Research paper

Thermodynamic properties for the sodium dimer

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ABSTRACT

We present a closed-form expression of the classical vibrational partition function for the improved Rosen-Morse potential energy model. We give explicit expressions for the vibrational mean energy, vibrational specific heat, vibrational free energy, and vibrational entropy for diatomic molecule systems. The properties of these thermodynamic functions for the Na_2 dimer are discussed in detail. We find that the improved Rosen-Morse potential model is superior to the harmonic oscillator in calculating the heat capacity for the Na_2 molecules.

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1. Introduction

The major contribution of molecular vibrations is to temperature-dependent thermodynamic functions through a partition function and its first two derivatives with respect to temperature. Acquiring an analytical expression for the partition function is very useful and informative. The molecular vibrational partition function can be calculated by direct summation over all possible vibrational energy levels. Many efforts have been made to acquire explicit expressions of partition functions for molecular potential energy models in diatomic molecules and polyatomic molecules [1–15]. The anharmonicity of molecular vibrations play an important role in calculations of thermodynamic functions. The Morse potential is the most simple and realistic anharmonic potential model, which has been widely used in the description of vibrational motion of diatomic molecules. By employing various approaches, ones constructed explicit expressions for the vibrational partition function of the Morse potential [1–3]. The vibrational partition function is of great importance to many issues in chemical physics and engineering, including calculations of thermodynamic functions [11–13], investigations of isotope fractionation during chemisorption reactions [14], and modeling of the equilibrium constant of gas phase reaction [15].

By employing the dissociation energy and the equilibrium bound length for diatomic molecules as explicit parameters, the authors in literature [16] generated an improved Rosen–Morse potential energy model based on the original Rosen–Morse potential function [17]. The improved Rosen-Morse potential serves as a simple and real model for describing vibration motion of diatomic molecules. By using the parametric Nikiforov–Uvarov method, Akanni1 and Kazeem [18] investigated analytical solutions of the Klein-Gordon equation with the improved Rosen-Morse potential, and Aguda [19] studied approximate analytical solutions of the Dirac equation with the improved Rosen-Morse potential under the conditions of spin and pseudospin symmetry. The improved Rosen-Morse potential model can well model the interaction potential curves for the $3^3\Sigma_g^+$ state of the Cs_2 molecule and the $5^1\Delta_g$ state of the Na_2 molecule [20,21]. Since the experimental realization of Bose-Einstein condensation in cold dilute gases of alkali-metal atoms [22–26], the investigation of various properties for alkali-metal dimers has long been an important field of activity.

In this work, we apply rotation-vibrational energy level expressions of the improved Rosen–Morse potential energy model to calculate the partition function of fundamental vibrations, and investigate thermodynamic properties for the sodium dimer.

2. Thermodynamic properties of a diatomic molecule

The improved Rosen-Morse potential model for diatomic molecules is given by [16]

$$U_{IRM}(r) = D_e \left(1 - \frac{e^{\alpha r_e} + 1}{e^{\alpha r} + 1} \right)^2, \tag{1}$$

where r the internuclear separation, r_e is the equilibrium bond length, D_e is the dissociation energy, and α is an adjustable parameter, which governs the range of the interaction. Conventionally, the range decreases as α increases. By employing the Pekeris approximation [27] scheme to deal with the centrifugal term, Liu et al. [20] solved the three-dimensional Schrödinger equation with the improved Rosen-Morse potential, and obtained the rotation-vibrational energy expression for diatomic molecules. They [20] found that the vibrational energy levels predicted by using the improved Rosen-Morse potential energy model are in good agreement with the experimental data for the $3^3\Sigma_g^+$ state of the Cs_2 molecule and the $5^1\Delta_g$ state of the Na_2 molecule. The value of parameter α can be determined in terms of the

expression $\alpha = \pi c \omega_e \sqrt{\frac{2\mu}{D_e}} + \frac{1}{r_e} W\left(\pi c \omega_e r_e \sqrt{\frac{2\mu}{D_e}} e^{-\pi c \omega_e r_e \sqrt{\frac{2\mu}{D_e}}}\right)$ [20],

where μ is the reduced mass of a diatomic molecule, c is the speed of light, ω_e is the equilibrium harmonic vibrational frequency, and W is the Lambert W function, which satisfies $z = W(z)e^{W(z)}$ [28].

