Anharmonic effect of the unimolecular dissociation of $\text{CF}_3\text{CX}_2\text{O}$ (X=F, H) Radicals

Qian Li, Li Yao^{*}, Ying Shao

Institute of Computational Physics, Department of Physics, Dalian Maritime University, Dalian 116026, China.

^{*}Corresponding author; E-mail: yaoli@dmlu.edu.cn; yshao@dmlu.edu.cn

doi:10.5618/chem.2012.v2.n1.1 || Received: 15-12-2011, Accepted: 22-1-2012, Available online: 02-2-2012

Abstract

The C-C bond scission of the three fluorinated ethoxy radicals $\text{CF}_3\text{CF}_2\text{O}$, CF_3CFHO , $\text{CF}_3\text{CH}_2\text{O}$ has been investigated using YL (Yao and Lin) method. Anharmonic and harmonic rate constants have been calculated for the reactions. In the canonical system of the three reactions at 1 atm pressure, the anharmonic (k_1) and harmonic (k_2) rate constants of the unimolecular decomposition reactions are $k_1(300\text{K})=6.35\times 10^6\text{ s}^{-1}$ and $k_2(300\text{K})=7.05\times 10^6\text{ s}^{-1}$ for $\text{CF}_3\text{CF}_2\text{O}$ radical, $k_1(300\text{K})=3.79\times 10^3\text{ s}^{-1}$ and $k_2(300\text{K})=3.88\times 10^3\text{ s}^{-1}$ for CF_3CFHO radical, and $k_1(300\text{K})=6.34\times 10^{-2}\text{ s}^{-1}$ and $k_2(300\text{K})=4.29\times 10^{-2}\text{ s}^{-1}$ for $\text{CF}_3\text{CH}_2\text{O}$ radical, respectively. The anharmonic effects on the decomposition reactions have also been examined. The different rate constants indicate that the anharmonic effect has most significant contributions to the decomposition reaction of CF_3CFHO radical, while the anharmonic effect has least contributions to the decomposition reaction of $\text{CF}_3\text{CF}_2\text{O}$ radical. It has also found that higher symmetry of the reactants results in less anharmonic effects on the decomposition reactions.

Keywords: Anharmonic effect; Unimolecular reaction; Rate constant; YL method.

1. Introduction

The chemical and physical properties of chlorofluorocarbons (CFCs) make them suited for a variety of industrial applications, while the stability of fully halogenated CFCs make them dangerous to the stratospheric ozone layer. Since 1974, many studies have indicated that the release of CFCs in the stratosphere through a series of catalytic reactions led to ozone-layer depletion increasing and global warming [1-5]. In 1987, with the threat of CFCs becoming more and more serious, Montreal Protocol was developed to prohibit production and use of CFCs. So, there was an urgent need to develop acceptable substitutes which had similar properties to CFCs

except its harmful environmental behavior such as depletion of ozone layer and global warming. In particular hydrofluorocarbons (HFCs) are now in widespread use because of their similar physical properties to CFCs but significantly shorter atmospheric lifetimes. Due to the presence of at least one H atom, HFCs were subject to tropospheric removal processes [6]. This was in contrast to the CFCs which eventually reach the stratosphere, where they were photolysed and the nascent Cl atoms initiated ozone destroying chain reactions [6-7]. Thus the alkoxy radicals' forming HFCs in the atmosphere plays an important role in the degradation mechanism of organic vapors in the troposphere. Recently, considerable theoretical studies had been performed on the similar alkoxy radicals [8-14]. H. Somnitz and R. Zellner had calculated the harmonic rate constants for C-C bond scission in $\text{CF}_3\text{CX}_2\text{O}$ (X=F, H) decomposition for the canonical case at 300K and 1 atm pressure, obtaining the values $k(\text{CF}_3\text{CF}_2\text{O})=5.3\times 10^6\text{ s}^{-1}$, $k(\text{CF}_3\text{CFHO})=1.1\times 10^4\text{ s}^{-1}$ and $k(\text{CF}_3\text{CH}_2\text{O})=7.4\times 10^{-5}\text{ s}^{-1}$, respectively [11]. Literature survey indicated that there was no experimental data available on $\text{CF}_3\text{CX}_2\text{O}$ (X=F, H) radicals.

On the other hand, many chemists observed that the anharmonic effect played an important role in molecular systems, especially in those of molecules and clusters with highly flexible transition states [15]. In 1962, Schlag and Sandmark discovered that anharmonicity corrections may be significant in practice [16]. Haarhoff then considered the anharmonic corrections about the density of vibrational energy levels which were applied to a system of simple Morse oscillators [17]. Recently, many chemists also observed that anharmonic effects were quite significant in dissociation of clusters and molecular systems [18-22]. Some chemists also recognized that the characteristic features of the anharmonic effects led to an increase in the bond lengths and distance of bond dissociation, and a decrease in vibrational bond-stretching frequencies. Several researches have concentrated on the requirements for the anharmonic corrections to previous reaction rate theories [23-25]. For this reason, using experimental thermodynamic

data, Troe [26] presented a simple empirical method for generating anharmonic vibrational densities of states. Recently, a method proposed by Yao and Lin(YL) [27] which could carry out the first principle calculations about the rate constants of molecular reactions within the framework of the transition state theory had been proposed. With this method, the anharmonic effects on the dissociation of molecular reactions have been examined. The results suggested that the YL method was appropriate for calculating rate constants of the unimolecular reactions, and investigating the anharmonic effects of rate constants.

