High-temperature partition functions, specific heats and spectral radiative properties of diatomic molecules with an improved calculation of energy levels

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ABSTRACT

The level energies of diatomic molecules calculated by the frequently used Dunham expansion will become less accurate for high-lying vibrational and rotational levels. In this paper, the potential curves for the lower-lying electronic states with accurate spectroscopic constants are reconstructed using the Rydberg–Klein–Rees (RKR) method, which are extrapolated to the dissociation limits by fitting of the theoretical potentials, and the rest of the potential curves are obtained from the ab-initio results in the literature. Solving the rotational dependence of the radial Schrödinger equation over the obtained potential curves, we determine the rovibrational level energies, which are then used to calculate the equilibrium and non-equilibrium thermodynamic properties of N_2, N_2^+, NO, O_2, CN, C_2, CO and CO^+. The partition functions and the specific heats are systematically validated by available data in the literature. Finally, we calculate the radiative source strengths of diatomic molecules in thermodynamic equilibrium, which agree well with the available values in the literature. The spectral radiative intensities for some diatomic molecules in thermodynamic non-equilibrium are calculated and validated by available experimental data.

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1. Introduction

The partition functions are key to the calculation of the energy level populations of high-temperature gases produced in Earth and Mars atmospheric entry [1,2]. And the energy level populations are input parameters in the calculation of the spectral radiative properties of high-temperature gases in equilibrium and local non-equilibrium systems [1]. The obtained spectral radiative properties can be used to predict the atmospheric radiative transfer [3] and the radiative heat flux of aircraft surface caused by shock waves in atmospheric entries [4]. Moreover, the partition functions can also be used to calculate the thermodynamic properties, which are required in the calculation of the aerothermodynamic flow field [5–8].

Strong shock waves can be formed in front of the vehicles during hypersonic flights, which translate part of the kinetic energy of the vehicles into the internal energy of gases. As a result, the gas temperature rises precipitously, leading to the non-equilibrium between the vibrational and rotational modes for molecular compo-

nents. However, the excitation of different energy modes will not occur at the same time, making it difficult to adopt a single temperature to accurately describe the thermal non-equilibrium phenomenon among different energy modes. To simplify the problem, Lee [9] and Park [10] assumed that various energy modes can be separated by the corresponding temperatures, known as the multi-temperature model. For instance, the frequently used two-temperature model uses T_r to represent the temperature of the rotational and translational energy levels with a Boltzmann and Maxwell distribution, and uses T_v to represent the temperature of the electronic and vibrational energy levels with Boltzmann distributions (shown in Fig. 1). Recently, the state-to-state model becomes more and more popular due to the availability of the ever-increasing ab-initio rate parameters for the elementary collisional processes. It was shown that the state-to-state model can predict better the number densities of the species in high-temperature non-equilibrium reacting flows [11–13], in which different vibrational temperatures are introduced for each corresponding molecule and even for each electronic state of the same molecule. For these two non-equilibrium models, the thermodynamic and spectral radiative properties of high-temperature gases cannot be described using one temperature. Instead, the rovibrational interaction energy should be divided into multiple parts with the cor-
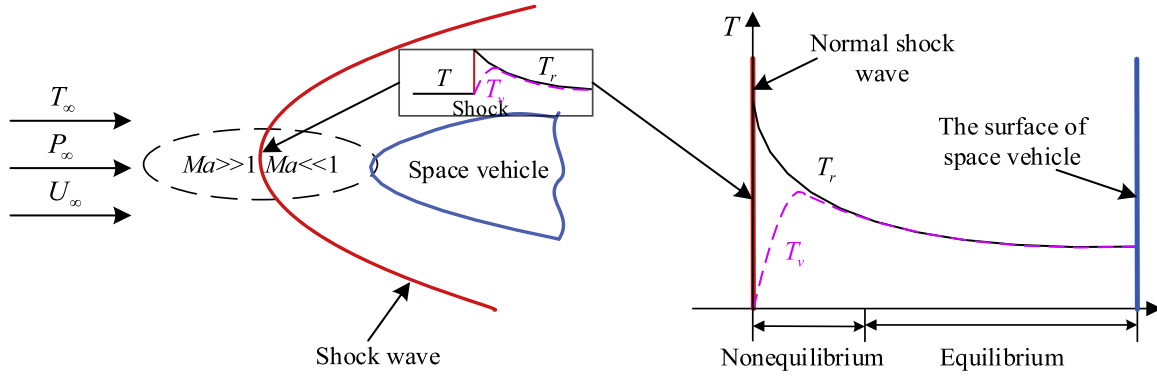
Fig. 1. Schematic diagram of thermodynamic parameters behind a shock in hypersonic flow (T_∞, P_∞, U_∞ are respectively the temperature, pressure and velocity before the shock, T_r, T_v are respectively the translational and vibrational temperature, *Ma* is the Mach number).

responding temperatures. Hence, Jaffe et al. [5] proposed the two limiting cases to split the rovibrational internal energy based on the two-temperature model. This method is the starting point to resolve the non-equilibrium thermodynamic and spectral radiative properties, which can also be generalized to the multi-temperature and state-to-state models if the summation over each internal energy mode is performed for its own temperature.

