The anharmonic effect study of coupled Morse oscillators for the unimolecular reaction

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The importance of anharmonic effect in dissociation of molecular systems especially clusters has been noted. In this paper, we shall study the effect of coupled anharmonic oscillator of the standard bilinear form (SBF) Morse oscillator (MO) potential on unimolecular reaction. We shall use the systematic theoretical approach, YL method, proposed by Yao and Lin (YAO L, et. al. J Phys Chem A, 2007, 111(29): 6722—6729), which can evaluate anharmonic effects on the rate constants based on the transition state theory. In treating the anharmonic effect with the Morse oscillator potential on unimolecular reactions under collision-free conditions by using the RRKM (Rice-Ramsperger-Kassel-Marcus) theory, the inverse Laplace transformation of the partition functions was used to obtain the total amount of state and density of state by using the first-order and the second-order approximations of the saddle-point method. To demonstrate the anharmonic effect of the SBF Morse model, we choose some model systems and a real reaction as examples.

anharmonic effect, standard bilinear form, Morse oscillator, rate constant, RRKM theory

1 Introduction

Recent reviews of the anharmonic effect on unimolecular reactions can be found in refs. [1—5]. Unimolecular reactions and dissociation of molecules are important for many different chemical processes, e.g., atmospheric and combustion chemistry [6], peptide fragmentation [7] and the dissociation of clusters. In molecules or clusters with some vibrational modes corresponding to relatively weak bonds, highly flexible transition state has been used [2,5], showing that anharmonic effects have become very important [3,4]. In this case, the anharmonic potential like Morse potential is commonly used to simulate the bonding; for comparison, the standard bilinear form Morse oscillator (SBFMO) will be used in this paper. During the last few years, there have been several attempts to observe anharmonic effect. Typical features of the anharmonic effect include a decrease in vibrational bond stretching frequencies (a red shift), and an increase in the bond lengths and distance of bond dissociation [3,4]. Several approximate formulas and anharmonic corrections are now available for estimating the anharmonic force field, partition functions, total amount of state, density of state and the rate constants [8,9]. A main purpose of this paper is to compare the anharmonic effect of the SBFMO model with the simple Morse oscillator (SMO) potential model by using the systematic theoretical method proposed by us to treat the anharmonic effect on unimolecular dissociation obtained from the RRKM (Rice-Ramsperger-Kassel-Marcus)10—12 theory.

The SBFMO model was proposed by Watson [13] in 1967. Nearly forty years have elapsed since Watson derived the above model used widely and accepted [14].

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as the simplest and most elegant quantum-mechanical form of Eckart’s[15] classical vibration-rotation Hamiltonian at present. Watson’s Hamiltonian differed by one term (the so-called ‘Watson term’) from that which had been commonly used on experimental grounds[16]. That Watson’s Hamiltonian is correct is now beyond doubt and has been widely used. However, as noted by Sayvetz[17], this formalism needs to be adapted for the case of large amplitude vibrational motion, and as shown by Watson himself[18], it is not appropriate for linear molecules for which the Watson term becomes singular.

Recently, Barone[19,20] used the Watson form of the kinetic-energy operator and a fourth-order expansion of the potential energy, and a second-order perturbative treatment to obtain a SBFMO of asymmetric tops. This model has been applied to the Gaussian03 to determine the anharmonic effect.

For the RRKM theory, the total amount of state and density of state play the crucial role in the calculation of the rate constants. The total amount of state and density of state can be obtained from the inverse Laplace transformations of canonical partition function and its related function. The inverse Laplace transformation can be performed by using the saddle-point method or method of steepest descent[21]. According to the above method, the central point is to calculate the partition function. The present investigations focus on the quantitative examination of the different anharmonic effects on the dissociation of molecules by using SBFMO and SMO, and the interpretation and analysis of the observed kinetic results from the viewpoint of the first-principle calculations will be also given in this paper.

In our previous papers[21,22], we performed ab initio calculations of the potential energy surface (PES) for photodissociation of some molecules and obtained rate constant of the dissociation by using RRKM theory in the harmonic oscillator (HO) approximation, and the importance of anharmonic effect was also discussed in a previous paper by using different potential models. In this paper, the anharmonic effect of SBFMO will be considered for some model systems and a real molecule.

\[
W = \frac{e^{\beta E} Q(\beta^*)}{2\pi \left[1 + \beta^* \left(\frac{\partial^2 \ln Q(\beta^*)}{\partial \beta^*} \right)\right]} \left[1 + \frac{6 \left(\frac{\partial \ln Q(\beta^*)}{\partial \beta^*} \right)}{\beta^*} + \frac{2 \left(\frac{\partial \ln Q(\beta^*)}{\partial \beta^*} \right)^2}{\beta^*} \right] + \ldots
\]

\[
2 \text{ RRKM theory and anharmonic effect}
\]

For a microcanonical system, using the RRKM theory, the unimolecular reaction rate constant for a system with energy \(E\) is given [12]

\[
k_r(E) = \frac{\sigma}{h} \frac{W^*(E - E^*_a)}{\rho(E)},
\]

(2-1)

where \(\sigma\) is the symmetry factor, and \(h\), Planck’s constant, \(W^*(E - E^*_a)\), the total amount of state of the activated complex with activation energy \(E^*_a\), and \(\rho(E)\), the density of the state of the reactant.

In general, from the definition of \(W(E)\), the total amount of state can be expressed as

\[
W(E) = \sum_i H(E - E_i),
\]

(2-2)

where \(H(E - E_i)\) is the Heaviside function. \(W(E)\) can be obtained by direct counting of those state which is below or equal to \(E\). By applying the Laplace transformation to eq. (2-2), we obtain

\[
\int_0^\infty de^{\beta E} W(E) = \frac{Q(\beta)}{\beta} = I[W(E)],
\]

(2-3)

where \(Q(\beta)\) is the partition function of the system, \(\beta = \frac{1}{kT}\), \(k\), Boltzmann’s constant, and \(T\), the temperature of the system. Similarly, from the definition of the density of state \(\rho(E) = \frac{dW(E)}{dE}\), we obtain,

\[
\int_0^\infty de^{\beta E} \rho(E) = Q(\beta) = I[\rho(E)],
\]

(2-4)

\(W(E)\) and \(\rho(E)\) can be obtained from eqs. (2-3) and (2-4) by inverse Laplace transformation respectively.

\[
W(E) = \frac{1}{2\pi i} \oint d\beta e^{\beta E} Q(\beta) = \frac{1}{2\pi i} \oint d\beta e^{\beta f^*(\beta)},
\]

(2-5)

and

\[
\rho(E) = \frac{1}{2\pi i} \oint d\beta e^{\beta E} Q(\beta) = \frac{1}{2\pi i} \oint d\beta e^{\beta f^*(\beta)}. \quad (2-6)
\]

The saddle-point method can be applied to evaluating the \(W(E)\) and \(\rho(E)\) by using the first- and second-order saddle-point approximation for the inverse Laplace transformations. Thus, to the second-order approximation of the steepest descent of \(W(E)\), it can be expressed as