



## Research paper

## Thermodynamic properties for the lithium dimer



Chun-Sheng Jia\*, Lie-Hui Zhang, Chao-Wen Wang

State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, People's Republic of China

## ARTICLE INFO

## Article history:

Received 10 November 2016

In final form 30 November 2016

Available online 1 December 2016

## Keywords:

Partition function

Thermochemistry

Lithium dimer

## ABSTRACT

We present an explicit expression of the vibrational partition function for the improved Manning-Rosen potential energy model. We give analytical expressions for the vibrational mean energy, vibrational specific heat, vibrational free energy, and vibrational entropy for diatomic molecules. The properties of these thermodynamic functions for the  $a^3\Sigma_u^+$  state of the  ${}^7\text{Li}_2$  molecule are discussed in detail.

© 2016 Published by Elsevier B.V.

## 1. Introduction

The lithium dimer,  ${}^7\text{Li}_2$  or  ${}^6\text{Li}_2$ , is the second smallest stable homonuclear molecule next to  $\text{H}_2$ , and due to that, it has received considerable attention both theoretically and experimentally [1–12]. Since the discovery by Bradley and coworkers [3] of Bose-Einstein condensation in  ${}^7\text{Li}_2$ , many efforts have been made to determine the scattering length of two ground state lithium atoms from an internuclear potential energy curve of the lowest triplet  $a^3\Sigma_u^+$  state of  ${}^7\text{Li}_2$ . The stability of the  ${}^7\text{Li}_2$  Bose-Einstein condensation is sensitive to the last bound vibrational level.  ${}^7\text{Li}$  atoms have a negative *s*-wave scattering length, it shows that the interatomic interactions are effectively attractive for a sufficiently cold and dilute gas. Many authors [5–12] have investigated the vibrational levels and the interatomic interaction potential for the  $a^3\Sigma_u^+$  state of  ${}^7\text{Li}_2$  in terms of the Rydberg-Klein-Rees (RKR) method [13–15] and ab initio approach [16]. Besides this contribution to the stability of Bose-Einstein condensation, the major contribution of vibrations is to temperature-dependent thermodynamic functions through the molecular partition function. However, as far as we know, one has not reported any investigation on vibrational contribution to thermodynamic properties of the  ${}^7\text{Li}_2$  molecular gas. Hence, the main topic of the present work is to carry out available calculations on the thermodynamic functions for the  $a^3\Sigma_u^+$  state of  ${}^7\text{Li}_2$ .

Analytical representations of thermodynamic functions of gases over the whole temperature range from zero to the thermal dissociation limit have aroused much interest in dealing with diatomic and polyatomic systems [17–26]. Vibrational contribution to vari-

ous thermodynamic properties of a molecular gas is expressed by using a partition function and its first two derivatives with respect to temperature. The vibrational partition function can be calculated in terms of molecular vibrational energy levels. Rotation-vibrational energy levels for diatomic molecules can be obtained from the direct solutions of the Schrödinger equation with diatomic molecule potential energy models [11,12]. The improved Manning-Rosen potential model [27] can well model the interaction potential curve for the  $a^3\Sigma_u^+$  state of the  ${}^7\text{Li}_2$  molecule [11]. The average absolute deviation of the improved Manning-Rosen potential for the  $a^3\Sigma_u^+$  state of  ${}^7\text{Li}_2$  from the ab initio potential reported by Halls et al. [6] is 0.178% of dissociation energy  $D_e$  [11]. This situation encourages us to apply rotation-vibrational energy level expressions derived in the previous work [11] to calculate the partition function of fundamental vibrations, and investigate thermodynamic properties for the lithium dimer.

## 2. Thermodynamic properties of a diatomic molecule

Based on a diatomic potential function proposed by Manning and Rosen [28], Wang et al. [27] proposed the improved Manning-Rosen potential model for diatomic molecules,

$$U_{\text{MR}}(r) = D_e \left( 1 - \frac{e^{\alpha r_e} - 1}{e^{\alpha r} - 1} \right)^2, \quad (1)$$

where  $r$  the internuclear separation,  $r_e$  is the equilibrium bond length,  $D_e$  is the dissociation energy, and  $\alpha$  is a adjustable parameter, which governs the range of the interaction. Conventionally, the range decreases as  $\alpha$  increases. The potential parameter  $\alpha$  can be determined by employing the expression  $\alpha = \pi C \omega_e \sqrt{\frac{2\mu}{D_e}} +$

$\frac{1}{r_e} W \left( -\pi C \omega_e r_e \sqrt{\frac{2\mu}{D_e}} e^{-\pi C \omega_e r_e \sqrt{\frac{2\mu}{D_e}}} \right)$  [11], where  $c$  is the speed of light,

\* Corresponding author.

