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Research paper

The ratios of partition functions at different temperatures – Sensitivity to potential energy shape II

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The ratios of partition functions at different temperatures are calculated and its dependence on potential energy shape is analyzed. The role of anharmonicity and non-rigidity of rotations is discussed in the context of the angular frequency and the shape of potential energy curve. A role of inflection point of potential energy curve for the quality of rigid rotor harmonic oscillator and rigid rotor Morse oscillator is elucidated.

1. Introduction

The ratios of partition functions at different temperatures, $Q(T)/Q(T_0)$, can be calculated exactly by the combination of thermodynamic integration [1] and path integral based simulations for energies [2]. Those ratios can be subsequently used for calculation of the temperature dependence of the equilibrium constant [3].

In this Letter the exact values of $Q(T)/Q(T_0)$ were calculated for the harmonic, Morse [4], and Wei-Hua [5] potential energy curves (PEC) and temperature range of 200–2000 K. The choice of PECs is justified in the previous publication [6]. Specifically, this study considers the influence of PEC shape on $Q(T)/Q(T_0)$. The PEC shapes are: the harmonic shape (i.e. parabola) and the shapes of non-harmonic PECs defined as the features of PECs left when the force constant and the depth of a potential are fixed.

H_2, H_2^+ and HF molecules were modeled on the harmonic, Morse and Wei-Hua potential energy curves:

$$\begin{aligned} V_{\mathrm{H}}(r) &= \frac{1}{2}k(r-r_0)^2, \\ V_{\mathrm{M}}(r) &= D_e\left[1-e^{-\alpha(r-r_0)}\right]^2, \\ V_{\mathrm{WH}}(r) &= D_e\left\{\frac{1-e^{-\alpha(1-c)(r-r_0)}}{1-ce^{-\alpha(1-c)(r-r_0)}}\right\}^2, \end{aligned} \tag{1}$$

where k is the force constant ($k_{\mathrm{H}_2} = 0.3693$, $k_{\mathrm{H}_2^+} = 0.1028, k_{\mathrm{HF}} = 0.6203$), r_0 is the bond length ($r_0(\mathrm{H}_2) = 1.4, r_0(\mathrm{H}_2^+) = 2.0, r_0(\mathrm{HF}) = 1.7$), D_e is the potential well depth ($D_e(\mathrm{H}_2) = 0.1646, D_e(\mathrm{H}_2^+) = 0.0974, D_e(\mathrm{HF}) = 0.2149$) [7]; α parameter values are given according to $\alpha = \sqrt{k/(2D_e)}$; c is the parameter of Wei-Hua potential ($c_{\mathrm{H}_2} = 0.17, c_{\mathrm{H}_2^+} = 0.3, c_{\mathrm{HF}} = 0.128$) [5]. For $c = 0$ the Wei-Hua potential becomes the Morse potential, so that parameter c measures the deviation from the latter one.

The rest of the Letter is organized as follows: Section 2 describes the TI/PIMC method for $Q(T)/Q(T_0)$ and the harmonic approximation; Section 3 presents approximation based on the vibrational partition function of the Morse oscillator; in Section 4 the results are analyzed and discussed; in Section 5 the general conclusions are drawn.

2. The exact path integral method and rigid rotor harmonic oscillator approximation

The TI/PIMC method [3] was used to calculate the $Q(200\,\mathrm{K})/Q(2000\,\mathrm{K})$, $Q(200\,\mathrm{K})/Q(400\,\mathrm{K})$, and $Q(400\,\mathrm{K})/Q(2000\,\mathrm{K})$ values for each molecule with the PECs described above. The method combines thermodynamic integration [1] of molecule's energy

$$\frac{Q(\beta)}{Q(\beta_0)} = \exp\left(-\int_{\beta_0}^{\beta} E_{\mathrm{PIMC}}(\beta)d\beta\right), \tag{2}$$

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where $\beta = 1/(k_B T)$ is the inverse temperature, with the PIMC (path integral Monte Carlo) simulations [2]. The Takahashi–Imada factorization [8] (to lower the effective dimension of simulations) and the centroid virial estimator for the energy [9] were used. The TI/PIMC method is the rigorous approach for the partition functions ratios and is not using any approximations or correction factors.

The standard rigid rotor harmonic oscillator (RRHO) approximation (analogous to the one used for isotope effects [10]), which assumes harmonicity of vibrations, separability of rotations, and vibrations and rigid rotor approximation for rotations, was calculated.

The ratio of partition functions for diatomic molecule in the RRHO approximation is

$$\frac{Q(T)}{Q(T_0)} = \frac{Q_{trans}(T)Q_{rot}(T)Q_{vib}(T)}{Q_{trans}(T_0)Q_{rot}(T_0)Q_{vib}(T_0)} = \left(\frac{\beta}{\beta_0}\right)^{-5/2} e^{-\omega(\beta-\beta_0)/2}\,\frac{1-e^{-\omega\beta_0}}{1-e^{-\omega\beta}}, \tag{3}$$

where ω is the angular frequency of the molecule's vibration.

The limiting cases with respect to the angular frequency (the temperatures T and T_0 are fixed) can be inferred:

$$\lim_{\omega\to 0}\frac{Q(T)}{Q(T_0)} = \left(\frac{\beta}{\beta_0}\right)^{-7/2}, \tag{4}$$

which is analogous to the high temperature limit for isotope effects and

$$\lim_{\omega\to \infty}\frac{Q(T)}{Q(T_0)} = 0, \tag{5}$$

which is analogous to the low temperature limit for isotope effects and in this case partition functions at different temperatures can differ by orders of magnitude.

