = 0$ ) molecular state by comparing the vibrational energy with the dissociation energy of the  $n$ th electronic state referenced to the energy of the first vibrational level  $D_0(n)$ .

The rotational energy for a nonrigid rotator associated with the  $v$ th vibrational level of the  $n$ th electronic state reads

$$\frac{E_{\text{rot}}(n, v, J)}{hc} = B_v J(J+1) - D_v J^2(J+1)^2 \quad (20)$$

where

$$B_v = B_e - \alpha_e \left( v + \frac{1}{2} \right) \quad (21)$$

$$D_v = D_e - \beta_e \left( v + \frac{1}{2} \right) \quad (22)$$

The maximum permissible value  $J_{\text{max}}$  of the rotational quantum number for each vibrational quantum number is determined comparing the vibrational-rotational energy with the dissociation energy relative to the electronic level we are considering. This represents a simplification in which the molecule is considered as a nonrotating system.

For a diatomic molecule the potential curve is given by<sup>15</sup>

$$U_0 = D_e \{1 - \exp[-\beta(r - r_e)]\}^2 \quad (23)$$

where  $\beta$  is a constant (in  $\text{cm}^{-1}$ ) whose value will be derived from

$$\beta = \sqrt{2\pi^2 c \mu / D_e h \cdot \omega_e} \quad (24)$$

When we consider, on the basis of classical mechanics, a rotating molecule, we must introduce an additional term in Eq. (23): a centrifugal potential.<sup>13</sup> Thus, when the angular momentum is  $J$ , the effective potential energy (in  $\text{cm}^{-1}$ ) becomes

$$U_J(r) = U_0 + (h/8\pi^2 c \mu r^2) J(J+1) \quad (25)$$

A series of potential curves for consecutive  $J$ s can be constructed. These potential curves show a maximum at a larger distance respect to the equilibrium distance for  $0 < J < J_{\text{max}}$ . For  $J = 0$  no centrifugal distortion occurs and there is some maximum value of  $J$  beyond which the potential curve no longer displays a minimum. This means that for  $J = 0$  all vibrational states with energy lower than the dissociation limit are present, whereas there are no stable states with  $J$  larger than  $J_{\text{max}}$ . See Fig. 1.

The centrifugal distortion of the potential energy determines the existence of “quasi-bound” states above the dissociation limit of the molecule. To calculate the number of rotational states above the dissociation limit for each vibrational state, we differentiate Eq. (25) respect to  $r$ , setting this derivative equal to zero and solve the resulting equation for the value of  $r$  at the hump (called  $r_m$ ) as a function of  $J$  for any electronic state of the molecule:

$$\begin{aligned} \frac{\partial U}{\partial r} &= 2D_e \beta \{ \exp[-\beta(r - r_e)] - \exp[-2\beta(r - r_e)] \} \\ &- \frac{2}{r^3} \frac{h}{8\pi^2 c \mu} J(J+1) = 0 \end{aligned} \quad (26)$$

Then the value of the potential at  $r_m$  is calculated for each  $J$ :

$$U_J(r_m) = D_e \{1 - \exp[-\beta(r_m - r_e)]\}^2 + (h/8\pi^2 c \mu r_m^2) J(J+1) \quad (27)$$

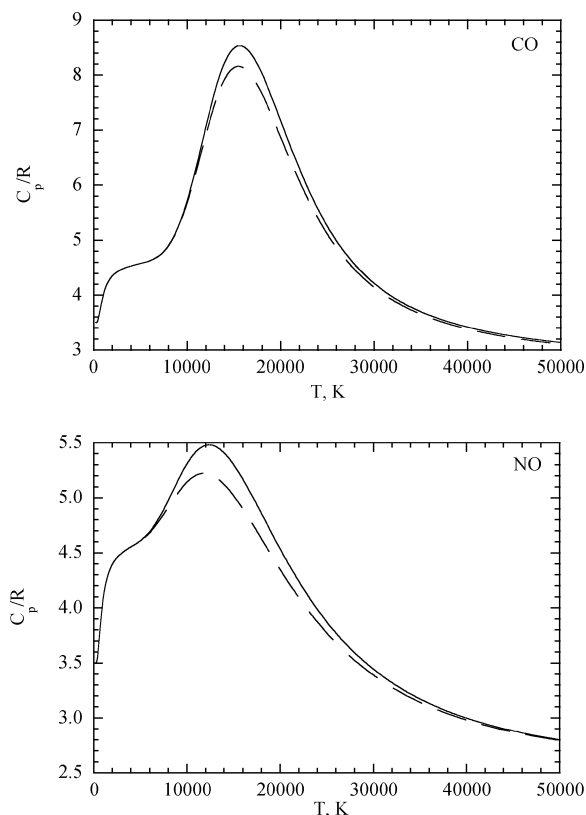
This potential is compared with the energy as calculated from the coupled vibrational-rotational energy expression for any assumed  $v$ :  $J$  is varied until these two energy values are equal. When this point is reached, one has a compatible  $v, J$  combination.

Once the maximum number of vibrational levels for each electronic state and the maximum number of rotational states for each vibrational state have been determined, the internal partition function can be calculated by the following expression:

$$\begin{aligned} Q_{\text{int}} &= \frac{1}{\sigma} \sum_n g_n \exp \left[ -\frac{E_{\text{el}}(n)}{k_B T} \right] \sum_v^{v_{\text{max}}(n)} \exp \left[ -\frac{E_{\text{vib}}(n, v)}{k_B T} \right] \\ &\times \sum_J^{J_{\text{max}}(v)} (2J+1) \exp \left[ -\frac{E_{\text{rot}}(n, v, J)}{k_B T} \right] \end{aligned} \quad (28)$$

where the symmetry factor  $\sigma$  equals one or two for, respectively, heteronuclear and homonuclear diatomic molecules.

In Sec. III, we will present results for selected diatomic molecules and compare them with data from other compilations. Here, we want



**Fig. 2** Nondimensional specific heat as a function of temperature for CO and NO without (---) and with (—) quasi-bound states.

to discuss the influence of quasi-bound states and of electronically excited states on the thermodynamic properties of molecular components.