The rotation-vibrational energy levels of the improved Rosen-Morse potential for diatomic molecules are given by [20]

$$E_{\nu J} = D_e + \frac{J(J+1)\hbar^2}{2\mu r_e^2} d_0$$
$$- \frac{\hbar^2\alpha^2}{2\mu}\left[\frac{\frac{2\mu}{\hbar^2\alpha^2}D_e(e^{2\alpha r_e}-1) + \frac{J(J+1)}{\alpha^2 r_e^2}(d_1+d_2)}{2\nu+1 - \sqrt{1 + \frac{4J(J+1)}{\alpha^2 r_e^2}d_2 + \frac{8\mu}{\hbar^2\alpha^2}D_e(e^{\alpha r_e}+1)^2}}\right.$$
$$\left. - \frac{2\nu+1 - \sqrt{1 + \frac{4J(J+1)}{\alpha^2 r_e^2}d_2 + \frac{8\mu}{\hbar^2\alpha^2}D_e(e^{\alpha r_e}+1)^2}}{4}\right]^2, \quad (2)$$

where $\nu = 0, 1, 2, 3, \ldots, \nu_{max}$, ν_{max} denotes the upper bound vibration quantum number, $\hbar = h/2\pi$, h denotes the Planck constant, ν and J are the vibrational and rotational quantum numbers, respectively. The coefficients d_0, d_1, and d_2 are given by [20]

$$d_0 = 1 + \frac{1}{\alpha^2 r_e^2}(3 - 3\alpha r_e + 6e^{-\alpha r_e} + 3e^{-2\alpha r_e} - 2\alpha r_e e^{-\alpha r_e} + \alpha r_e e^{-2\alpha r_e}), \quad (3)$$

$$d_1 = \frac{2}{\alpha^2 r_e^2}(-9 + 3\alpha r_e - 3e^{\alpha r_e} + 2\alpha r_e e^{\alpha r_e} - 9e^{-\alpha r_e} - 3e^{-2\alpha r_e} - \alpha r_e e^{-2\alpha r_e}), \quad (4)$$

$$d_2 = \frac{1}{\alpha^2 r_e^2}(18 + 12e^{\alpha r_e} + 3e^{2\alpha r_e} - 2\alpha r_e e^{\alpha r_e} - \alpha r_e e^{2\alpha r_e} + 12e^{-\alpha r_e}$$
$$+ 3e^{-2\alpha r_e} + 2\alpha r_e e^{-\alpha r_e} + \alpha r_e e^{-2\alpha r_e}). \quad (5)$$

The pure vibrational energy levels read as

$$E_\nu = D_e - \frac{\hbar^2\alpha^2}{2\mu}\left[\frac{\frac{2\mu}{\hbar^2\alpha^2}D_e(e^{2\alpha r_e}-1)}{2\nu+1 - \sqrt{1 + \frac{8\mu}{\hbar^2\alpha^2}D_e(e^{\alpha r_e}+1)^2}}\right.$$
$$\left. - \frac{2\nu+1 - \sqrt{1 + \frac{8\mu}{\hbar^2\alpha^2}D_e(e^{\alpha r_e}+1)^2}}{4}\right]^2. \quad (6)$$

Eq. (6) is not valid once the vibrational energy levels to decrease with increasing ν. The closest to the maximum value allowed can be determined by putting $dE_\nu/d\nu = 0$,

$$\nu_{max} = \left[\sqrt{\frac{1}{4} + \frac{2\mu D_e(e^{\alpha r_e}+1)^2}{\hbar^2\alpha^2}} - \frac{1}{2}(1 + \sqrt{\frac{8\mu D_e(e^{2\alpha r_e}-1)}{\hbar^2\alpha^2}})\right], \quad (7)$$

where square bracket in Eq. (7) means the biggest integer inferior to ν.