Although many efforts have been made to the study of the unimolecular dissociation of $\text{CF}_3\text{CX}_2\text{O}$ ($\text{X}=\text{F}, \text{H}$) radicals, the study of their rate constants and the anharmonic effects on the reactions are very rare. The purpose of this paper is to calculate the harmonic and anharmonic rate constants of the unimolecular dissociation of $\text{CF}_3\text{CX}_2\text{O}$ ($\text{X}=\text{F}, \text{H}$) radicals, and to investigate the anharmonic effects on the reactions using YL method. The computational methods will be described in detail in section 2. Section 3 concludes numerical results and detailed discussions. Finally, concluding remarks and a summary of this work are presented in section 4.

2. Computational Methods

2.1. Ab Initio Calculations. The C-C bond scission of the three fluorinated ethoxy radicals $\text{CF}_3\text{CF}_2\text{O}$, CF_3CFHO , $\text{CF}_3\text{CH}_2\text{O}$ are investigated, the reactions as given below:

The geometries of the reactants and transition states had been optimized, with 6-311G(d,p) basis set, by the MP2 method. The vibrational harmonic and anharmonic frequencies, calculated with the same method, were used for the characterization of stationary points, zero-point-energy (ZPE) corrections, and the calculations of reaction rate constants using transition state and RRKM theory. To obtain more accurate and reliable data, the single point energies were recalculated by employing the coupled cluster CCSD(T) method with 6-311G(d,p) basis set. To confirm that the transition state connected smoothly to reactant and products, the transition state was subjected to an intrinsic reaction coordinate (IRC) with the same level of theory at which optimization and frequency calculation are performed. The frequencies, energies of reactants and TS structures in this paper were all calculated at in 1 atm and 298K (room temperature). The Gaussian 03 program was applied for all ab initio calculations [28].

2.2. Rice-Ramsperger-Kassel-Marcus (RRKM)

theory. According to the RRKM theory, for the microcanonical system, the rate constant $k(E)$ for unimolecular reaction can be expressed as [29]:

$$k(E) = \frac{\sigma}{h} \frac{W^\ddagger(E - E^\ddagger)}{\rho(E)} \quad (1)$$

where σ is the symmetry factor (here we set $\sigma = 1$). h is Planck's constant, $\rho(E)$ stands for the density of the states of the reactant, $W^\ddagger(E)$ represents the total number of states for the transition state, E and $E^\ddagger$ are the total energy and the activation energy in the microcanonical case, respectively. From the definition of $W(E)$ and $\rho(E)$, we can obtain [30-32]:

$$W(E) = \sum_i H(E - E_i) \quad (2)$$

$$\rho(E) = \frac{dW(E)}{dE} \quad (3)$$

where $H(E - E_i)$ denotes Heaviside function, E_i are energy levels.

The Laplace transformation is employed for $W(E)$ and $\rho(E)$ we obtain[30-32]:

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

$$\int_0^\infty dE e^{-\beta E} \rho(E) = Q(\beta) = L[\rho(E)] \quad (5)$$

where $\beta = 1/kT$, k is Boltzmann's constant, T is the temperature of the system, and $Q(\beta)$ is the partition function of the system. That is, approximate $W(E)$ and $\rho(E)$ can be determined by eqs. (4) and (5) by applying the inverse Laplace transformation after $Q(\beta)$ are given. The details can be found in Ref. [27].

For a canonical system, the rate constant $k(T)$ for unimolecular reaction can be expressed as [30, 32-34]

$$k(T) = \frac{kT}{h} \frac{Q^\ddagger(T)}{Q(T)} e^{-\frac{E^\ddagger}{kT}} \quad (6)$$

where $Q(T)$ and $Q^\ddagger(T)$ are the partition functions of the reactant and the activated complex, respectively. In this case, we obtain

$$Q^\ddagger(T) = \prod_i^{N-1} q_i^\ddagger(T) \quad (7)$$

$$Q(T) = \prod_i^N q_i(T) \quad (8)$$

where N is the number of the vibrational modes of the reactant, $q_i^\ddagger(T)$ and $q_i(T)$ represent the vibrational partition functions of the activated complex and the reactant for the single mode,

respectively.

According to the above discussion, it is worth noting that the partition function plays a very important role in calculating the total number of states, the density of states and the rate constant. To calculate the partition function of both microcanonical and canonical cases and investigate the anharmonic effect on a unimolecular reaction, Morse Oscillator (MO) is taken as the simple form. For the MO, we have

$$E_{n_i} = (n_i + \frac{1}{2})\hbar\omega_i - x_i(n_i + \frac{1}{2})\hbar\omega_i \quad (9)$$

where n_i is the vibrational quantum number of the vibrational mode, ω_i is the frequency of the i th vibrational mode. Actually, Morse model and harmonic model are given similar results at low energy, just like equilibrium position of the stretching bond. We can use Morse model to simulate all the degrees of freedom, include non-stretching and stretching bonds. x_i is the MO parameter, which is a measure for the deviation of the potential from the harmonic case. It is related to the dissociation energy and the energy of the fundamental transition. For $x_i = 0$, the anharmonic potential is reduced to the harmonic case. x_i can be expressed as

$$x_i = \hbar\omega_i / 4D_{ie},$$

where D_{ie} is the well depth of the MO, and the maximum of n_i is given by

$$n_i(m) = \frac{1}{2x_i} - \frac{1}{2}.$$

It is necessary to pointed out that the anharmonic constant x_i for various molecules can be determined by ab initio calculation. In this case, it is known that the anharmonic model has two features, compared with harmonic model: one is that the energy spacings are not equal, and the other is that there is a maximum quantum number $n_i(m)$ in MO. In YL method, all of the vibrational modes are treated as anharmonic Morse oscillator (MO). In the calculation of the density of states $\rho(E)$, harmonic and anharmonic vibrational degrees of freedom of the reactants are 18 (3N-6, N=7). To calculate the total number of states $W(E)$, harmonic and anharmonic imaginary frequencies are excluded and the degrees of freedom of the transition states are 17. In this paper, we shall discuss the anharmonic effect of the dissociation rate constant for the unimolecular decomposition reaction of $\text{CF}_3\text{CX}_2\text{O}$ (X=F, H) radical.