Eq. (3) exploits the form of rotational partition function in which summation is approximated by integral. Such form can be insufficient in situations when the summation of only few factors is needed. The exact expression of rotational partition function can be cast in a series form based on the Euler–Maclaurin summation formula and sometimes is called the Mulholland formula [11]

$$Q_{rot} \approx \frac{2I}{\sigma\beta}\left(1+\frac{1}{3}\left(\frac{\beta}{2I}\right)+\frac{1}{15}\left(\frac{\beta}{2I}\right)^2\right), \tag{6}$$

where I stands for the moment of inertia and σ for symmetry number. The harmonic approximation with this improvement will be abbreviated MRRHO. The use of MRRHO is crucial for molecules with light atoms and at low temperatures.

The angular frequencies for the RRHO and MRRHO were calculated from the PECs described above.

3. Rigid rotor Morse oscillator approximation

Apart from the RRHO approximation, a useful insight is provided by the almost exact vibrational partition function of the Morse oscillator for which the closed form is known [12].

$$Q_{vib,Morse} = \frac{1}{2\sinh(\omega\beta/2)}\exp\left[\frac{\omega^2\beta}{4D_e}\left(\frac{1}{4}+\frac{1}{2\sinh^2(\omega\beta/2)}\right)\right]. \tag{7}$$

For the approximation based on this partition function the RRMO (rigid rotor Morse oscillator) abbreviation will be used. The version with Mulholland formula will be abbreviated MRRMO and it will provide interesting insight because the only factor not included is the non-rigidity of rotations.

Other expressions for the partition function of Morse oscillator can also be the basis of the RRMO and MRRMO approximations like the expression based on algebraic thermodynamics method [13] or the expression in terms of Jacobi elliptic function [14].

4. Results

Tables 1–3 report values of $Q(200\text{ K})/Q(2000\text{ K})$, $Q(200\text{ K})/Q(400\text{ K})$, and $Q(400\text{ K})/Q(2000\text{ K})$ for the H_2, H_2^+ and HF molecules respectively. The values are calculated with the TI/PIMC method on the harmonic, Morse, and Wei-Hua PECs. Uncertainties of the last digit are also given. Additionally, for easier comparison, the relative percent differences from the values in the preceding column are given.

The average energy of a quantum oscillator at the inverse temperature β is given by [15]:

$$E = -\frac{\partial Q(\beta)}{\partial\beta} = \frac{\omega}{2}+\frac{\omega}{e^{\omega\beta}-1}, \tag{8}$$

so that the "quantumness" of the molecule (strictly – of the harmonic molecule) increases with ω i.e. if $\omega \to \infty$ the energy becomes the ground state quantum.

Similarly to the isotope effect case, the deviations form harmonicity are sensitive to the quantumness of the system increasing with the angular frequency ω. The frequencies (in atomic units) are the following: $\omega_{H_2} = 0.02, \omega_{H_2^+} = 0.011, \omega_{HF} = 0.019$ and indeed the respective partition function ratios deviates from harmonicity more for H_2 and HF which have higher ω than H_2^+ (see TI/PIMC Morse columns). Those deviations are not proportional to ω so it is difficult to predict their magnitude.

The deviations of Wei-Hua from Morse values (see TI/PIMC WH columns) are generally small, however can be comparable with deviations from harmonicity at high c parameter in Wei-Hua PEC (H_2^+) especially at high temperatures ($Q(400\text{ K})/Q(2000\text{ K})$). Correlation with force constant is not clear (in contrary to the isotope effect case [6]).

Importance of non-rigidity of molecules is highlighted when the comparison with the MRRMO results is made. The values of $Q(T)/Q(T_0)$ in the MRRMO approximation (Tables 4–6) provides almost always a significant correction of the harmonic values. The remaining difference between the MRRMO approximation and the TI/PIMC Morse values has to be attributed to non-rigidity of rotations. That difference is sometimes significant in comparison with deviations from harmonicity.

Note that comparison with RRMO often overestimates importance non-rigidity of rotations (i.e. deviates from the TI/PIMC values more than MRRMO) especially at low temperatures where RRMO is less accurate than at higher temperatures.

Similar anharmonic correction for isotope effect also gives very good results. $Q(HD)/Q(H_2)$ at 200 K is 39.4 in MRRHO approximation, 36.3 in MRRMO, and 36.9 in TI/PIMC method on Morse PEC [6].

Table 1
The partition function ratios values for H_2 ($k = 0.3693$). The TI/PIMC method (with statistical errors) on the harmonic, Morse and Wei-Hua potential energy curves. Percentage differences from the values in the previous columns are given below.

	TI/PIMC HO	TI/PIMC Morse	TI/PIMC Wei-Hua
Q(200 K)/Q(2000 K)	$2.21(1)\cdot 10^{-9}$	$2.70(1)\cdot 10^{-9}$ 22%	$2.73(1)\cdot 10^{-9}$ 1%
Q(200 K)/Q(400 K)	$7.00(2)\cdot 10^{-5}$	$7.93(2)\cdot 10^{-5}$ 13%	$7.97(2)\cdot 10^{-5}$ 0.5%
Q(400 K)/Q(2000 K)	$3.16(1)\cdot 10^{-5}$	$3.41(1)\cdot 10^{-5}$ 8%	$3.43(1)\cdot 10^{-5}$ 0.5%