Figure 2 illustrates the effect of quasi-bound states on nondimensional specific heat of CO and NO. Consideration of the quasi-bound states can introduce differences of up to 10% of the maximum specific heat. Note also that the nondimensional specific heat at constant pressure starts from the value 3.5 (activation of translational and rotational degrees of freedom) and rapidly reaches the value 4.5, which includes the vibrational contribution from the ground electronic state. The maximum is due to the contribution of the electronically excited states.

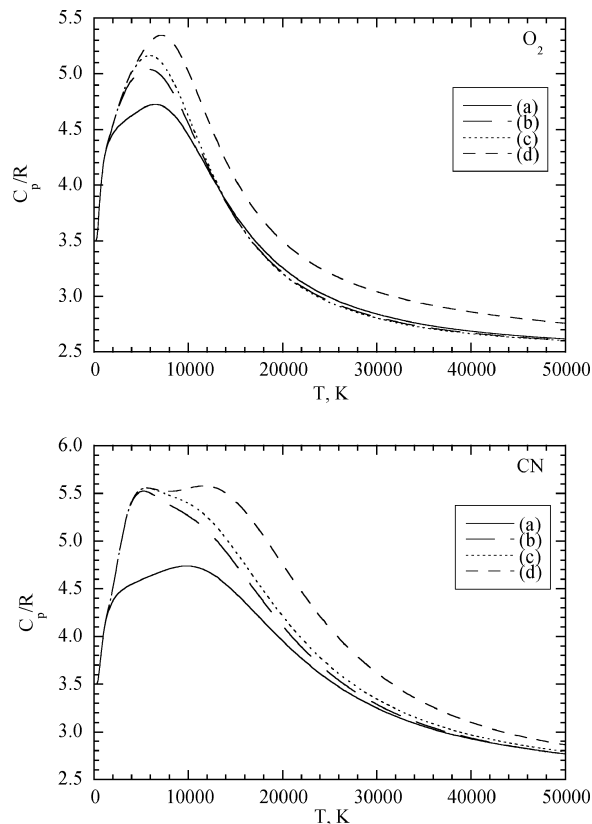
In any case, depending on the number of electronically excited states considered in the partition function and on the energy values, the nondimensional specific heat slowly converges after the maximum to the translational contribution ( $3/2R + R$ ). This behavior is typical for systems containing a finite number of rotational, vibrational, and electronic states.

The last observation is better understood by inspection of Fig. 3, which shows the role of electronically excited states in forming and enhancing the specific heat of O<sub>2</sub> and CN.

Curves a represent the specific heat of the ground state of the molecules, which rapidly passes from 3.5 to 4.5 for the reasons explained earlier. Then, there is the presence of a small maximum, after which the specific heat smoothly declines toward the translational contribution. The successive inclusion of electronically excited states b, c, and d produces a well-defined maximum, the absolute value of which depends on the specific molecule. Case b refers to the inclusion of the ground state and the first excited state. Case c refers to the inclusion of the second excited state also. Finally, in case d, all of the excited levels as given by Herzberg<sup>11</sup> are included in the calculation.

## 2. Polyatomic Molecules

The internal partition function of polyatomic molecules by analogy with diatomic molecules can be written in the general case in



**Fig. 3** Contribution of electronically excited states to the nondimensional specific heat as a function of temperature for O<sub>2</sub> and CN.

the following way<sup>4,16</sup>:

$$Q_{\text{int}} = \frac{1}{\sigma} \sum_i p_i \exp\left(-\frac{hc}{k_B T} T_0^{(i)}\right) \cdot \sum_{v_1} \sum_{v_2} \cdots \sum_{v_m} p_v \exp\left[-\frac{hc}{k_B T} G_0^{(i)}(v_1, v_2, \dots, v_m)\right] \times \sum_J \sum_{k=-J}^{k=J} (2J+1) \exp[-F_v^{(i)}(j, k)] \quad (29)$$

In this expression, the first sum is taken over the electronic states (in general the valence ones) of the molecule, characterized by the energy of excitation  $T_0^{(i)}$  and the statistical weight  $p_i$ . The electronic states of nonlinear polyatomic molecules are nondegenerate and therefore the statistical weight of these states is determined only by multiplicity  $p_i = 2S + 1$ . In the case of linear polyatomic molecules, the statistical weights are the same as for the corresponding states of diatomic molecules. Sum over  $v$  is carried out for all the  $m$  normal vibrations of the molecule. If a molecule, consisting of  $N$  atoms, has  $t$  degenerate normal vibrations with degeneracy  $d_n$ , then  $m = 3N - 5 - t$  for linear molecules and

$$m = 3N - 6 - \sum_{n=1}^i (d_n - 1)$$

for nonlinear molecules. The statistical weight  $p_v$  of the state  $(v_1, v_2, \dots, v_m)$  is equal to

$$p_v = \prod_{n=1}^m \frac{(v_n + d_n - 1)!}{v_n! (d_n - 1)!} \quad (30)$$

The energy of the vibrational levels has been calculated in the approximation of harmonic oscillator:

$$G_0(v_1, v_2, \dots, v_m) = \sum_{n=1}^m \omega_n \left(v_n + \frac{d_n}{2}\right) \quad (31)$$

An additional simplification that can be included consists in factorizing the vibrational partition function. Then it can be written as

$$\sum_{v_1} \sum_{v_2} \dots \sum_{v_m} p_v \exp \left[ -\frac{hc}{k_B T} G_0^{(i)}(v_1, v_2 \dots v_m) \right] \\ = \prod_{n=1}^m \left\{ \sum_{v=1}^{v_{\max}} p_n(v) \exp \left[ -\frac{hc}{k_B T} G_n^{(i)}(v) \right] \right\} \quad (32)$$

where  $p_n(v)$  is the statistical weight of  $v$ th level in the  $n$ th vibrational mode

$$p_n(v) = \frac{(v_n + d_n - 1)!}{v_n! (d_n - 1)!} \quad (33)$$

and  $G_n^{(i)}(v)$  is the energy of the  $v$ th level in the  $n$ th vibrational mode

$$G_n^{(i)}(v) = \omega_n(v_n + d_n/2) \quad (34)$$

Summation over  $J$  in Eq. (29) has been carried out for the value  $v=0$ . The energy of the rotational levels of the polyatomic molecules is expressed differently, depending on the symmetry of the molecule.