3. Results and discussions

3.1 Unimolecular dissociation of the $\text{CF}_3\text{CF}_2\text{O}$ radical. Firstly, we investigate the reaction $\text{CF}_3\text{CF}_2\text{O} \rightarrow \text{CF}_3 + \text{CF}_2\text{O}$ employing the MP2/6-311G (d,p) method. The geometric and the energetic parameters

of the reactant and transition state are illustrated in **Tab.1**. From **Tab.1**, it can be seen that the elongation of the C-C bond is found changed from 1.553 to 1.835Å, with a decrease in C-O bond distance from 1.346 to 1.210Å. The barrier height that is obtained using MP2 method of the reaction is 11.07 kcal/mol, with zero-point-energy (ZPE) corrected. To obtain high accuracy and reliability, we re-computed the single point energies at CCSD(T)/6-311G(d,p) level, and obtained the energy barrier of 8.28 kcal/mol, which is also given in **Tab. 1**. The result is in good agreement with the values (8.15-8.51 kcal/mol) obtained by H. Somnitz and R. Zellner [11]. The CCSD(T)/6-311G(d,p) result is used in the rate constants calculation. The anharmonic parameters x_i of the unimolecular dissociation of the $\text{CF}_3\text{CF}_2\text{O}$ radical are presented in **Tab.2**.

For the reaction of $\text{CF}_3\text{CF}_2\text{O}$, the anharmonic and harmonic rate constants for canonical case are presented in **Tab.3**, with temperatures ranging from 300 to 2000 K. Corresponding to **Tab.3**, the rate constants for the reaction are plotted in **Fig.1**. From the **Tab.3** and **Fig.1**, it is clear that both the harmonic and anharmonic rate constants increase with the increasing temperature. With the temperature increasing from 300 to 2000 K, the harmonic rate constant increases from 7.05×10^6 to $3.54 \times 10^{12} \text{ s}^{-1}$, while the anharmonic rate constant is in the range from 6.35×10^6 to $3.26 \times 10^{12} \text{ s}^{-1}$. The values of anharmonic rate constants and the harmonic ones are closer at all range of temperatures. When temperature is 300 K, the anharmonic rate constant ($6.35 \times 10^6 \text{ s}^{-1}$) is 9.9% lower than the harmonic rate constant ($7.05 \times 10^6 \text{ s}^{-1}$), while the anharmonic rate constant ($3.26 \times 10^{12} \text{ s}^{-1}$) is 7.9% lower than the harmonic rate constant ($3.54 \times 10^{12} \text{ s}^{-1}$) at temperature 2000 K. We can draw the conclusion that the anharmonic effect is not obvious in the canonical system. It is worth noting in **Tab.3** that the first two energies are all lower than the calculated activation energy 8.28 kcal/mol. Hence, we have to calculate the rate constant in the micro-canonical system at higher energy.

To calculate the energy corresponding to the above temperature, we employ the relation between the total energy of a microcanonical system and the temperature of a canonical system by:

$$E = - \left[\frac{\partial \ln Q}{\partial \beta} \right] \quad (10)$$

The energy in the microcanonical system can be obtained with Eq.(10).

The total energies are 3288, 5313, 7502, 9783, 12119, 14497, 16900, 19324, 24206 and 27889 cm^{-1} , corresponding to the temperatures of 600, 800, 1000, 1200, 1400, 1600, 1800, 2000, 2400 and 2700 K, respectively. **Tab.4** shows the harmonic and an-

harmonic total number of states, density of states and rate constants of the title reaction obtained from the YL method for microcanonical case. The rate constants for the microcanonical case are also illustrated in **Fig.2**.

Table 1. Parameters of the CF₃CF₂O radical used in rate constant calculations, obtained from MP2/6-311G(d,p) calculations. The bond lengths are in Å.

	CF ₃ CF ₂ O	TS
Zero-point energy(MP2) (Hartree)	0.0292335	0.0270586
Imaginary frequencies	---	1151.249i
C-C distance	1.553	1.835
C-O distance	1.346	1.210
Energies (MP2) (Hartree)	-649.3527740	-649.3329541
Single-point energy(CCSd(t)) (Hartree)	-649.4089671	-649.3935932
Barrier (kcal/mol)	11.07(for MP2 method)	8.28(for CCSD(T) method)

Table 2 The anharmonic parameters x_i of the unimolecular dissociation of the CF₃CF₂O radical.

CF ₃ CF ₂ O	0.0117 0.0058	0.0105 0.0094	0.0105 0.0249	0.0149 0.0211	0.0102 0.0268	0.0112 0.0099	0.0086 0.0026	0.0078 0.0106	0.0081 0.0342
TS	0.0001 0.0031	0.0103 0.0043	0.0076 0.0001	0.0112 0.0115	0.0030 0.0072	0.0041 0.0128	0.0049 0.0079	0.0042 0.0189	0.0049

Table 3. The rate constants of the CF₃CF₂O radical at different temperatures in the canonical system. The units of temperature, total energy and rate constants are K, kcal/mol and s⁻¹, respectively. The values are calculated at MP2/6-311G(d,p) level.