The vibrational partition function can be determined by direct summation over all possible vibrational energy levels,

$$Q = \sum_{\nu=0}^{\nu_{max}} e^{-\beta E_\nu}, \quad (8)$$

where $\beta = \frac{1}{kT}$, k is the Boltzmann's constant, and T is the temperature. With the help of the closed-form expression (6) for the vibrational energy levels, we obtain the following expression

$$Q = \sum_{\nu=0}^{\nu_{max}} e^{-\beta\left(D_e - \frac{\hbar^2\alpha^2}{2\mu}\left(\frac{\frac{2\mu}{\hbar^2\alpha^2}D_e(e^{2\alpha r_e}-1)}{2\nu+1 - \sqrt{1 + \frac{8\mu}{\hbar^2\alpha^2}D_e(e^{\alpha r_e}+1)^2}} - \frac{2\nu+1 - \sqrt{1 + \frac{8\mu}{\hbar^2\alpha^2}D_e(e^{\alpha r_e}+1)^2}}{4}\right)^2\right)}. \quad (9)$$

For a finite summation with the upper bound ν_{max}, the Poisson summation formula reads as [2]

$$\sum_{\nu=0}^{\nu_{max}} f(\nu) = \frac{1}{2}[f(0) - f(\nu_{max}+1)] + \sum_{m=-\infty}^{\infty} \int_0^{\nu_{max}+1} f(x)e^{-i2\pi mx}dx. \quad (10)$$

We only consider the lowest-order approximation which retains only the term with $m = 0$ in above equation, and omit the quantum corrections which include the terms with $m \neq 0$. In this case, the corresponding partition function is recognized as the classical partition function. In the case of neglecting the terms with $m \neq 0$, the summation formula (10) turns to the following form

$$\sum_{\nu=0}^{\nu_{max}} f(\nu) = \frac{1}{2}[f(0) - f(\nu_{max}+1)] + \int_0^{\nu_{max}+1} f(x)dx. \quad (11)$$

In terms of expression (11), we rewrite Eq. (9) as

$$Q = \frac{1}{2}\left[e^{-\beta(D_e-\lambda k_1^2)} - e^{-\beta(D_e-\lambda k_2^2)}\right] + \int_0^{\nu_{max}+1} e^{-\beta\left(D_e - \lambda\left(\frac{a}{x+b} - \frac{x+b}{2}\right)^2\right)}dx, \quad (12)$$

where $\lambda = \frac{\hbar^2\alpha^2}{2\mu}$, $a = \frac{\mu}{\hbar^2\alpha^2}D_e(e^{2\alpha r_e}-1)$, $b = \frac{1}{2}\left(1 - \sqrt{1 + \frac{8\mu D_e(e^{\alpha r_e}+1)^2}{\hbar^2\alpha^2}}\right)$, $k_1 = \frac{a}{b} - \frac{b}{2}$, and $k_2 = \frac{a}{\nu_{max}+1+b} - \frac{\nu_{max}+1+b}{2}$. With the help of the imaginary error function, we calculate the integral part in the right-hand side of Eq. (12), and obtain the following vibrational partition function for diatomic molecules represented by the improved Rosen-Morse potential model,

$$Q = \frac{1}{2}e^{-\beta D_e}\left[e^{\beta\lambda k_1^2} - e^{\beta\lambda k_2^2} + \sqrt{\frac{\pi}{\lambda}}\frac{1}{\sqrt{\beta}}\left(\text{erfi}(\sqrt{\beta\lambda}k_1) - \text{erfi}(\sqrt{\beta\lambda}k_2)\right.\right.$$
$$\left.\left. - e^{-2\beta\lambda a}\text{erfi}(\sqrt{\beta\lambda}(2a+k_1)) + e^{-2\beta\lambda a}\text{erfi}\left(\sqrt{\beta\lambda}(2a+k_2)\right)\right)\right]. \quad (13)$$

This partition function is the classical partition function, not including quantum corrections. The imaginary error function, denoted erfi, is defined as [29]

$$\text{erfi}(z) = -i\,\text{erf}(iz) = \frac{2}{\sqrt{\pi}}\int_0^z e^{t^2}dt, \quad (14)$$