For linear polyatomic molecules and molecules of the type of a spherical top, such as diatomic molecules, the energy of the rotational levels is described by the expression

$$F_v(J) = B_v J(J+1) \quad (35)$$

For molecules of the type of a symmetrical top

$$F_v(J, k) = B_v J(J+1) + (A_v - B_v)k^2 \quad (36)$$

where  $k$  assumes values from  $-J$  to  $+J$ .

For asymmetric top molecules

$$F_v(J) = \frac{1}{2}(B_v + C_v)J(J+1) + (A_v - B_v)k^2 \quad (37)$$

In expressions (35–37), the quantities  $A_v$ ,  $B_v$ , and  $C_v$  are the rotational constants related to the principal moments of inertia of the molecule. In particular

$$A_0 = h/8\pi^2 c I_A, \quad B_0 = h/8\pi^2 c I_B, \quad C_0 = h/8\pi^2 c I_C \quad (38)$$

where  $I_A$ ,  $I_B$ , and  $I_C$  correspond to some average structure of the molecule in the ground vibrational state.

It is important to note that different electronic excited states of the same polyatomic molecule can have different geometries, thus affecting the symmetry number and also determining a different rotational behavior. Then to include these excited states in our calculations it is necessary to take into account this geometry variation.

With increasing temperature, the use of the direct summation method becomes impossible both because of the absence of data for the high vibrational–rotational energy levels including the ground electronic state of almost all polyatomic molecules, as well as the absence of sufficiently accurate knowledge of the dependence of the energy of these levels on the quantum numbers  $v_n$  and  $J$ . Then calculations of the thermodynamic functions of polyatomic molecules still use the “rigid rotator–harmonic oscillator” approximation. Deviations from this model, the presence of excited electronic states, and other effects are taken into account in the form of corrections.

This approximation assumes the vibrations of the molecule in its electronic ground state as harmonic, and then the upper limits for  $v_n$  and  $J$  in the partition function and its derivatives approach infinity. Then, the internal partition function for the molecule in the electronic ground state is given by

$$Q_{\text{int}} = p_X Q_{\text{r.r.}, \text{h.o.}}^{(X)} = p_X Q_{\text{r.r.}}^{(X)} Q_{\text{h.o.}}^{(X)} \quad (39)$$

where

$$Q_{\text{h.o.}} = \prod_{n=1}^m \left[ 1 - \exp \left( -\frac{hc}{k_B T} v_n \right) \right]^{-d_n} \quad (40)$$

$$Q_{\text{r.r.}} = \frac{1}{\sigma} \frac{k_B T}{hc B_0} \quad (41)$$

for linear molecules, and

$$Q_{\text{r.r.}} = 1/\sigma \sqrt{(\pi/A_0 B_0 C_0)(k_B T/hc)^3} \quad (42)$$

for nonlinear molecules.

According to expression (39), the thermodynamic functions can be represented as the sum of the corresponding components:

$$\frac{[H^0(T) - H^0(0)]_{\text{h.o.}}}{RT} = \sum_{n=1}^m d_n u_n \exp(-u_n) [1 - \exp(-u_n)]^{-1} \quad (43)$$

$$\frac{[C_p^0(T)]_{\text{h.o.}}}{R} = \sum_{n=1}^m d_n u_n^2 \exp(-u_n) [1 - \exp(-u_n)]^{-2} \quad (44)$$

where  $u_n = (hc/k_B T)v_n$ , and

$$\frac{[H^0(T) - H^0(0)]_{\text{r.r.}}}{RT} = \frac{[C_p^0(T)]_{\text{r.r.}}}{R} = 1 \quad (45)$$

for linear molecules, and

$$\frac{[H^0(T) - H^0(0)]_{\text{r.r.}}}{RT} = \frac{[C_p^0(T)]_{\text{r.r.}}}{R} = \frac{3}{2} \quad (46)$$

for nonlinear molecules.

If we assume that the vibrational–rotational partition function of the excited states is equal to that of the ground state, the components of the excited electronic states can be calculated as the corrections to the components of the ground electronic state

$$\frac{[H^0(T) - H^0(0)]_{\text{e.s.}}}{RT} = \sum_i \frac{p_i}{p_X} \frac{hc}{k_B T} T_0^{(i)} \exp \left( -\frac{hc}{k_B T} T_0^{(i)} \right) / \left[ 1 + \sum_i \frac{p_i}{p_X} \exp \left( -\frac{hc}{k_B T} T_0^{(i)} \right) \right] \quad (47)$$

$$\frac{[C_p^0(T)]_{\text{e.s.}}}{R} = \left\{ \sum_i \frac{p_i}{p_X} \exp \left( -\frac{hc}{k_B T} T_0^{(i)} \right) + 1 \right\} \\ \times \sum_i \frac{p_i}{p_X} \left[ \frac{hc}{k_B T} T_0^{(i)} \right]^2 \exp \left( -\frac{hc}{k_B T} T_0^{(i)} \right) / \left\{ 1 + \sum_i \frac{p_i}{p_X} \exp \left( -\frac{hc}{k_B T} T_0^{(i)} \right) \right\}^2 \\ - \left\{ \sum_i \frac{p_i}{p_X} \frac{hc}{k_B T} T_0^{(i)} \exp \left( -\frac{hc}{k_B T} T_0^{(i)} \right) \right\}^2 / \left\{ 1 + \sum_i \frac{p_i}{p_X} \exp \left( -\frac{hc}{k_B T} T_0^{(i)} \right) \right\}^2 \quad (48)$$

where  $T_0^{(i)}$  and  $p_i$  are the energy and the statistical weight of the  $i$ th electronic state respectively and  $p_X$  is the statistical weight of the ground state.