E-mail address: [chshjia@263.net](mailto:chshjia@263.net) (C.-S. Jia).

$\omega_e$  is the equilibrium harmonic vibrational frequency, and  $W$  is the Lambert  $W$  function, which satisfies  $z = W(z)e^{W(z)}$  [29]. By solving the Schrödinger equation with the improved Manning-Rosen potential, Liu et al. [11] obtained the rotation-vibrational energy level expression for a diatomic molecule represented by the same potential model. It is given by [11]

$$E_{vj} = D_e + \frac{\hbar^2 \omega_e^2 J(J+1)}{2\mu} - \frac{\hbar^2 \omega_e^2}{2\mu} \left( \frac{\frac{2\mu}{\hbar^2 \omega_e^2} D_e (e^{2xre} - 1)}{2\nu+1 + \sqrt{(1+2J)^2 + \frac{8\mu D_e (e^{2xre} - 1)^2}{\hbar^2 \omega_e^2}}} - \frac{2\nu+1 + \sqrt{(1+2J)^2 + \frac{8\mu D_e (e^{2xre} - 1)^2}{\hbar^2 \omega_e^2}}}{4} \right)^2, \quad (2)$$

where  $\nu = 0, 1, 2, 3, \dots, \nu_{\max}$ ,  $\mu$  is the reduced mass of a diatomic molecule,  $\hbar$  denotes the reduced Planck constant,  $\nu$  and  $J$  are the vibrational and rotational quantum numbers, respectively. The upper bound vibrational quantum number  $\nu_{\max}$  reads as  $\nu_{\max} = \left\lfloor \sqrt{\frac{2\mu D_e (e^{2xre} - 1)}{\hbar^2 \omega_e^2}} - \frac{1}{2} \left( 1 + \sqrt{(1+2J)^2 + \frac{8\mu D_e (e^{2xre} - 1)^2}{\hbar^2 \omega_e^2}} \right) \right\rfloor$ ,  $\lfloor n \rfloor$  means the biggest integer inferior to  $n$ . The pure vibrational energy levels can be written as

$$E_\nu = D_e - \frac{\hbar^2 \omega_e^2}{2\mu} \left( \frac{\frac{2\mu}{\hbar^2 \omega_e^2} D_e (e^{2xre} - 1)}{2\nu+1 + \sqrt{1 + \frac{8\mu D_e (e^{2xre} - 1)^2}{\hbar^2 \omega_e^2}}} - \frac{2\nu+1 + \sqrt{1 + \frac{8\mu D_e (e^{2xre} - 1)^2}{\hbar^2 \omega_e^2}}}{4} \right)^2. \quad (3)$$

Partition functions are the starting point to derive thermodynamic data. The vibrational partition function can be calculated by direct summation over all possible vibrational energy levels available to the system,

$$Q = \sum_{\nu=0}^{\nu_{\max}} e^{-\beta E_\nu}, \quad (4)$$

where  $\beta = \frac{1}{kT}$ ,  $k$  is the Boltzmann's constant, and  $T$  is the temperature. Substituting expression (3) into Eq. (4), we have

$$Q = \sum_{\nu=0}^{\nu_{\max}} e^{-\beta \left( D_e - \frac{\hbar^2 \omega_e^2}{2\mu} \left( \frac{\frac{2\mu}{\hbar^2 \omega_e^2} D_e (e^{2xre} - 1)}{2\nu+1 + \sqrt{1 + \frac{8\mu D_e (e^{2xre} - 1)^2}{\hbar^2 \omega_e^2}}} - \frac{2\nu+1 + \sqrt{1 + \frac{8\mu D_e (e^{2xre} - 1)^2}{\hbar^2 \omega_e^2}}}{4} \right)^2 \right)} \quad (5)$$

