

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]

Received May 30, 2008; accepted July 20, 2008

doi: 10.1007/s11426-008-0125-1

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Supported by the National Natural Science Foundation of China (Grant No. 10704012), NSC (Taiwan), Academia Sinica, and the Natural Science Foundation of Liaoning Province (Grant No. 2006Z064)

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.

2 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]

$$k_u(E) = \frac{\sigma}{h} \cdot \frac{W^\ddagger(E - E_a^\ddagger)}{\rho(E)}, \quad (2-1)$$

where σ is the symmetry factor, and h , Planck's constant, $W^\ddagger(E - E_a^\ddagger)$, the total amount of state of the activated complex with activation energy $E_a^\ddagger$, 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

$$W(E) = \sum_i^{\text{states}} H(E - E_i), \quad (2-2)$$

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

$$\int_0^\infty dE e^{-\beta E} W(E) = \frac{Q(\beta)}{\beta} = L[W(E)], \quad (2-3)$$

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,

$$\int_0^\infty dE e^{-\beta E} \rho(E) = Q(\beta) = L[\rho(E)], \quad (2-4)$$

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

$$W(E) = \frac{1}{2\pi i} \oint d\beta e^{\beta E} \frac{Q(\beta)}{\beta} = \frac{1}{2\pi i} \oint d\beta e^{f_1(\beta)}, \quad (2-5)$$

and

$$\rho(E) = \frac{1}{2\pi i} \oint d\beta e^{\beta E} Q(\beta) = \frac{1}{2\pi i} \oint d\beta e^{f_2(\beta)}. \quad (2-6)$$

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

$$W = \frac{e^{\beta_1^* E} Q(\beta_1^*)}{\sqrt{2\pi \left(1 + \beta_1^{*2} \left(\frac{\partial^2 \ln Q(\beta_1^*)}{\partial \beta_1^{*2}} \right) \right)}} \left[1 + \frac{\left(\frac{\partial^4 \ln Q(\beta_1^*)}{\partial \beta_1^{*4}} \right) + \frac{6}{\beta_1^{*4}}}{8 \left(\left(\frac{\partial^2 \ln Q(\beta_1^*)}{\partial \beta_1^{*2}} \right) + \frac{1}{\beta_1^{*2}} \right)^2} - \frac{5 \left(\left(\frac{\partial^3 \ln Q(\beta_1^*)}{\partial \beta_1^{*3}} \right) - \frac{2}{\beta_1^{*3}} \right)^2}{24 \left(\left(\frac{\partial^2 \ln Q(\beta_1^*)}{\partial \beta_1^{*2}} \right) + \frac{1}{\beta_1^{*2}} \right)^3} + \dots \right], \quad (2-7)$$

where

$$E = \frac{1}{\beta_1^*} - \left[\frac{\partial}{\partial \beta} \ln Q(\beta) \right]_{\beta_1^*}, \quad (2-8)$$

and β_1^* denotes the saddle-point value of β . Similarly, for $\rho(E)$, we have

$$\rho(E) = \frac{e^{\beta_2^* E} Q(\beta_2^*)}{\sqrt{2\pi \left(\frac{\partial^2 \ln Q(\beta_2^*)}{\partial \beta_2^{*2}} \right)}} \left[1 + \frac{\left(\frac{\partial^4 \ln Q(\beta_2^*)}{\partial \beta_2^{*4}} \right)}{8 \left(\frac{\partial^2 \ln Q(\beta_2^*)}{\partial \beta_2^{*2}} \right)^2} - \frac{5 \left(\frac{\partial^3 \ln Q(\beta_2^*)}{\partial \beta_2^{*3}} \right)^2}{24 \left(\frac{\partial^2 \ln Q(\beta_2^*)}{\partial \beta_2^{*2}} \right)^3} + \dots \right], \quad (2-9)$$

where

$$E = - \left[\frac{\partial}{\partial \beta} \ln Q(\beta) \right]_{\beta_2^*}, \quad (2-10)$$

and β_1^* denotes the saddle-point value of β .