### III. Results and Discussion

#### A. Monoatomic Components

In this section we compare the present results with similar ones from the literature. In particular we will compare the present results (called new) with the results obtained by our group some years ago<sup>17,18</sup> (called old), the recent calculations performed by Wang and Rhodes<sup>7</sup> (called Wang), the old and new calculations of the NASA group,<sup>2</sup> and the old calculations performed by Browne.<sup>5</sup>

The main differences among the calculations are in the set of levels inserted in the partition function and its derivatives.

The present calculations complete the observed levels reported in the tables by Moore<sup>6</sup> and the National Institute of Standards and Technology (NIST)<sup>10</sup> with Rydberg and Ritz extrapolation laws for principal quantum number lower than 20, using the hydrogen-like formulation for  $n > 20$  (see Appendix). The calculations are then presented with the lowering of the ionization potential as a parameter to control the cutoff. The same procedure was used in our previous calculations<sup>17,18</sup> even though in this case we considered a less complete set of energy levels.

Wang and Rhodes<sup>7</sup> have recently presented new calculations of thermodynamic properties for very high-temperature air components by including a complete set of hydrogen-like levels. Moreover, the results presented by those authors are self-consistent because they calculated the lowering of the ionization potential provided by the Debye–Hückel theory in their equilibrium code. In principle, their results cannot be directly compared with ours. However, a rough estimate of the lowering of the ionization potential for atmospheric air plasmas in the temperature range 20,000–35,000 K should be in the range of 600–500 cm<sup>-1</sup> for neutral atomic components,<sup>19</sup> proportionally scaling with the charge of the considered ion [see Eq. (7)]. This point can be understood by looking at Fig. 4, in which we have reported the lowering of the ionization potential for equilibrium oxygen plasmas as a function of temperature for different pressures. The same lowering should be approximately applied to air plasmas.

Gordon and McBride,<sup>2</sup> on the other hand, used the few-level approximation to calculate the partition function of atomic components up to 6000 K. They extended their results above  $T > 6000$  K essentially by using the well-known Gurvich's tables. The last tabulations also account for a very limited number of excited levels.

Finally, the Browne's tables<sup>5</sup> are based on the observed levels as reported in the Moore's tables.<sup>6</sup> In general, we should expect a good agreement about the thermodynamic properties of atomic (neutral and ionized) components for temperatures below 10,000 K when only the low-lying excited states contribute to the partition function. Strong differences should appear above 10,000 K when the high-lying excited states begin to contribute. The effect becomes evident when complete sets of energy levels are inserted in the partition function. It should be also noted that only our results (new and old) depend on the cutoff.

These qualitative observations can be drawn from the results shown in Figs. 5 and 6, where a comparison of the nondimensional specific heats ( $C_p/R$ ) for the components N and N<sup>+</sup> is illustrated as

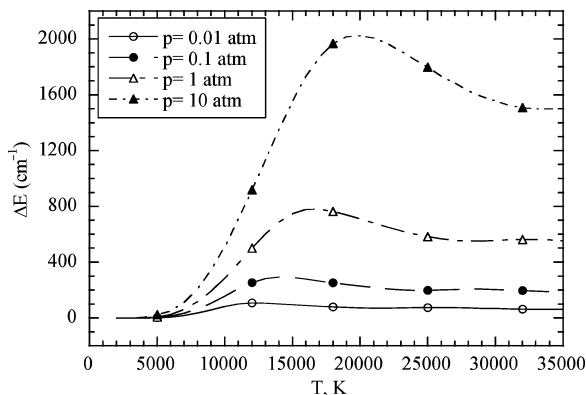


Fig. 4 Lowering of the ionization potential ( $\Delta E$ ) of neutral species in a oxygen plasma as a function of temperature at different pressures.

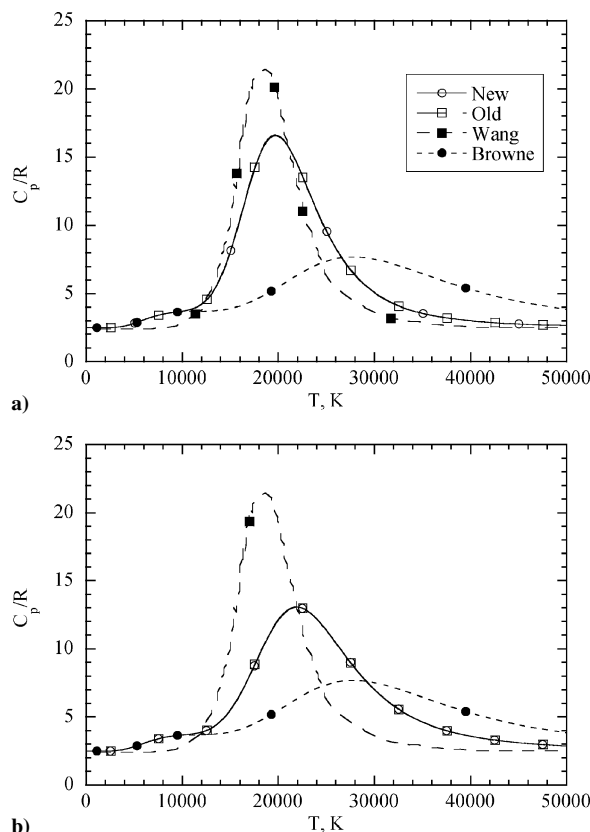


Fig. 5 Comparison of nondimensional specific heat as a function of temperature for N for a)  $\Delta E = 500$  cm<sup>-1</sup> and b)  $\Delta E = 1000$  cm<sup>-1</sup>.

