



Short Communication

Enthalpy of gaseous phosphorus dimer

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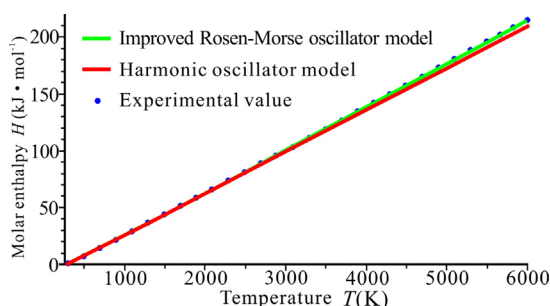
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HIGHLIGHTS

- We present an explicit representation of molar entropy for gaseous substances.
- Improved Rosen-Morse oscillator is used to describe the internal vibration.
- Entropy values of gaseous phosphorus dimer are excellently predicted.

GRAPHICAL ABSTRACT



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ABSTRACT

We present an explicit representation of molar enthalpy for gaseous substances based on the improved Rosen-Morse oscillator to describe the internal vibration of a molecule. We calculate molar enthalpy values of gaseous phosphorus dimer in terms of experimental values of three molecular constants, and obtain excellent agreement between the calculated values and experimental data in a temperature range of 298–6000 K.

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1. Introduction

Investigations of structure and spectrum for phosphorus-containing radicals have attracted much attention. The interest possibly arises from the contribution to the etching and epitaxial growth of phosphorus-containing semiconductors (Donnelly and Karlicek, 1982; Howe et al., 1993). Phosphorus is known to form a wide range of homoatomic clusters. The simplest phosphorus-containing radical is the homonuclear species, phosphorus dimer

(P₂), the second-row analogue of nitrogen molecule. The P₂ radical has received considerable experimental and theoretical interests in its molecular properties. Howe et al. (1993) generated the P₂ radicals by passing a spark discharge through a pulsed supersonic expansion of PCl₃ (or PH₃) in argon, and performed the first laser spectroscopic study of the P₂ radical in the gas phase. Heimbrook et al. (1985) examined several forbidden electronic transitions of the dimer P₂ in solid neon. Wu et al. (2012) made assignments of approximately 500 rotational spectral lines and analyzed the rotationally resolved spectra of the P₂ radical in the 16620–17860 cm⁻¹ region. Yilmaz (1992) studied the geometries of the low-lying isomers of the phosphorus

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microclusters P_2 to P_{10} by means of the modified neglect of diatomic overlap method. Bu (1995) carried out calculations of the inner-sphere reorganization energies of the gaseous P_2 radical using an accurate potential energy function and the vibrational spectroscopic experimental data. Wang et al. (2006) investigated the molecular structures and electron affinities of the phosphorus clusters P_n ($n = 1-6$) in terms of seven density functional theory methods. To the best of our knowledge, one has not reported any theoretical investigation on variations of molar enthalpy of the gaseous P_2 radical with respect to temperature. Enthalpy is a combination of the internal energy and the product of the pressure and volume in a thermodynamic system. Calculations of enthalpy changes are important in dealing with various processes, including chemical reaction (Hany et al., 2010; Hughes and Navrotsky, 2011; Suslova et al., 2017), dissolution (Wilder and Smith, 2004), and adsorption (Wu et al., 2013; Stadie et al., 2013; Kim et al., 2009; Mondal et al., 2017). Temperature affects the solubility of a gas in a liquid, and its derivative of the solubility is directly related to the partial molar enthalpy of the gaseous solute in the liquid phase (Wilder and Smith, 2004). The negative or positive value of the enthalpy change determines whether an adsorption process is exothermic or endothermic, respectively (Wu et al., 2013). Measuring enthalpy and calculating enthalpy have been a recurring theme in many fields. Establishing an analytical representation of the molar enthalpy for gaseous substances is of significant interest.

By introducing the dissociation energy and equilibrium bond length as explicit parameters in the original Rosen-Morse potential energy function (Rosen and Morse, 1932), an improved Rosen-Morse potential model has been generated (Jia et al., 2012). Recently, the vibrational partition function of the improved Rosen-Morse oscillator has been analytically derived (Song et al., 2017). Analytical expressions of the vibrational partition functions for some other diatomic molecule potentials have also been obtained and applied to calculate thermodynamic quantities (Jia et al., 2017a,b; Wang et al., 2017; Strelakov, 2007; Toutounji, 2011; Lasaga et al., 2008; Buchowiecki, 2015). By employing the improved Manning-Rosen oscillator to represent the internal vibration of a boron monobromide molecule, Wang et al. (2017) calculated the molar entropy values of gaseous boron monobromide, and obtained a good agreement between the theoretical predictions and experimental values.

The purposes of this paper are twofold. Firstly, we present a molar enthalpy calculation model for the gaseous diatomic molecule substances based on the use of the improved Rosen-Morse oscillator to describe the internal vibration of a molecule. Secondly, molar enthalpy values of the gaseous phosphorus dimer are calculated and compared with the experimental data reported from the literature. The comparison essentially shows that the proposed enthalpy calculation model is suitable for predicting molar enthalpy values of some gaseous substances.