From the above discussion, we can see that obtaining the partition function $Q(\beta)$ is crucial in calculating the total amount of state, density of state and the rate constants. For comparison with the anharmonic effect of the SBFMO case, we shall also consider the harmonic oscillator (HO), and SMO cases. For this purpose, we start with

$$Q^\#(E) = \prod_i^{N-1} q_{i,ib}^\#(E), \quad Q(E) = \prod_i^N q_{i,ib}(E), \quad (2-11)$$

where N is the number of the vibration modes of the reactant, and the subscript i and ib are for the SMO and for the SBFMO respectively. That is, $q_{i,ib}^\#(E)$ and $q_{i,ib}(E)$ are the vibrational partition functions of SBFMO for the activated complex and reactant. Then

$$q_i = \sum_{n_i}^{n_i(m)} e^{-\beta E_{n_i}}, \quad q_{ib} = \prod_{j \leq i} \sum_{n_i}^{n_i(m)} \sum_{n_j}^{n_j(m)} e^{-\beta E_{n_i n_j}}, \quad (2-12)$$

where q_i and q_{ib} are for SMO and SBFMO cases, respectively. The anharmonic amount of state and density of state for a system of SMO take a particularly simple form because of the simple energy level expression,

$$E_{n_i} = (n_i + \frac{1}{2})\hbar\omega_i - x_i(n_i + \frac{1}{2})^2\hbar\omega_i. \quad (2-13)$$

The SMO parameter x_i is given by $x_i = \frac{\hbar\omega_i}{4D_{ie}}$, where

D_{ie} is the well depth of the SMO.

For a given molecule, the potential function of nuclear motion can be expanded in terms of normal coordinates Q_i as

$$V(Q) = \frac{1}{2} \sum_i \left(\frac{\partial^2 V}{\partial Q_i^2} \right)_0 Q_i^2 + \frac{1}{3!} \sum_i \sum_j \sum_k \left(\frac{\partial^3 V}{\partial Q_i \partial Q_j \partial Q_k} \right)_0 Q_i Q_j Q_k + \frac{1}{4!} \sum_i \sum_j \sum_k \sum_l \left(\frac{\partial^4 V}{\partial Q_i \partial Q_j \partial Q_k \partial Q_l} \right)_0 Q_i Q_j Q_k Q_l + \dots \quad (2-14)$$

The Morse oscillator is the out-come of Eq. (10) when considering only

$$V_M(Q) = \sum_i \left[\frac{1}{2} \left(\frac{\partial^2 V}{\partial Q_i^2} \right)_0 Q_i^2 + \frac{1}{3!} \left(\frac{\partial^3 V}{\partial Q_i^3} \right)_0 Q_i^3 + \frac{1}{4!} \left(\frac{\partial^4 V}{\partial Q_i^4} \right)_0 Q_i^4 \right] + \dots \quad (2-15)$$

and carrying out the quantum-mechanical perturbation calculation of energy to the second-order approximation using the harmonic-oscillator approximation as the zeroth-order basis set. For the case of coupled Morse oscillators, we use

$$V(Q) = V_M(Q) + \sum_i \sum_{j \neq i} \left[\frac{1}{3!} \left(\frac{\partial^3 V}{\partial Q_i^2 \partial Q_j} \right)_0 Q_i^2 Q_j + \frac{1}{4!} \left(\frac{\partial^4 V}{\partial Q_i^2 \partial Q_j^2} \right)_0 Q_i^2 Q_j^2 \right] + \dots \quad (2-16)$$

and perform the second-order perturbation calculations.