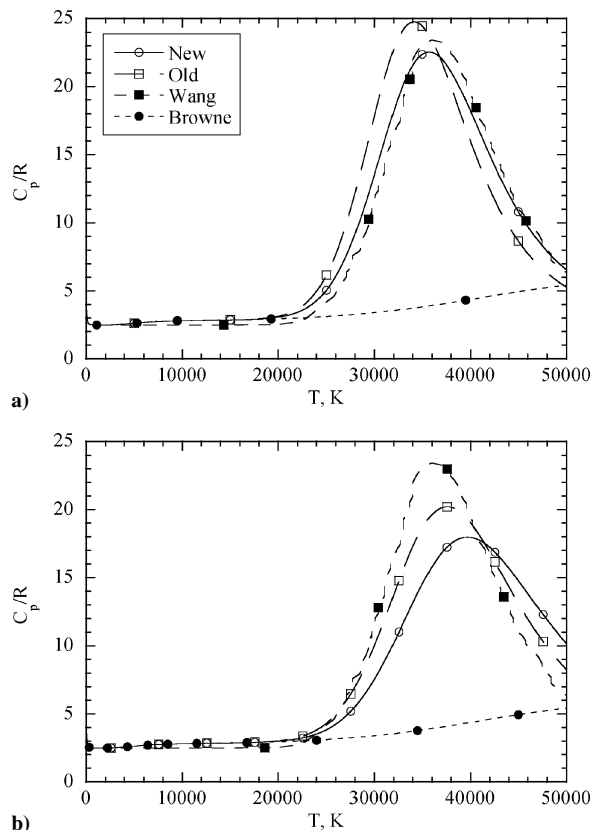


Fig. 6 Comparison of nondimensional specific heat as a function of temperature for N<sup>+</sup> for a)  $\Delta E = 500$  cm<sup>-1</sup> and b)  $\Delta E = 1000$  cm<sup>-1</sup>.

a function of temperature for different cutoff values in the temperature range 0–50,000 K.

Wang and Rhodes's<sup>7</sup> results at high temperature are in satisfactory agreement with the present results. This means that the hydrogen-like approximation for higher excited states is a good one. On the other hand, we can observe strong differences in the low-temperature regime. Apparently, Wang and Rhodes have completely disregarded the presence of low-lying levels of the different components. Thus, their specific heats present a flat behavior (that is, only the translational contribution  $C_p/R = 2.5$ ) below 10,000 K and a dramatic increase when high-lying excited states are populated.

Gordon and McBride's specific heats closely follow our results below 10,000 K, but are largely underestimated above 10,000 K because of the insufficient number of levels considered by these authors. The same behavior is observed in relation to Browne's calculations. The insufficient number of levels considered by Gordon and McBride is determined by the cutoff criterion adopted in their calculations. This cutoff criterion is temperature dependent: the partition function includes only those levels below the ionization potential lowered by  $k_B T$ , then as temperature increases, fewer energy levels are used, which results in an underestimation of thermodynamic properties at high temperature.

It is also interesting to compare the present results with those obtained by our group some years ago. A satisfactory agreement is observed and the minor differences are due to the improvement of the energy-level sets we have used.

Similar considerations can be made from Fig. 7 in which we have plotted the nondimensional specific heats of C and C<sup>+</sup>. In this case, we limit our comparison to Gordon and McBride's and Browne's data. As in the previous case, the agreement is excellent below 10,000 K but becomes poor above that temperature, namely when high-lying excited states begin to contribute substantially to the partition function.

Before concluding this section, we want to emphasize the problem related to the inclusion of the so-called autoionization states. These states derive by considering other series in the completion of

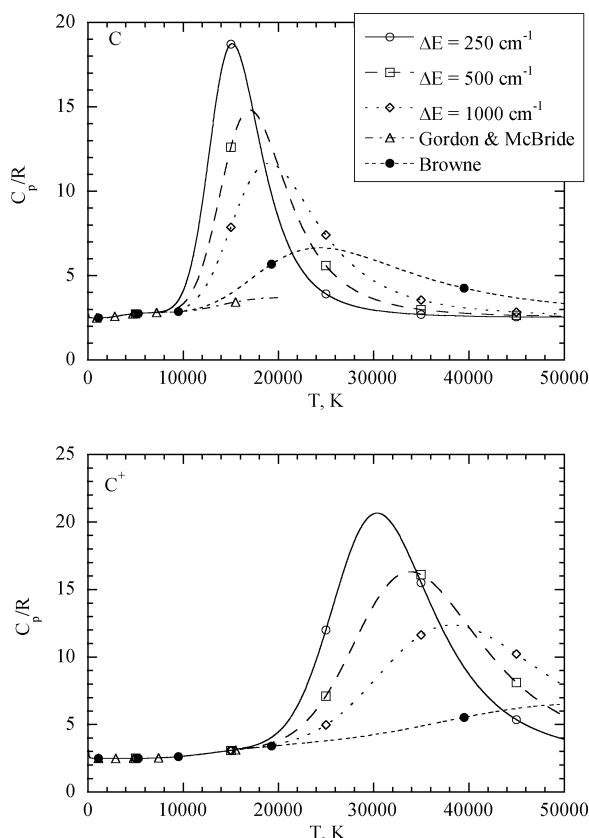


Fig. 7 Comparison of nondimensional specific heat as a function of temperature for C and C<sup>+</sup> for different cutoff.