Temperature (K)	300	400	600	800	1000	1200	1400	1600	1800	2000
Correspond energy (kcal/mol)	2.5	4.45	9.4	15.19	21.45	27.97	34.65	41.45	48.32	55.25
Correspond (cm ⁻¹)	874	1556	3288	5313	7502	9783	12119	14497	16900	19324
Anharmonic rate constant (1/s)	6.35×10 ⁶	2.88×10 ⁸	1.43×10 ¹⁰	1.03×10 ¹¹	3.31×10 ¹¹	7.13×10 ¹¹	1.22×10 ¹²	1.84×10 ¹²	2.52×10 ¹²	3.26×10 ¹²
Harmonic rate constant (1/s)	7.05×10 ⁶	3.06×10 ⁸	1.43×10 ¹⁰	1.00×10 ¹¹	3.27×10 ¹¹	7.21×10 ¹¹	1.27×10 ¹²	1.95×10 ¹²	2.71×10 ¹²	3.54×10 ¹²

Figure 1. The canonical rate constants at MP2/6-311G(d,p) level for the $\text{CF}_3\text{CF}_2\text{O} \rightarrow \text{CF}_3 + \text{CF}_2\text{O}$ reaction. The unit of rate constant is s^{-1} .

Figure 2. The microcanonical rate constants at MP2/6-311G(d,p) level for the $\text{CF}_3\text{CF}_2\text{O} \rightarrow \text{CF}_3 + \text{CF}_2\text{O}$ reaction. The unit of rate constant is s^{-1} .

From **Tab.4** and **Fig.2**, we can see that the harmonic and anharmonic rate constants increase with the increasing of the total energy in the microcanonical system. With the energy increasing from 3288 to 27889 cm^{-1} , the harmonic rate constant increases from 5.95×10^8 to $6.66 \times 10^{12} \text{ s}^{-1}$, while the anharmonic rate constant is in the range from 4.23×10^8 to $5.94 \times 10^{12} \text{ s}^{-1}$. Although the harmonic rate constants are higher than the anharmonic ones at all energies, the values of harmonic rate constants and the anharmonic ones are closer at all range of energies. When total energy is 5313 cm^{-1} , the anharmonic rate constant ($3.44 \times 10^{10} \text{ s}^{-1}$) is 4.2% lower than the harmonic rate constant ($3.59 \times 10^{10} \text{ s}^{-1}$), while the anharmonic rate constant ($5.94 \times 10^{12} \text{ s}^{-1}$) is 10.8%

lower than the harmonic rate constant ($6.66 \times 10^{12} \text{ s}^{-1}$) at total energy of 27889 cm^{-1} . It can be seen that, the anharmonic effect is not significant at all energies in the microcanonical system.

From **Tabs.3-4** and **Figs.1-2**, it can be seen that the calculated harmonic and anharmonic rate constants are $7.05 \times 10^6 \text{ s}^{-1}$ and $6.35 \times 10^6 \text{ s}^{-1}$ at the temperature 300 K. The results are in good agreement with the value ($5.3 \times 10^6 \text{ s}^{-1}$) given by H. Somnitz and R. Zellner [11]. On the other hand, both in the canonical system and the microcanonical system, the values of anharmonic rate constants and harmonic rate constants are closer. In other words, the anharmonic effect is not obvious for the reaction of $\text{CF}_3\text{CF}_2\text{O}$ radical for either canonical case or microcanonical case.

3.2 Unimolecular dissociation of the CF_3CFHO radical. Similarly, we investigate the reaction $\text{CF}_3\text{CFHO} \rightarrow \text{CF}_3 + \text{CFHO}$ using MP2/6-311G(d,p) method. The geometric and the energetic parameters of the reactant and transition state are shown in **Tab.5**. From **Tab.5**, we can see that the elongation of the C-C bond is found changed from 1.538 to 1.901 Å, with a decrease in C-O bond distance from 1.334 to 1.199 Å. The barrier height that is obtained using MP2 method of the reaction is 14.86 kcal/mol, with zero-point-energy (ZPE) corrected. To obtain high accuracy and reliability, we recompute the single point energies by employing the CCSD(T)/6-311G(d,p) method, then get the value of the energy barrier 12.34 kcal/mol, which is also illustrated in **Tab.5**. The result is lower than the values (12.60-13.10 kcal/mol) obtained by H. Somnitz and R. Zellner[11]. This is because the geometries of the reactant and transition states were optimized using different method and levels by H. Somnitz and R. Zellner[11]. The value of the energy barrier obtained by the CCSD(T)/6-311G(d,p) method is used to calculate the rate constants. The anharmonic parameters χ_i of the unimolecular dissociation of the CF_3CFHO radical are presented in **Tab.6**.

For the reaction of CF_3CFHO , the anharmonic and harmonic rate constants for canonical case are presented in **Tab.7**, with temperatures ranging from 300 to 2000 K. Corresponding to **Tab.7**, the rate constants for the title reaction is plotted in **Fig.3**. From the **Tab.7** and **Fig.3**, we can see that both the harmonic and anharmonic rate constants increase with the increasing temperature. With the temperature increasing from 300 to 2000 K, the harmonic rate constant increases from 3.88×10^3 to $6.92 \times 10^{11} \text{ s}^{-1}$, while the anharmonic rate constant is in the range from 3.79×10^3 to $4.71 \times 10^{12} \text{ s}^{-1}$. The anharmonic rate constants are higher than the harmonic ones in the range of temperatures from 400 to 2000 K. When temperature is 400K, the harmonic rate constant ($8.21 \times 10^5 \text{ s}^{-1}$) is 12.3% lower than the anharmonic rate constant ($9.36 \times 10^5 \text{ s}^{-1}$), while the harmonic rate constant ($6.92 \times 10^{11} \text{ s}^{-1}$) is 85.3% lower than the

anharmonic rate constant ($4.71 \times 10^{12} \text{ s}^{-1}$) at temperature 2000 K. We can draw the conclusion that the difference between the two cases becomes larger with the increasing of temperature. In other words, the anharmonic effect becomes more significant with the increasing temperature in the canonical system. It is worth noting in **Tab.5** that the first five energies are all lower than the calculated activation energy of 12.34 kcal/mol. Hence, we have to calculate the rate constant in the microcanonical system at higher energy.