The energy expression for the SBFMO in the quantum numbers of coupled normal modes is given by^[19,20]

$$E_n = \chi_0 + \sum_i \hbar\omega_i (n_i + 1/2) + \sum_i \sum_i \chi_{ii} (n_i + 1/2)^2 \hbar\omega_i + \sum_i \sum_{j < i} \chi_{ij} (n_i + 1/2)(n_j + 1/2), \quad (2-17)$$

where ω_i is the harmonic frequency of the i th vibrational mode, n_i and n_j denote the vibrational quantum numbers of the i th mode and j th mode, respectively. And $n_i(m)$ and $n_j(m)$ denote the maximum values of SBFMO beyond which the oscillator dissociates. The maximum values $n_i(m)$, $n_j(m)$ for eqs. (2-13) and (2-17) are decided by the relation, $\frac{\partial E_{n_i}}{\partial n_i} = 0$. We only include the

possibility of every two modes coupled when three or more modes are considered. Then the smallest $n_i(m)$ value is chosen which is used in the program to calculate the total amount of state and the density of state. For two modes, we have

$$E_n = (n_1 + 1/2)\hbar\omega_1 + (n_2 + 1/2)\hbar\omega_2 + \chi_{11}(n_1 + 1/2)^2\hbar\omega_1 + \chi_{22}(n_2 + 1/2)^2\hbar\omega_2 + \chi_{21}(n_1 + 1/2)(n_2 + 1/2), \quad (2-18)$$

$$\begin{cases} n_1(m) = \frac{\chi_{21}\hbar\omega_2 - 2\chi_{22}\hbar\omega_1\hbar\omega_2}{4\chi_{11}\chi_{22}\hbar\omega_1\hbar\omega_2 - \chi_{21}^2} - \frac{1}{2} \\ n_2(m) = \frac{\chi_{21}\hbar\omega_1 - 2\chi_{11}\hbar\omega_1\hbar\omega_2}{4\chi_{11}\chi_{22}\hbar\omega_1\hbar\omega_2 - \chi_{21}^2} - \frac{1}{2} \end{cases} \quad (2-19)$$

where the maximum values should not exceed the maximum vales obtained from the single mode relation, $\frac{\partial E_{n_i}}{\partial n_i} = 0$.

For the SBFMO, the anharmonic constants (χ) are simple functions of the cubic and quadric force constant, the third (F_{ijk}) and semidiagonal fourth (F_{ijij}) energy derivatives with respect to normal coordinates. We think that the contribution of quadrature scheme, with all indices different, is unimportant. The neglect of them means that in the quadrature scheme, it should not be necessary to include more than three normal coordinates simultaneously. Using a fourth-order expansion of the potential energy, a second-order perturbative treatment results in the above expression for the vibrational energy

(in wave numbers) of asymmetric tops^[19]. It should be noted that the anharmonic constants x_{ij} for various molecules can be obtained by *ab initio* calculations^[19].

It should be noted that there are cases where rotational effects on the rate constants have been experimentally and theoretically demonstrated. However, in most cases, the reaction rate is relatively little affected by rotation. So for simplicity, only the vibrational degrees of freedom will be considered in this paper; the rotational contribution can easily be included.

3 Numerical demonstration

3.1 Application of the SBFMO method to some modeling systems

A main purpose of the present paper is to discuss how the anharmonic effect works due to SBFMO when comparing with that due to SMO from *ab initio* calculations within the framework of the transition state theory. To test the performance of the anharmonic effect of SBFMO discussed in this paper, Tables 1–7 present the comparison of the total amount of state, density of state and rate constants of the HO, SMO and SBFMO cases, and for this purpose, the second-order approximation of saddle-point method is used. In the calculation of the SBFMO case, all the results are obtained by coupling two modes for all the Tables. The total amount of state $W(E)$ for SMO with anharmonic constants $x_i=0.01$ and $x_i=0.1$ is also given for comparing with the results of

Table 1 A comparison of $W(E)$ for the results of the HO case and the SMO case, and the SBFMO case with and without coupling the two modes with $x_{ii}=0.1, 0.01$ and $x_{ij}=0.1, 0.01$, and frequencies $\varepsilon_i=349.75(2) \text{ cm}^{-1}$