For a finite summation with the upper bound  $N$ , the Poisson summation formula can be written as [18]

$$\sum_{n=0}^N f(n) = \frac{1}{2} [f(0) + f(N+1)] + \sum_{m=-\infty}^{\infty} \int_0^{N+1} f(x) e^{-i2\pi mx} dx. \quad (6)$$

Under the lowest-order approximation, the above summation formula becomes the following form

$$\sum_{n=0}^N f(n) = \frac{1}{2} [f(0) + f(N+1)] + \int_0^{N+1} f(x) dx. \quad (7)$$

With the help of expression (7), we write Eq. (5) in the following form

$$Q = \frac{1}{2} \left[ e^{-\beta(D_e - \lambda c_1^2)} - e^{-\beta(D_e - \lambda c_2^2)} \right] + \int_0^{\nu_{\max}+1} e^{-\beta \left( D_e - \lambda \left( \frac{a}{x+b} \right)^2 \right)} dx, \quad (8)$$

where  $\lambda = \frac{\hbar^2 \omega_e^2}{2\mu}$ ,  $a = \frac{\mu}{\hbar^2 \omega_e^2} D_e (e^{2xre} - 1)$ ,  $b = \frac{1}{2} \left( 1 + \sqrt{1 + \frac{8\mu D_e (e^{2xre} - 1)^2}{\hbar^2 \omega_e^2}} \right)$ ,  $c_1 = \frac{a}{b} - \frac{b}{2}$ , and  $c_2 = \frac{a}{\nu_{\max}+1+b} - \frac{\nu_{\max}+1+b}{2}$ . The integral in the right-hand side of Eq. (8) is expressed in terms of the imaginary error function. After some manipulations, we obtain the following expression of the vibrational partition function for a diatomic mole-

cule represented by the improved Manning-Rosen potential energy model,

$$Q = \frac{1}{2} e^{-\beta D_e} \left[ e^{\beta \lambda c_1^2} - e^{\beta \lambda c_2^2} + \sqrt{\frac{\pi}{\lambda}} \frac{1}{\sqrt{\beta}} \left( \operatorname{erfi}(\sqrt{\beta \lambda} c_1) - \operatorname{erfi}(\sqrt{\beta \lambda} c_2) - e^{-2\beta \lambda a} \operatorname{erfi}(\sqrt{\beta \lambda} (2a + c_1)) + e^{-2\beta \lambda a} \operatorname{erfi}(\sqrt{\beta \lambda} (2a + c_2)) \right) \right]. \quad (9)$$

The imaginary error function, denoted  $\operatorname{erfi}$ , is defined as [30]

$$\operatorname{erfi}(z) = -i \operatorname{erf}(iz) = \frac{2}{\sqrt{\pi}} \int_0^z e^{t^2} dt, \quad (10)$$

where  $\operatorname{erf}$  denotes the error function, which is a special function of sigmoid shape. The imaginary error function is implemented in Maple as  $\operatorname{erfi}(z)$ , and can easily be calculated numerically.

In deducing expression (9) from Eq. (5), we have used the lowest-order approximation which retains only the term with  $m = 0$  in Eq. (6). This term is recognized as the classical partition function, the terms with  $m \neq 0$  give the quantum corrections [18]. The partition function (9) is the classical vibrational partition function, all quantum corrections are omitted. At high temperatures, when  $\beta \ll 1$ , expression (9) of the vibrational partition function  $Q$  can be represented as a power series,