As required in the study of the plasma flow for atmospheric entry, a large amount of data of the partition functions, the thermodynamic and spectral radiative properties for high-temperature gases have been calculated over the past few years. For the partition functions and thermodynamic properties, Drellishak et al. [14,15] calculated the equilibrium chemical composition and the thermodynamic properties of argon, nitrogen and oxygen plasma for temperatures as high as 35000 K. In order to derive the entropy and enthalpy of gas mixtures for the calculation of non-equilibrium flow field, Jaffe [5] proposed a scheme for partitioning the internal energy into vibrational, rotational and electronic parts, in which two extreme cases of splitting the rovibrational interaction energy are considered. With the aid of this scheme, the two-temperature energies of N_2, O_2 and NO were found to be insensitive to the two extreme cases [5]. Employing the two-temperature partitioning scheme, Babou et al. [2] calculated the two-temperature internal partition functions, internal energies, vibrational and rotational specific heats of N_2, N_2^+, NO, O_2, CN, C_2, CO and CO^+ from 1000 to 50000 K. McBride et al. [16] reported a library of thermodynamic data of more than 2000 individual species, from which the equilibrium thermodynamic properties ranging from 200 to 20000 K can be found for the gaseous chemical species related to planetary atmosphere. Capitelli et al. [7] presented the thermodynamic properties of the components related to the Martian atmosphere. In addition, a spectroscopic database is built by the EM2C laboratory in France [1] for radiative transfer calculations in air and CO_2–N_2 plasmas.

Notice that all the rovibrational level energies for the bound and quasi-bound electronic states of diatomic molecules in previous published papers are calculated based on the Dunham expansion, which is given by [17]

$$E_{n,vJ} = hc \sum_{i=0,j=0} Y_{ij}\left(v+\frac{1}{2}\right)^i [J(J+1)]^j \quad (1)$$

where Y_{ij} is the Dunham coefficients. For $j=0$, Eq. (1) reduces to the vibrational level energy, which is generally expressed as expansions of the anharmonic oscillator limit [17]

$$G_v = \sum_{i=0} Y_{i0}\left(v+\frac{1}{2}\right)^i = T_e + \omega_e\left(v+\frac{1}{2}\right) - \omega_e\chi_e\left(v+\frac{1}{2}\right)^2$$

$$+ \omega_e y_e\left(v+\frac{1}{2}\right)^3 + \cdots \quad (2)$$

And the internal rotational constant for this vibrational level can be expanded as [17]

$$B_v = \sum_{i=0} Y_{i1}\left(v+\frac{1}{2}\right)^i = B_e - \alpha_e\left(v+\frac{1}{2}\right) + \gamma_e\left(v+\frac{1}{2}\right)^2 + \cdots \quad (3)$$

Moreover, analogous power series expansions in $(v+1/2)$ are used to express the *v*-dependence of the other rotational constants D_v (for *j*=2), H_v (for *j*=3), etc. [24]. It is simple and convenient to calculate the level energies by Dunham expansion. However, the Dunham coefficients in the literature are usually fitted by lower-lying levels due to the difficulty in measuring the higher-lying levels. Hence, the Dunham coefficients are only valid for the lower-lying rovibrational levels. Thus, the higher-lying rovibrational levels calculated by the fitted Dunham coefficients maybe diverge from the exact energies, which are very important in the calculation of the partition function at high temperatures.

Inspired by the work of da Silva et al. [18], we present a more precise calculation of the rovibrational level energies for all the electronic states of N_2, N_2^+, NO, O_2, CN, C_2, CO and CO^+ by resolving the rotational dependence of the radial Schrödinger equation over the accurate potential curves. And the potential curves are reconstructed by combining the well-known Rydberg–Klein–Rees (RKR) method [19–21] and ab-initio calculations [26,27]. Using the same cut-off criterion, the number of the vibrational and rotational levels predicted by this method is larger than those derived from the Dunham expansion. The increment of the level number is investigated due to its importance in the partition functions. After obtaining the rovibrational level energies, we calculate the equilibrium partition functions and thermodynamic properties of N_2, N_2^+, NO, O_2, CN, C_2, CO and CO^+. The non-equilibrium partition functions and thermodynamic properties of these molecules in the framework of the two-temperature model are also computed and studied considering the vibrational and rotational temperatures ranging from 1000 K to 50000 K. Moreover, the spectral radiative properties of diatomic molecules in air and CO_2–N_2 plasmas are investigated. This paper is organized as follows. In Section 2, we briefly describe the improved approach for the energy level calculation. The method to determine the maximum vibrational and rotational quantum number is also given. In Sections 3 and 4, the equilibrium and non-equilibrium thermodynamic properties are given and discussed. In Section 5, the spectral radiative properties of diatomic molecules required for radiative transfer calculations in air and CO_2–N_2 plasmas are investigated. In Section 6, conclusions are drawn.