$E \text{ (kcal}\cdot\text{mol}^{-1})$		$W(E)$ two modes model for $\varepsilon_i=349.75(2) \text{ cm}^{-1}$							
	Exact results	HO	SMO $x_i=0.01$	SBFMO $x_{ii}=0.01$ $x_{ij}=0.001$	SBFMO $x_{ii}=x_{ij}=0.01$	SMO $x_i=0.1$	SBFMO $x_{ii}=0.1$ $x_{ij}=0.001$	SBFMO $x_{ii}=0.1$ $x_{ij}=0.01$	SBFMO $x_{ii}=x_{ij}=0.1$
1	2	2	2	2	5	2	2	2	4
2	4	4	4	5	14	9	9	9	14
3	8	8	9	9	28	17	17	17	22
4	13	13	14	14	47	22	22	23	24
5	18	18	20	20	74	24	24	24	24
10	60	62	74	75	364	24	24	24	24
20	216	227	364	394	1691	24	24	24	24
30	456	494	982	1083	2404	24	24	24	24
40	850	864	1691	1820	2587	24	24	24	24
50	1313	1337	2164	2257	2646	24	24	24	24
100	5210	5244	2646	2658	2700	24	24	24	24
150	11700	11720	2689	2693	2707	24	24	24	24

Table 2 A comparison of $W(E)$ for the results of the HO case and the SMO case, and the SBFMO case of two coupling modes (612,612) with $x_{ii}=0.1$, 0.01 and $x_{ij}=0.1$, 0.01 and frequencies $\omega_i=612(2)$, 729(2), 1974(1), 3287(1), 3374(1) cm^{-1} for acetylene

E (kcal·mol ⁻¹)	$W(E)$ for acetylene								
	Exact results	HO	SMO $x_i=0.01$	SBFMO $x_{ii}=0.01$ $x_{ij}=0.001$	SBFMO $x_{ii}=0.01$ $x_{ij}=0.01$	SMO $x_i=0.1$	SBFMO $x_{ii}=0.1$ $x_{ij}=0.001$	SBFMO $x_{ii}=0.1$ $x_{ij}=0.01$	SBFMO $x_{ii}=0.1$ $x_{ij}=0.1$
2.31	5	4	4	4	4	6	6	6	6
4.61	15	15	15	15	15	38	35	35	34
9.23	94	99	107	108	110	341	271	275	213
13.8	387	398	450	451	464	1225	915	924	658
18.5	1.21×10^3	1259	1489	1495	1570	3253	2354	2374	1615
23.1	3.23×10^3	3266	4028	4048	4375	7002	4959	4995	3291
27.7	7.34×10^3	7493	9623	9686	10805	13127	9137	9193	5897
36.9	2.98×10^4	30406	42486	42954	50582	33036	22308	22398	13692

Table 3 A comparison of $W(E)$ for the results of the HO case and the SMO case, and the SBFMO case of two coupling modes (3287, 3374) with $x_{ii}=0.1$, 0.01 and $x_{ij}=0.1$, 0.01 and frequencies $\omega_i=612(2)$, 729(2), 1974(1), 3287(1), 3374(1) cm^{-1} for acetylene

E (kcal·mol ⁻¹)	$W(E)$ for acetylene								
	Exact results	HO	SMO $x_i=0.01$	SBFMO $x_{ii}=0.01$ $x_{ij}=0.001$	SBFMO $x_{ii}=0.01$ $x_{ij}=0.01$	SMO $x_i=0.1$	SBFMO $x_{ii}=0.1$ $x_{ij}=0.001$	SBFMO $x_{ii}=0.1$ $x_{ij}=0.01$	SBFMO $x_{ii}=0.1$ $x_{ij}=0.1$
2.31	5	4	4	4	4	6	6	6	6
4.61	15	15	15	15	15	38	38	38	39
9.23	94	99	107	107	107	341	341	341	345
13.8	387	398	450	450	450	1225	1225	1237	1329
18.5	1.21×10^3	1259	1489	1490	1493	3253	3257	3309	3670
23.1	3.23×10^3	3266	4028	4029	4042	7002	7017	7037	7690
27.7	7.34×10^3	7493	9623	9627	9666	13127	13167	12794	13113
36.9	2.98×10^4	30406	42485	42513	42764	33036	33161	28635	22858