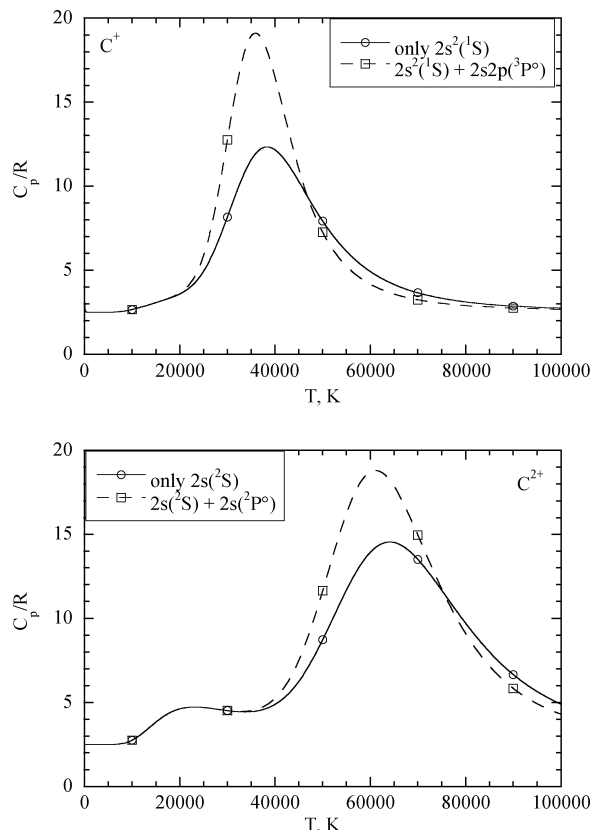


Fig. 8 Nondimensional specific heat for C<sup>+</sup> and C<sup>2+</sup> as a function of temperature calculated with and without autoionizing levels (up to  $n = 20$ ).

energy levels, which converge to ionization potentials greater than the first ionization potential of the considered component. These levels are usually eliminated in the partition-function calculations by the cutoff procedure even though in many cases those are observed experimentally. To understand their influence, we present in Fig. 8 the nondimensional specific heat for the C<sup>+</sup> and C<sup>2+</sup> calculated with and without the inclusion of autoionizing levels. For both series, we consider levels up to  $n = 20$ . The figure shows that the autoionization affects the results above 20,000 K and, therefore, originates a further problem for the determination of the electronic partition function.

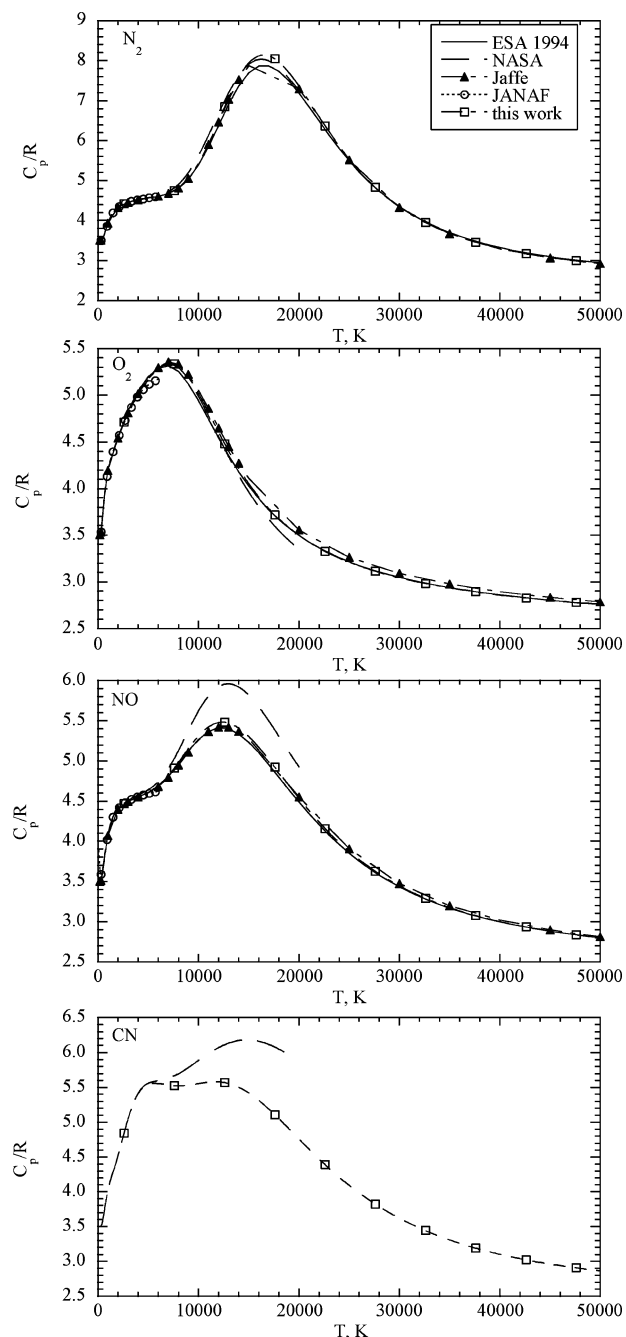
The extension of the results up to 100,000 K is reported only for a better appreciation of the differences in the two calculations. Indeed, C<sup>+</sup> and C<sup>2+</sup> ions will disappear for  $T > 50,000$  K in realistic pressure ranges.

## B. Diatomic Species

In this section, we will compare the present results with those given in the JANAF tables,<sup>1</sup> by McBride et al.,<sup>3</sup> in ESA tables,<sup>17,18</sup> and by Jaffe.<sup>20</sup> The present results are calculated by using spectroscopic data from Huber and Herzberg.<sup>21</sup> The various calculations differ because of the number of electronically excited states included in the partition function and, in some cases, because of the way to account for the rotational and vibrational levels.

Results for N<sub>2</sub>, O<sub>2</sub>, NO, and CN are shown in Fig. 9. In the low-temperature range ( $T < 6000$  K) our results are in perfect agreement with all other calculations. Small differences emerge at higher temperatures when the contribution of electronically excited states becomes important. Deviations for NO are present only with the recent calculations of Gordon and McBride, who have fitted the Gurvich data<sup>2</sup> with polynomial curves.