Using Eq.(10), we get the total energies 4648, 6138, 7733, 9412, 11153, 12951, 14787, 18551, 22408 and 26333 cm^{-1} , corresponding to the temperatures of 1200, 1400, 1600, 1800, 2000, 2200, 2400, 2800, 3200 and 3600 K. **Tab.8** gives the harmonic and anharmonic total number of states, density of states and rate constants of the reaction obtained from the YL method for microcanonical case. The rate constants of the microcanonical total energies are also illustrated in **Fig.4**.

Table 4. The rate constants of the $\text{CF}_3\text{CF}_2\text{O}$ radicals at different energies in the microcanonical system. The units of total energy, $\rho(E)$ and rate constants are kcal/mol, $1/\text{cm}^{-1}$ and s^{-1} , respectively. The values are calculated at MP2/6-311G(d,p) level.

Total energy (cm^{-1})	3288	5313	7502	9783	12119	14497	16900	19324	24206	27889
Correspond total energy(kcal/mol)	9.4	15.19	21.45	27.97	34.65	41.45	48.32	55.25	69.21	79.74
Anharmonic W(E) of TS	21.84	8.46×10^4	1.31×10^7	6.05×10^8	1.39×10^{10}	2.00×10^{11}	2.03×10^{12}	1.58×10^{13}	5.29×10^{14}	4.94×10^{15}
Anharmonic $\rho(E)$ of reactant ($1/\text{cm}^{-1}$)	1.55×10^3	7.38×10^4	2.01×10^6	3.47×10^7	4.19×10^8	3.80×10^9	2.72×10^{10}	1.60×10^{11}	3.46×10^{12}	2.50×10^{13}
Anharmonic rate constant (1/s)	4.23×10^8	3.44×10^{10}	1.95×10^{11}	5.22×10^{11}	9.34×10^{11}	1.57×10^{12}	2.24×10^{12}	2.97×10^{12}	4.59×10^{12}	5.94×10^{12}
Harmonic W(E) of TS	20.38	5.74×10^4	8.27×10^6	3.71×10^8	8.30×10^9	1.16×10^{11}	1.14×10^{12}	8.63×10^{12}	2.71×10^{14}	2.43×10^{15}
Harmonic $\rho(E)$ of reactant($1/\text{cm}^{-1}$)	1.03×10^3	4.79×10^4	1.25×10^6	2.04×10^7	2.31×10^8	1.97×10^9	1.34×10^{10}	7.55×10^{10}	1.54×10^{12}	1.10×10^{13}
harmonic rate constant (1/s)	5.95×10^8	3.59×10^{10}	1.98×10^{11}	5.46×10^{11}	1.08×10^{12}	1.76×10^{12}	2.56×10^{12}	3.43×10^{12}	5.27×10^{12}	6.66×10^{12}

Table 5. Parameters of the CF_3CFHO radical used in rate constant calculations, obtained from MP2/6-311G(d,p) calculations. The bond lengths are in Å.

	CF_3CFHO	TS
Zero-point energy(MP2) (Hartree)	0.0372551	0.034794
Imaginary frequencies	---	915.961i
C-C distance	1.538	1.901
C-O distance	1.334	1.199
Energies (MP2) (Hartree)	-550.2775184	-550.251382
Single-point energy(CCS(D(t)) (Hartree)	-550.3346555	-550.3121349
Barrier (kcal/mol)	14.86(for MP2 method)	12.34(for CCSD(T) method)

Table 6. The anharmonic parameters x_i of the unimolecular dissociation of the CF_3CFHO radical.

CF_3CFHO	0.0256	0.0150	0.0131	0.0135	0.0112	0.0114	0.0107	0.0119	0.0088
	0.0067	0.0044	0.0062	0.0045	0.0064	0.0053	0.0001	0.0013	0.0057
TS	0.0238	0.0001	0.0123	0.0141	0.0116	0.0099	0.0077	0.0001	0.0051
	0.0001	0.0089	0.0025	0.0063	0.0126	0.0241	0.0166	0.0081	

Table 7. The rate constants of the CF₃CFHO radical at different temperatures in the canonical system. The units of temperature, total energy and rate constants are K, kcal/mol and s⁻¹, respectively. The values are calculated at MP2/6-311G(d,p) level.

Temperature (K)	300	400	600	800	1000	1200	1400	1600	1800	2000
Correspond energy (kcal/mol)	0.68	1.31	3.27	6.03	9.41	13.29	17.55	22.11	26.91	31.89
Correspond (cm ⁻¹)	238	458	1144	2109	3291	4648	6138	7733	9412	11133
Anharmonic rate constant (1/s)	3.79×10 ³	9.36×10 ⁵	3.01×10 ⁸	6.72×10 ⁹	4.97×10 ¹⁰	2.06×10 ¹¹	6.03×10 ¹¹	1.39×10 ¹²	2.72×10 ¹²	4.71×10 ¹²
Harmonic rate constant (1/s)	3.88×10 ³	8.21×10 ⁵	1.94×10 ⁸	3.25×10 ⁹	1.84×10 ¹⁰	6.00×10 ¹⁰	1.42×10 ¹¹	2.73×10 ¹¹	4.57×10 ¹¹	6.92×10 ¹¹

Table 8. The rate constants of the CF₃CFHO radicals at different energies in the microcanonical system. The units of total energy, p(E) and rate constants are kcal/mol, 1/cm⁻¹ and s⁻¹, respectively. The values are calculated at MP2/6-311G(d,p) level.