SBFMO. Generally, the results of SBFMO are more than those of SMO, except for the energy which is high enough to break some weak bonds in the system. As mentioned above, the anharmonic constants can be approximately determined by *ab initio* calculations using Gaussian03 program.

Firstly, we take two identical modes model system for an example. In Table 1, the first column of $W(E)$ is for the harmonic results. The second and fifth columns are for SMO with anharmonic constant $x_i=0.01$ and 0.1, which are bigger than the results of the harmonic case generally at the low energy. The third and sixth columns are for SBFMO with the anharmonic constant of the coupling term $x_{ij}=0.001$ ($i \neq j$) and the diagonal anharmonic constant $x_{ii}=0.01$ and 0.1 separately. For the small coupling constant, there are no a lot of differences between the SBFMO results and the SMO results. For the forth and seventh columns, the same x_{ij} ($i \neq j$) value of 0.01 has been used, while for the diagonal anharmonic constant, $x_{ii}=0.01$ and 0.1 have been used. The $W(E)$ values of the forth and seventh columns are much bigger than those above-discussed columns. The last column in

Table 1 is for $x_{ii} = x_{ij} = 0.1$, and the significant anharmonic effect is shown. The $W(E)$ values reach their maxima at very low energy of 10.0 kcal/mol (1 cal = 4.184 J). The bigger the anharmonic constant x_{ij} , the bigger the anharmonic effect. The most pronounced anharmonic effect is given in the columns with $x_{ii} = x_{ij}$ ($i \neq j$), and in this case, the SBFMO results reach the maximum values very quickly. Comparing the SMO case with the SBFMO case for $x_{ii} = x_{ij} = 0.01$, the difference is not significant with E increasing from 1.0 kcal/mol to 150.0 kcal/mol as shown in Table 1.

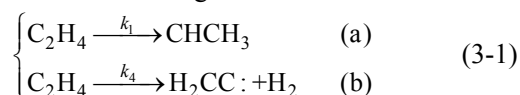
As expected, at low energy, the total amount of state of SMO is bigger than the HO results, and the corresponding SBFMO results with large coupling anharmonic constant are much bigger than the SMO results. As E increases, $W(E)$ increases for all results in Tables 1–3 except for these in Table 1 at energy of 100.0 kcal/mol and 150.0 kcal/mol, which are larger than the energy that breaks all bonds in the system. In most cases, the amount of state for the HO case is much smaller than that of the SMO and SBFMO case for a given anharmonic parameter x_{ii} in the energy range up to the disso-

ciation energy. In Table 1, the difference is from 125.7% to 0.65% in columns 2 and 4. From Table 1, we can see that the $W(E)$ increases rapidly to the maximum at the energy lower than 100.0 kcal/mol with $x_{ii}=0.01$, while in the range of high energy, the $W(E)$ almost does not increase. The results reach the maximum value at 10.0 kcal/mol with $x_{ii}=0.1$ in column 7. The harmonic $W(E)$ invariably increases with the increasing of the energy.

In Table 2, we take the real molecule acetylene as an example. Here only the two smallest modes (612, 612 cm^{-1}) are coupled among the seven modes of acetylene. The other modes are treated as SMO model. The similar conclusion can be derived from Table 2 for acetylene. The total amount of state increases with the energy increasing from 2.31 kcal/mol to 36.9 kcal/mol. In Table 3, for comparison, we take the two biggest modes (3287, 3374 cm^{-1}) among the seven modes of acetylene to be coupled. As expected, the behavior of $W(E)$ vs. E is quite similar except in the high energy range. Compared with Table 2, we are surprised to find that when we couple the big frequencies, no more significant anharmonic effect information is given.