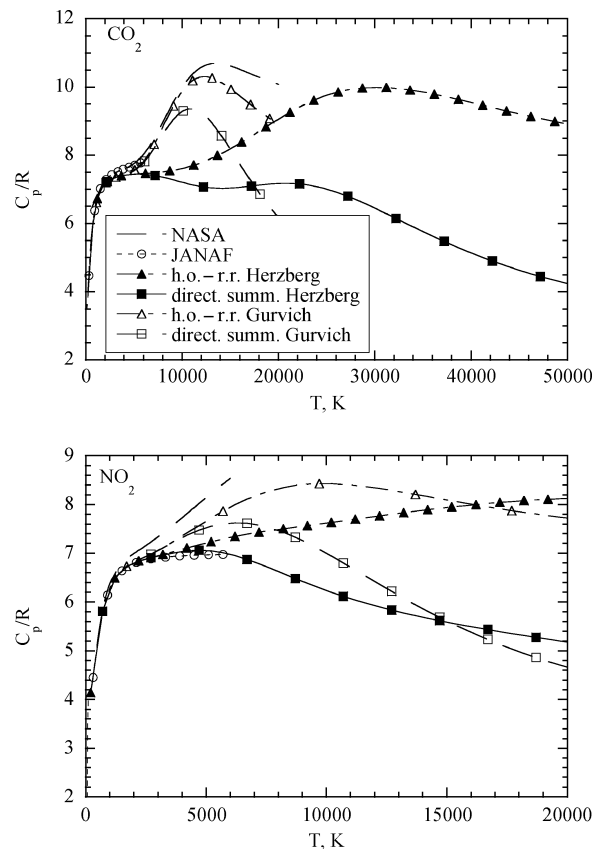
It should be noted again that diatomic molecules do not survive for temperatures higher than 10,000 K in realistic pressure ranges. The extension to higher temperatures is interesting to emphasize the decline of the specific heat and its convergence to the translational specific heat.



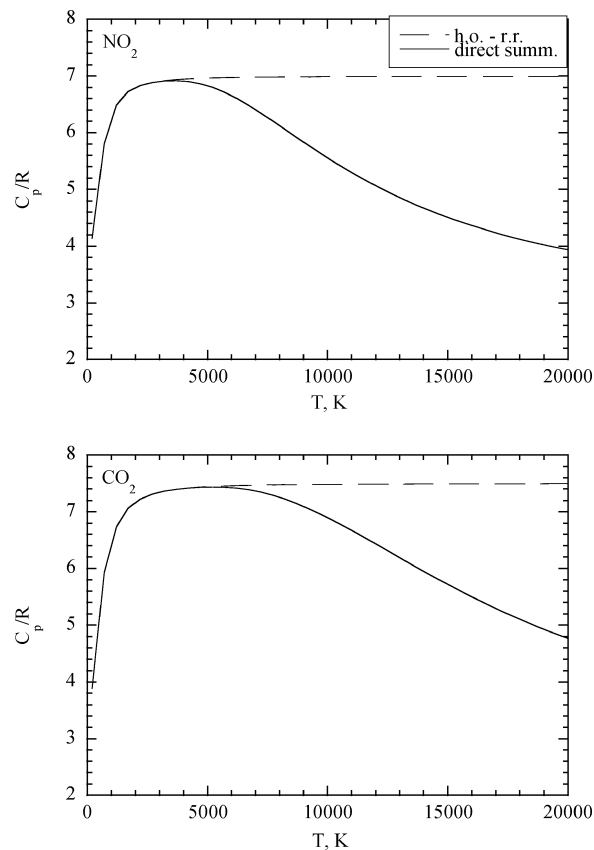
**Fig. 9** Comparison of nondimensional specific heat as a function of temperature for some selected diatomic species.

### C. Triatomic Species

In this section, we show results for  $NO_2$  and  $CO_2$  (Fig. 10), calculated by using two different methods and two different data sets. The first method consists of the direct summation method extending the vibrational part of electronic excited states with data from the fundamental state if absent, as suggested by Gurvich. The second method uses the “rigid rotator–harmonic oscillator” approximation for the electronic ground state, including the correction for the electronic excited states in which the vibrational–rotational partition functions of the ground and excited electronic states are equal. Both data sets include spectroscopic data from Herzberg<sup>16</sup> (vibrational frequencies and rotational constants), while for the electronic levels’ energies, in one case we use data from Herzberg and in the second case data are taken from Gurvich et al.<sup>4</sup> These results are compared with those reported by McBride et al.<sup>3</sup> and in JANAF tables.<sup>1</sup> Also, for triatomic species the agreement is perfect in the low-temperature range, while differences arise at high temperature



**Fig. 10** Comparison of nondimensional specific heat as a function of temperature for  $NO_2$  and  $CO_2$ .



**Fig. 11** Comparison of nondimensional specific heat as a function of temperature for  $NO_2$  and  $CO_2$  calculated with the direct summation method and the rigid rotator–harmonic oscillator method, considering only the ground electronic level.



when electronically excited states begin contributing to the partition function. These strong differences reflect the differences in the two data sets for the electronic levels' energies. The contribution of electronically excited states modulates the corresponding contribution for vibrational partition function of the ground electronic states.

In Fig. 11 we report the nondimensional specific heat calculated either by direct summation method or by the rigid rotator-harmonic oscillator method as a function of temperature. Note that in the analytical model the specific heat converge to the value of 7.5R and 7R, respectively, for CO<sub>2</sub> and NO<sub>2</sub> as expected by classical theory.

Before concluding this section we want to point out that all the results will be collected in a special report, which can be obtained from the authors upon request.<sup>22</sup>

#### IV. Conclusions

In this paper we have described and discussed a recent effort to calculate the high-temperature thermodynamic properties of Mars-atmosphere components. Associated problems, such as the effects of quasi-bound vibrational states, cutoff criteria, energy-level completion of the monatomic components, and autoionizing states have been considered and have shown to be nonnegligible, particularly at high temperatures. Indeed, we find agreement with data from other published tables at low temperatures and marked differences at high temperatures. In particular, for monatomic components, the discrepancies are mainly due to the insufficient number of electronic levels usually accounted for in the other tabulations.

#### Appendix: Estimation of Energy Levels for Neutral Carbon

The available database for observed atomic electronic energy levels are Moore's tables<sup>6</sup> and the more complete NIST's table.<sup>9</sup> However, many predicted electronic levels are missing, especially for the higher quantum numbers, so the set of electronic levels should be completed using semi-empirical methods.