Total energy (cm ⁻¹)	4648	6138	7733	9412	11153	12951	14787	18551	22408	26333
Correspond total energy (kcal/mol)	13.29	17.55	22.11	26.91	31.89	37.03	42.28	53.04	64.07	75.29
Anharmonic W(E) of TS	1.36	44.14	5.97×10 ²	5.27×10 ³	3.50×10 ⁴	1.88×10 ⁵	8.43×10 ⁵	1.13×10 ⁷	9.96×10 ⁷	6.49×10 ⁸
Anharmonic p(E) of reactant (1/cm ⁻¹)	2.41	9.53	34.86	1.18×10 ²	3.71×10 ²	1.09×10 ³	2.98×10 ³	1.90×10 ⁴	9.94×10 ⁴	4.46×10 ⁵
Anharmonic rate constant (1/s)	1.69×10 ¹⁰	1.39×10 ¹¹	5.13×10 ¹¹	1.34×10 ¹²	2.83×10 ¹²	5.18×10 ¹²	8.47×10 ¹²	1.78×10 ¹³	3.00×10 ¹³	4.37×10 ¹³
Harmonic W(E) of TS	1.52	37.57	4.26×10 ²	3.20×10 ³	1.83×10 ⁴	8.67×10 ⁴	3.51×10 ⁵	4.06×10 ⁶	3.31×10 ⁷	2.07×10 ⁸
Harmonic p(E) of reactant (1/cm ⁻¹)	5.33	22.89	90.00	3.25×10 ²	1.08×10 ³	3.31×10 ³	9.50×10 ³	6.47×10 ⁴	3.58×10 ⁵	1.67×10 ⁶
harmonic rate constant (1/s)	8.67×10 ⁹	4.92×10 ¹⁰	1.42×10 ¹¹	2.95×10 ¹¹	5.10×10 ¹¹	7.84×10 ¹¹	1.11×10 ¹²	1.88×10 ¹²	2.78×10 ¹²	3.73×10 ¹²

Figure 3. The canonical rate constants at MP2/6-311G(d,p) level for the $\text{CF}_3\text{CFHO} \rightarrow \text{CF}_3 + \text{CFHO}$ reaction. The unit of rate constant is s^{-1} .

Figure 4. The microcanonical rate constants at MP2/6-311G(d,p) level for the $\text{CF}_3\text{CFHO} \rightarrow \text{CF}_3 + \text{CFHO}$ reaction. The unit of rate constant is s^{-1} .

From **Tab.8** and **Fig.4**, we can see that for the microcanonical system the harmonic and anharmonic rate constants increase with the increasing of the total energy. With the energy increasing from 4648 to 26333 cm^{-1} , the harmonic rate constant increases from 8.67×10^9 to $3.73 \times 10^{12} \text{ s}^{-1}$, while the anharmonic rate constant is in the range from 1.69×10^{10} to $4.37 \times 10^{13} \text{ s}^{-1}$. The anharmonic rate constants are higher than the harmonic ones at all range of energies. When total energy is 4648 cm^{-1} , the harmonic rate constant ($8.67 \times 10^9 \text{ s}^{-1}$) is 48.7% lower than the anharmonic rate constant ($1.69 \times 10^{10} \text{ s}^{-1}$), while the harmonic rate constant ($3.73 \times 10^{12} \text{ s}^{-1}$) is 91.5% lower than the anharmonic rate constant ($4.37 \times 10^{13} \text{ s}^{-1}$) at the total

energy 26333 cm^{-1} . It can be seen that, the anharmonic effect is so obvious at all energies especially in case of high energies that it is not negligible. On the other hand, with the increment of total energy, the anharmonic effect becomes more significant in the microcanonical system.

From **Tabs.7-8** and **Figs.3-4**, it can be seen that the calculated harmonic and anharmonic rate constants are $3.88 \times 10^3 \text{ s}^{-1}$ and $3.79 \times 10^3 \text{ s}^{-1}$, respectively, at the temperature 300K. The results are smaller than the value ($1.1 \times 10^4 \text{ s}^{-1}$) given by H. Somnitz and R. Zellner[11], the main reason for which is that the value of the energy barrier used in the rate constants' calculation is different from that obtained by H. Somnitz and R. Zellner[11]. On the other hand, both in the canonical system and the microcanonical system, the anharmonic rate constants are higher than the harmonic ones. The difference between the anharmonic rate constants and harmonic rate constants become larger with the increasing of energy. The difference in rate constants results from the difference in harmonic potential and anharmonic potential, which are utilized to simulate the vibrational bonds. The total number of states and density of states are also counted. They affect the dissociation rate constants. In summary, the anharmonic effect is so obvious for the reaction of CF_3CFHO radical at all energies especially in the case of high energies that it is not negligible for either canonical case or microcanonical case.