2. Analytical representation of enthalpy

The vibrational partition function of the improved Rosen-Morse oscillator can be read as (Song et al., 2017)

$$Q_{\text{IRMO}}^{\nu} = \frac{1}{2} e^{-\frac{D_e}{kT}} \left[e^{\frac{\eta_1^2}{kT}} - e^{\frac{\eta_2^2}{kT}} + \sqrt{\frac{\pi kT}{\lambda}} \left(\operatorname{erfi} \left(\sqrt{\frac{\lambda}{kT}} \eta_1 \right) - \operatorname{erfi} \left(\sqrt{\frac{\lambda}{kT}} \eta_2 \right) \right) - e^{-\frac{2\mu}{kT}} \operatorname{erfi} \left(\sqrt{\frac{\lambda}{kT}} (2a + \eta_1) \right) + e^{-\frac{2\mu}{kT}} \operatorname{erfi} \left(\sqrt{\frac{\lambda}{kT}} (2a + \eta_2) \right) \right] \quad (1)$$

where $\lambda = \frac{h^2 \alpha^2}{2\mu}$, $a = \frac{\mu}{h^2 \alpha^2} D_e (e^{2\alpha r_e} - 1)$, $b = \frac{1}{2} \left(1 - \sqrt{1 + \frac{8\mu D_e (e^{2\alpha r_e} + 1)^2}{h^2 \alpha^2}} \right)$, $\eta_1 = \frac{a}{b} - \frac{b}{2}$, $\eta_2 = \frac{a}{v_{\max} + 1 + b} - \frac{v_{\max} + 1 + b}{2}$, $\alpha = \pi c \omega_e \sqrt{\frac{2\mu}{D_e}}$, $+ \frac{1}{r_e} W \left(\pi c \omega_e r_e \sqrt{\frac{2\mu}{D_e}} e^{-\pi c \omega_e r_e \sqrt{\frac{2\mu}{D_e}}} \right)$, and $h = h/2\pi$. Here k denotes the Boltzmann's constant, T denotes the temperature, h denotes the Planck constant, c denotes the speed of light, μ denotes the reduced mass of a diatomic molecule, D_e represents the dissociation energy, r_e represents the equilibrium bond length, ω_e represents the frequency of the molecule's equilibrium harmonic vibration, W represents the Lambert W function, which is defined by $z = W(z)e^{W(z)}$ (Corless et al., 1996); v_{\max} is the upper bound vibration quantum number and given according to $v_{\max} = \left\lfloor \sqrt{\frac{1}{4} + \frac{2\mu D_e (e^{2\alpha r_e} + 1)^2}{h^2 \alpha^2}} - \frac{1}{2} \left(1 + \sqrt{\frac{8\mu D_e (e^{2\alpha r_e} - 1)}{h^2 \alpha^2}} \right) \right\rfloor$, where $\lfloor n \rfloor$ denotes the biggest integer referring to n . In expression (1), $\operatorname{erfi}(z)$ denotes the imaginary error function, $\operatorname{erfi}(z) = -i \operatorname{erf}(iz) = \frac{2}{\sqrt{\pi}} \int_0^z e^{t^2} dt$, where erf denotes the usual error function.

The vibrational partition function of a harmonic oscillator can be expressed by the following equation (Schwabl, 2006);

$$Q_{\text{HO}} = \frac{e^{\Theta_v/2T}}{e^{\Theta_v/T} - 1}, \quad (2)$$

where the vibrational characteristic temperature is defined as $\Theta_v = hc\omega_e/k$.

We treat the diatomic molecules as rigid rotors and neglect the interaction between two molecules. Restricting the diatomic molecules in a spatial volume V , the translational partition function and rotational partition function for a molecule are given as (Schwabl, 2006), respectively,

$$Q^t = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V, \quad (3)$$

$$Q^r = \frac{T}{\sigma \Theta_r} \left(1 + \frac{1}{3} \frac{\Theta_r}{T} + \frac{1}{15} \left(\frac{\Theta_r}{T} \right)^2 + \frac{4}{315} \left(\frac{\Theta_r}{T} \right)^3 \right), \quad (4)$$

where m denotes the molecule mass, Θ_r represents the rotational characteristic temperature, $\Theta_r = \frac{h^2}{8\pi^2 \mu r_e^2 k}$ and the values of σ are taken as 1 and 2 for a heteronuclear diatomic molecule and homonuclear diatomic molecule, respectively.

The enthalpy of a quantum oscillator at the temperature T is given by the following expression (Schwabl, 2006);

$$H = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V + kTV \left(\frac{\partial \ln Q}{\partial V} \right)_T. \quad (5)$$

According to this formula, the molar translational, rotational, and vibrational enthalpies are obtained by using expressions (1)–(4), respectively,

$$H^t = \frac{5}{2} RT, \quad (6)$$

$$H^r = RT \frac{315T^3 - 21\Theta_r^2 T - 8\Theta_r^3}{315T^3 + 105\Theta_r T^2 + 21\Theta_r^2 T + 4\Theta_r^3}, \quad (7)$$

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