3.2 Application of the SBFMO potential to dissociation of ethylene

Two possible separate reaction channels are shown here for the C_2H_4 photodissociation at 193 and 157 nm under the collision-free condition. The rate equations of the C_2H_4 photodissociation are given^[22]



In Table 4, we apply the SBFMO potential with two coupling modes 1057.169 and 1128.609 (in cm^{-1}) to their large anharmonic coupling constant, to obtain the total amount of state of the transition state 1 (TS1). The TS1 structure is shown in Figure 1, and obtained by using the *ab initio* calculation of Gaussian03 at B3LYP/6-311G** level. The coupling constant x_{21} obtained from *ab initio* calculation is 108.769 cm^{-1} . From Table 4, as expected, the total amount of state of SMO is bigger than HO results, and SBFMO results are bigger than HO and SMO results generally. To our surprise, the SBFMO results decrease with increasing the coupled anharmonic constant (Table 4), which denotes the strength of the mode coupling. Table 5 gives the total amount of state of TS4, whose structure is shown in Figure 1, of ethylene with modes 584.052 and 601.183

(cm^{-1}) coupled. For comparison, the density of state for reactant ethylene is all obtained with HO SMO and SBFMO models in Table 6, which are also necessary for obtaining the rate constants.

Table 4 Total amount of state of ethylene TS1, where the activation energy is 73.36 kcal/mol. The sequence of the TS1 frequency is $\varepsilon_i=1057.169, 1128.609, 1259.723, 1272.358, 1371.866, 1532.73, 2254.256, 2953.27, 2987.303, 3089.01, 960.327$, and corresponding diagonal anharmonic constant is $x_{ii}=32.829, 41.293, 10.707, 1.242, 5.265, 6.498, 3.313, 0.102, 3.675, 0.969, 56.904 \text{ cm}^{-1}$ (the corresponding frequencies are included for couple anharmonic constant). The coupling anharmonic constant is $x_{21}=108.769 \text{ cm}^{-1}$ when coupling the modes 1057.169, 1128.609 cm^{-1}

E (kcal·mol ⁻¹)	HO	SMO	SBFMO $x_{21}=108.769 \text{ cm}^{-1}$
147.584 (193 nm)	1.16×10^7	2.52×10^7	3.97×10^8
182.1146 (157 nm)	3.02×10^8	6.12×10^8	6.96×10^9

Table 5 Total amount of state of ethylene TS4, where the activation energy is 92.80 kcal/mol. The sequence of the TS4 frequency is $\varepsilon_i=584.052, 601.183, 763.5, 859.65, 888.076, 1342.864, 1433.394, 1683.345, 3056.967, 3116.83, 3222.578 \text{ cm}^{-1}$ and corresponding anharmonic constants are $x_{ii}=57.628, 63.157, 115.346, 12.680, 13.54, 73.845, 72.082, 3.776, 2.964, 6.555, 2.504 \text{ cm}^{-1}$ (the corresponding frequencies are included for couple anharmonic constant). The coupling anharmonic constant is $x_{ij}=89.923 \text{ cm}^{-1}$ when coupling the modes 584.052, 601.183 cm^{-1}

E (kcal·mol ⁻¹)	HO	SMO	SBFMO $x_{21}=89.923 \text{ cm}^{-1}$
147.584 (193 nm)	7.92×10^6	7.66×10^6	1.41×10^7
182.1146 (157 nm)	4.66×10^8	2.21×10^8	3.73×10^8