$$\begin{aligned} Q &= c_1 - c_2 - \sqrt{2a+c_1} + \sqrt{2a+c_2} + \left[ \frac{1}{2} \lambda c_1^2 - \frac{1}{2} \lambda c_2^2 + \frac{1}{3} \lambda c_1^3 - \frac{1}{3} \lambda c_2^3 \right. \\ &\quad - \frac{1}{3} \lambda (2a+c_1) \sqrt{2a+c_1} + 2\lambda a \sqrt{2a+c_1} + \frac{1}{3} \lambda (2a+c_2) \sqrt{2a+c_2} \\ &\quad \left. - 2\lambda a \sqrt{2a+c_2} - D_e (c_1 - c_2 - \sqrt{2a+c_1} + \sqrt{2a+c_2}) \right] \beta \\ &\quad + \left[ \frac{1}{4} \lambda^2 c_1^4 - \frac{1}{4} \lambda^2 c_2^4 + \frac{1}{2} (\frac{1}{5} \lambda^2 c_1^5 - \frac{1}{5} \lambda^2 c_2^5 - \frac{1}{5} \lambda^2 (2a+c_1)^2 \sqrt{2a+c_1} \right. \\ &\quad \left. - 4\lambda^2 a^2 \sqrt{2a+c_1} + \frac{4}{3} \lambda^2 a (2a+c_1) \sqrt{2a+c_1} + \frac{1}{5} \lambda^2 (2a+c_2)^2 \sqrt{2a+c_2} \right. \\ &\quad \left. + 4\lambda^2 a^2 \sqrt{2a+c_2} - \frac{4}{3} \lambda^2 a (2a+c_2) \sqrt{2a+c_2} \right] \beta^2 \\ &\quad + \frac{1}{2} D_e^2 (c_1 - c_2 - \sqrt{2a+c_1} + \sqrt{2a+c_2}) - \frac{1}{2} D_e (\lambda c_1^2 - \lambda c_2^2 + \frac{2}{3} \lambda c_1^3 \\ &\quad - \frac{2}{3} \lambda c_2^3 - \frac{2}{3} \lambda (2a+c_1) \sqrt{2a+c_1} + 4\lambda a \sqrt{2a+c_1} \\ &\quad \left. + \frac{2}{3} \lambda (2a+c_2) \sqrt{2a+c_2} - 4\lambda a \sqrt{2a+c_2}) \right] \beta^3 + \dots \end{aligned} \quad (11)$$

With the help of the vibrational partition function, one can determine the thermodynamic functions for the diatomic molecule system by using following formulas:

#### (1) Vibrational mean energy $U$

$$\begin{aligned} U &= -\frac{\partial \ln Q}{\partial \beta} \\ &= - \left[ e^{\beta \lambda c_1^2} - e^{\beta \lambda c_2^2} + \sqrt{\frac{\pi}{\lambda}} \frac{1}{\sqrt{\beta}} \left( \operatorname{erfi}(\sqrt{\beta \lambda} c_1) - \operatorname{erfi}(\sqrt{\beta \lambda} c_2) - e^{-2\beta \lambda a} \operatorname{erfi}(\sqrt{\beta \lambda} (2a + c_1)) + e^{-2\beta \lambda a} \operatorname{erfi}(\sqrt{\beta \lambda} (2a + c_2)) \right) \right]^{-1} \\ &\quad \times \left[ - (D_e - \lambda c_1^2) e^{\beta \lambda c_1^2} + (D_e - \lambda c_2^2) e^{\beta \lambda c_2^2} - \sqrt{\frac{\pi}{\lambda}} \left( \frac{D_e}{\sqrt{\beta}} + \frac{1}{2\beta^{3/2}} \right) \right. \\ &\quad \times \left( \operatorname{erfi}(\sqrt{\beta \lambda} c_1) - \operatorname{erfi}(\sqrt{\beta \lambda} c_2) - e^{-2\beta \lambda a} \operatorname{erfi}(\sqrt{\beta \lambda} (2a + c_1)) \right. \\ &\quad \left. \left. + e^{-2\beta \lambda a} \operatorname{erfi}(\sqrt{\beta \lambda} (2a + c_2)) \right) \right. \\ &\quad \left. + \frac{c_1}{\beta} e^{\beta \lambda c_1^2} - \frac{c_2}{\beta} e^{\beta \lambda c_2^2} + \frac{2a\sqrt{\pi}\lambda e^{-2\beta \lambda a}}{\sqrt{\beta}} \operatorname{erfi}(\sqrt{\beta \lambda} (2a + c_1)) - \frac{\sqrt{2a+c_1}}{\beta} e^{\beta \lambda c_1} \right. \\ &\quad \left. - \frac{2a\sqrt{\pi}\lambda e^{-2\beta \lambda a}}{\sqrt{\beta}} \operatorname{erfi}(\sqrt{\beta \lambda} (2a + c_2)) + \frac{\sqrt{2a+c_2}}{\beta} e^{\beta \lambda c_2} \right] \end{aligned} \quad (12)$$

Download English Version:

<https://daneshyari.com/en/article/5378496>

Download Persian Version:

<https://daneshyari.com/article/5378496>

[Daneshyari.com](https://daneshyari.com)