3.3 Unimolecular dissociation of the $\text{CF}_3\text{CH}_2\text{O}$ radical.

At last, we employ the MP2/6-311G(d,p) method to investigate the reaction $\text{CF}_3\text{CH}_2\text{O} \rightarrow \text{CF}_3 + \text{CH}_2\text{O}$. The geometric and the energetic parameters of the reactant and transition state are presented in **Tab.9**. The elongation of the C-C bond is found changed from 1.525 to $2.050 \text{ \AA}$, with a decrease in C-O bond distance from 1.383 to $1.209 \text{ \AA}$. The barrier height obtained using MP2 method of the reaction is 24.20 kcal/mol, with zero-point-energy (ZPE) corrected. To obtain higher accuracy and reliability in calculations, we re-computed the single point energies at CCSD(T)/6-311G(d,p) level, and obtained the energy barrier of 20.07 kcal/mol, which is also shown in **Tab. 9**. The result is lower than the values (24.31-25.19 kcal/mol) obtained by H. Somnitz and R. Zellner [11]. The geometries of the reactant and transition states are optimized using different method and levels by H. Somnitz and R. Zellner [11]. The value of the energy barrier obtained by CCSD(T)/6-311G(d,p) method is used in the rate constants calculation. The anharmonic parameters χ_i of the unimolecular dissociation of the $\text{CF}_3\text{CH}_2\text{O}$ radical are presented in **Tab.10**.

For the reaction of $\text{CF}_3\text{CH}_2\text{O}$, the anharmonic and harmonic rate constants in canonical case are present-

ed in **Tab.11**, with the temperatures ranging from 300 to 2000 K. Corresponding to **Tab.11**, the rate constant for the title reaction is plotted in **Fig.5**. As shown in the **Tab.11**, it is clear that both the harmonic and anharmonic rate constants increase with the increasing temperature. With the temperature increasing from 300 to 2000 K, the harmonic rate constant increases from 4.29×10^{-2} to $9.97 \times 10^{11} \text{ s}^{-1}$, while the anharmonic rate constant is in the range from 6.00×10^{-2} to $2.72 \times 10^{12} \text{ s}^{-1}$. The anharmonic rate constants are higher than the harmonic ones at all range of temperatures. When temperature is 300 K, the harmonic rate constant ($4.29 \times 10^{-2} \text{ s}^{-1}$) is 32.3% lower than

the harmonic rate constant ($6.34 \times 10^{-2} \text{ s}^{-1}$), while the harmonic rate constant ($9.97 \times 10^{11} \text{ s}^{-1}$) is 63.3% lower than the anharmonic rate constant ($2.72 \times 10^{12} \text{ s}^{-1}$) at temperature 2000K. We can draw the conclusion that the difference between the harmonic and anharmonic cases increases with the increasing of temperature. In other words, the anharmonic effect becomes more significant with the increasing temperature in the canonical system. It is worth noting in **Tab.9** that the first five energies are all lower than the calculated activation energy of 20.07 kcal/mol. Hence, we have to calculate the rate constant in the microcanonical system at the higher energy.

Table 9. Parameters of the $\text{CF}_3\text{CH}_2\text{O}$ radical in rate constant calculations, obtained from MP2/6-311G(d,p) calculations. The bond lengths in Å.

CF ₃ CH ₂ O	TS	
Zero-point energy(MP2) (Hartree)	0.046495	0.041821
Imaginary frequencies	---	625.234i
C-C distance	1.525	2.050
C-O distance	1.383	1.209
Energies (MP2) (Hartree)	-451.1957523	-451.1525169
Single-point energy(CCSd(t)) (Hartree)	-451.2522912	-451.2156317
Barrier (kcal/mol)	24.20(for MP2 method) 20.07(for CCSd(T) method)	

Table 10. The anharmonic parameters x_i of the unimolecular dissociation of the $\text{CF}_3\text{CH}_2\text{O}$ radical.

CF ₃ CH ₂ O	0.0241 0.0072	0.0448 0.0065	0.0714 0.0001	0.0991 0.0030	0.0001 0.0007	0.0086 0.0001	0.0090 0.0001	0.0030 0.0001	0.0124 0.1441
TS	0.0238 0.0178	0.0242 0.0001	0.0001 0.0084	0.0063 0.0056	0.0135 0.0289	0.0127 0.0134	0.0083 0.0176	0.0166 0.0427	0.0001

Table 11. The rate constants of the $\text{CF}_3\text{CH}_2\text{O}$ radical at different temperatures in the canonical system. The units of temperature, total energy and rate constants are K, kcal/mol and s^{-1} , respectively. The values are calculated at MP2/6-311G(d,p) level.

Temperature (K)	300	400	600	800	1000	1200	1400	1600	1800	2000
Correspond energy(kcal/mol)	1.61	2.99	6.78	11.53	16.90	22.70	28.78	35.08	41.53	48.11
Correspond (cm^{-1})	563	1046	2371	4033	5911	7939	10066	12269	14525	16826
Anharmonic rate constant (1/s)	6.34×10^{-2}	5.33×10^2	5.44×10^6	6.07×10^8	1.05×10^{10}	7.04×10^{10}	2.68×10^{11}	7.18×10^{11}	1.52×10^{12}	2.72×10^{12}
Harmonic rate constant (1/s)	4.29×10^{-2}	3.05×10^2	2.47×10^6	2.36×10^8	3.73×10^9	2.38×10^{10}	8.98×10^{10}	2.44×10^{11}	5.33×10^{11}	9.97×10^{11}

Table 12. The rate constants of the $\text{CF}_3\text{CH}_2\text{O}$ radicals at different energies in the microcanonical system. The units of total energy, $\rho(E)$ and rate constants are kcal/mol, $1/\text{cm}^{-1}$ and s^{-1} , respectively. The values are calculated at MP2/6-311G(d,p) level.