Table 6 Density of state of ethylene C_2H_4 for HO, SMO, SBFMO models

E (kcal·mol ⁻¹)	HO	SMO	SBFMO $x_{21}=56.61 \text{ cm}^{-1}$
147.584 (193 nm)	3.92×10^6	5.00×10^8	7.21×10^{11}
182.1146 (157 nm)	2.76×10^7	2.56×10^9	1.33×10^{12}

The sequence of the frequencies of ethylene used in Table 6 is $\varepsilon_i=3121.7, 3136.9, 834.6, 972.7, 973.3, 1066.4, 1238.7, 1379.5, 1472.0, 1691.6, 3193.2$ and 3221.6 (in cm^{-1}) which are calculated at the B3LYP/6-311G** level by using Gaussian03 program. The corresponding diagonal anharmonic constants are $x_{ii}=16.050, 13.635, 16.312, 13.693, 2.490, 0.570, 0.486, 1.134, 0.1, 0.1, 13.635, 3.498$ and 0.1, and the coupling anharmonic constant is $x_{ij} (i>j)=57.610$ for two modes coupling (the corresponding frequencies are included for couple anharmonic constant).

Using the data in Tables 4–6, we obtain the decomposition rate constants of C_2H_4 corresponding to TS1 and TS4 which are given in Table 7. From the results of

Table 7 Rate constants of decomposition of ethylene C₂H₄ to TS1 and TS4^{a)}

E (kcal·mol ⁻¹)		HO	SMO	SBFMO
k_1	193 nm	8.91×10^{10}	1.51×10^9	$1.65 \times 10^7 (x_{21}=108.769 \text{ cm}^{-1})$
	157 nm	3.28×10^{11}	7.17×10^9	$1.57 \times 10^8 (x_{21}=108.769 \text{ cm}^{-1})$
k_4	193 nm	6.06×10^{10}	4.59×10^8	$5.86 \times 10^5 (x_{21}=89.923 \text{ cm}^{-1})$
	157 nm	5.05×10^{11}	2.59×10^9	$8.41 \times 10^6 (x_{21}=89.923 \text{ cm}^{-1})$

Here we use the value of density of state with $x_{21}=56.61$ for C₂H₄, to get all the data in this table.

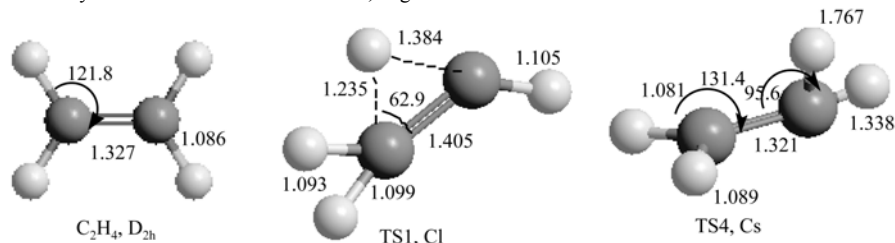
**Figure 1** The B3LYP/6-311G** optimized geometry of transition state and intermediates in the hydrogen molecule and atom elimination channels on the C₂H₄ ground state potential energy surface. The bond lengths are in Å and the angles are in degrees.

Table 7, we find that the rate constants of SBFMO are lower than those of HO and SMO, and the SMO results are lower than the HO results.

4 Conclusion

In a previous paper, we employed the Morse potential to treat the anharmonic effect on unimolecular reactions based on RRKM theory. In this paper, we study the anharmonic effect of coupled oscillators on unimolecular reactions. For this purpose, the SBFMO model has been

used.

From all the tables and figure shown in this paper, we can see that the SBFMO model gives more significant anharmonic effect than the SMO model, after comparing the total amount of state, density of state and rate constants. The anharmonic effect, of course, depends on the magnitude of the anharmonic constant. An important feature is that the anharmonic constants x_{ij} can be obtained from the *ab initio* calculations. We believe that the SBFMO model will be suitable for studying the decompositions of molecular clusters.

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