To extend the electronic levels of the ground-state configuration we use the iso-electronic sequence method. Let us consider carbon atom C(I) as an example.

For carbon, the ground state configuration we shall consider is

2s<sup>2</sup>2p<sup>2</sup>(<sup>1</sup>S, <sup>3</sup>P, <sup>1</sup>D);  
2s<sup>2</sup>p<sup>3</sup>(<sup>5</sup>S°, <sup>3</sup>S°, <sup>3</sup>P°, <sup>1</sup>P°, <sup>3</sup>D°, <sup>1</sup>D°);  
2p<sup>4</sup>(<sup>1</sup>S, <sup>3</sup>P, <sup>1</sup>D).

If one of these terms has not yet been observed, it can be derived through extrapolation from energy levels of isoelectronic species. Practically, for carbon C(I), one missing term is 2p<sup>4</sup> [<sup>1</sup>S], so, for example, we consider the energies of N(II), O(III), and F(IV), corresponding to the same term, and reporting them as a function of the atomic number Z, we perform an extrapolation to obtain the missing energy corresponding to the C(I) (Z = 6). The method works well; as a matter of fact extrapolating isoelectronic sequences corresponding to 2s<sup>2</sup>p<sup>3</sup>(<sup>5</sup>S°) term we obtain a value very close to the observed one.

The excited states come from the excitation of one electron toward higher values of the principal quantum numbers ( $n > 2$ ); such series for C(I) are

2s<sup>2</sup>2p(2P°)nx  
2s2p<sup>2</sup>(4P)nx  
2s2p<sup>2</sup>(2D)nx'  
2s2p<sup>2</sup>(2S)nx''  
2s2p<sup>2</sup>(2P)nx'''  
2p<sup>3</sup>(4S°)nx<sup>IV</sup>

These series arise from the interaction of the atomic core (2s<sup>2</sup>2p(2P°), 2s2p<sup>2</sup>(4P), ...) with the excited electron (nx, nx', ...) with x = s, p, d, ...

Let us focus our attention on the first excited series. In the case of x = s, there are two spectroscopic terms: <sup>3</sup>P° (L = 1, S = 1), and <sup>1</sup>P° (L = 1, S = 0). NIST's tables report observed levels up to  $n = 10$  for the former and  $n = 14$  (missing values  $n = 11$  and  $n = 12$ ) for the latter. To extrapolate to higher principal quantum numbers, the

following Ritz-Rydberg series can be used:

$$E_n = E_i - \frac{Ry^*}{(n + A + B/n^2)^2} \quad (A1)$$

where  $E_i$  is the ionization potential,  $Ry^*$  is the Rydberg constant of the selected series, and  $A$ ,  $B$  are adjustable parameters. For each excited series,  $E_i$  is calculated as the sum between the ionization energy of the selected species [in this case C(I)] and the core energy of the successive ionized species [that is, C(II)]. For example, if we consider the 2s2p<sup>2</sup>(4P)nx series,  $E_i$  is calculated as the sum between the ionization potential of C(I) (for example, 90,820.42 cm<sup>-1</sup>) and the energy of the core 2s2p<sup>2</sup>(4P) for C(II) (for example, 43,035.78 cm<sup>-1</sup>).

$Ry^*$  is given by the following equation:

$$Ry^* = Ry \cdot (Z' - Z_H)^2 \quad (A2)$$

where  $Ry$  is the Rydberg constant (109,737 cm<sup>-1</sup>),  $Z'$  is the nuclear charge (atomic number) (for C,  $Z' = 6$ ), and  $Z_H$  is the number of core electrons which should be extracted to obtain a hydrogen-like atom [for C(I)  $Z_H = 5$ ]. The constants  $A$  and  $B$  can be determined when at least two observed levels are available. If we have only two levels it is straightforward to solve a system of two equations, while if we have more than two levels it is possible to fit these energy levels as a function of the principal quantum number using Eq. (34). To extend the spectroscopic term 2s2p<sup>2</sup>(2P°)ns (<sup>3</sup>P°) for  $n > 10$ , using last method, we obtain  $A = -1.0288$  and  $B = -0.66479$ .

If there is only one observed energy level, instead of Eq. (49) the following formula should be used:

$$E_n = E_i - Ry^*/(n + C)^2 \quad (A3)$$

where  $C$  is an adjustable parameter.

For the spectroscopic series 2s<sup>2</sup>2p(2P°)nx, all the spectroscopic terms corresponding to  $x = g$  ( $n \geq 5$ ) have not been observed. In this case to obtain the energy level of the terms corresponding to 5g, we report in graph the energy levels (5s, 5p, 5d, 5f) as a function of the azimuthal quantum number  $l$ , and extrapolate to  $l = 4$ . The energy levels of 5s, 5p, 5d, 5f are the average values over all the spectroscopic terms; for example, for 5s we have

$$\bar{E}_{5s} = \frac{g(^3P^\circ) * E_{5s}^{3P^\circ} + g(^1P^\circ) * E_{5s}^{1P^\circ}}{g(^3P^\circ) + g(^1P^\circ)} \quad (A4)$$

where  $g$  is statistical weights.

The total statistical weight associated to 5g energy level, obtained as previously, is the sum over the statistical weights of all the corresponding predicted spectroscopic terms.

From this last energy value, we extrapolate to  $n > 5$  using the formula (A2).

This method has been applied on  $n = 20$  and  $l = 19$ , with the exception of those series where no observed energies are present.

For  $n > 20$  energy levels, we assume an hydrogen-like behavior and use the following formulas:

$$E_n = E_i - Ry^*/n^2 \quad (A5)$$

It is possible to demonstrate that, at fixed  $n$  and for each series, the sum over the statistical weights of all the corresponding predicted spectroscopic terms for different  $l$  is equal to

$$g_n = 2n^2 \cdot g_{\text{core}} \quad (A6)$$

so for  $n > 20$  we have applied this last equation to determine the total statistical weight.

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