Total energy(cm^{-1})	8992	11161	13392	14525	16826	19159	21513	23891	26287	28693
Correspond total energy(kcal/mol)	25.71	31.91	38.29	41.53	48.11	54.78	61.51	68.31	75.16	82.04
Anharmonic $W(E)$ of TS	8.44×10^3	9.20×10^5	3.01×10^7	1.32×10^8	1.75×10^9	1.60×10^{10}	1.10×10^{11}	6.11×10^{11}	2.86×10^{12}	1.16×10^{13}
Anharmonic $\rho(E)$ of reactant($1/\text{cm}^{-1}$)	6.06×10^4	4.85×10^5	3.20×10^6	7.71×10^6	4.01×10^7	1.82×10^8	7.33×10^8	2.67×10^9	8.67×10^9	2.72×10^{10}
Anharmonic rate constant($1/\text{s}$)	4.18×10^9	5.68×10^{10}	2.82×10^{11}	5.13×10^{11}	1.31×10^{12}	2.64×10^{12}	4.50×10^{12}	6.86×10^{12}	9.66×10^{12}	1.28×10^{13}
Harmonic $W(E)$ of TS	5.38×10^3	5.40×10^5	1.66×10^7	7.11×10^7	9.25×10^8	8.48×10^9	5.97×10^{10}	3.44×10^{11}	1.69×10^{12}	7.21×10^{12}
Harmonic $\rho(E)$ of reactant($1/\text{cm}^{-1}$)	1.00×10^5	7.96×10^5	5.18×10^6	1.24×10^7	6.32×10^7	2.82×10^8	1.13×10^9	4.08×10^9	1.35×10^{10}	4.16×10^{10}
harmonic rate constant($1/\text{s}$)	1.61×10^9	2.04×10^{10}	9.61×10^{10}	1.72×10^{11}	4.39×10^{11}	8.99×10^{11}	1.59×10^{12}	2.53×10^{12}	3.73×10^{12}	5.19×10^{12}

Figure 5. The canonical rate constants at MP2/6-311G(d,p) level for the $\text{CF}_3\text{CH}_2\text{O} \rightarrow \text{CF}_3 + \text{CH}_2\text{O}$ reaction. The unit of rate constant is s^{-1} .

Figure 6. The microcanonical rate constants at MP2/6-311G(d,p) level for the $\text{CF}_3\text{CH}_2\text{O} \rightarrow \text{CF}_3 + \text{CH}_2\text{O}$ reaction. The unit of rate constant is s^{-1} .

Using Eq.(10), we get the total energies 8992, 11161, 13392, 14525, 16826, 19159, 21513, 23891, 26287 and 28693 cm^{-1} , corresponding to the temperatures of 1300, 1500, 1700, 1800, 2000, 2200, 2400, 2600, 2800 and 3000 K. **Tab.12** shows the harmonic and anharmonic total number of states, density of states and rate constants of the title reaction obtained from the YL method for microcanonical case. The rate constants of the microcanonical total energies are also illustrated in **Fig.6**.

From **Tab.12** and **Fig.6**, we can see that for the microcanonical system the harmonic and anharmonic rate constants increase with the increasing of the total energy. With the energy increasing from 8992 to 28693 cm^{-1} , the harmonic rate constant increases from 1.61×10^9 to $5.19 \times 10^{12} \text{ s}^{-1}$, while the anharmonic rate constant is in the range of 4.18×10^9 to $1.28 \times 10^{13} \text{ s}^{-1}$. The anharmonic rate constants are higher than the harmonic ones at all range of the energies. When total energy is 8992 cm^{-1} , the harmonic rate constant ($1.61 \times 10^9 \text{ s}^{-1}$) is 61.5% lower than the anharmonic rate constant ($4.18 \times 10^9 \text{ s}^{-1}$), while the harmonic rate constant ($5.19 \times 10^{12} \text{ s}^{-1}$) is 59.5% lower than the anharmonic rate constant ($1.28 \times 10^{13} \text{ s}^{-1}$) at total energy 28693 cm^{-1} . It can be seen that, the difference between the anharmonic rate constants and the harmonic constants are large. In other words, the anharmonic effect is so obvious at all energies that it is not negligible in the microcanonical system.

From **Tabs.11-12** and **Figs.5-6**, it can be seen that the calculated harmonic and anharmonic rate constant are $6.34 \times 10^{-2} \text{ s}^{-1}$ and $4.29 \times 10^{-2} \text{ s}^{-1}$ at the temperature 300K. The results are larger than the value ($7.4 \times 10^{-5} \text{ s}^{-1}$) given by H. Somnitz and R. Zellner[11]. The main reason is that the value of the energy barrier used in the rate constants calculation is lower than that obtained by H. Somnitz and R. Zellner[11]. On the other hand, both in the canonical system and the microcanonical system, the anharmonic rate constants are higher than the harmonic ones. Their differences are so obvious that the anharmonic effect is then significant for the reaction of $\text{CF}_3\text{CH}_2\text{O}$ radical. Therefore the anharmonic effect cannot be neglected in either canonical case or microcanonical case.

From all the Tables and Figures, we can conclude that the anharmonic effect on the decomposition reaction of CF_3CFHO radical is the most obvious, while the anharmonic effect on the decomposition reaction of $\text{CF}_3\text{CF}_2\text{O}$ radical is the least one. Through analyzing the configurations of the reactants and transition states, we conclude two reasons for the condition. First, the elongation of the C-C bond, comparing the bond of reactants and TSs, of three radicals $\text{CF}_3\text{CF}_2\text{O}$, CF_3CFHO and $\text{CF}_3\text{CH}_2\text{O}$ are 18.16%, 23.60% and 34.43%, respectively. Second, the symmetry of the CF_3CFHO radical is the least for all the three radicals. The energies are used to break

the good symmetry of the whole molecules firstly, then using the energies left, to break the C-C bond then form the product. Therefore the structure of the $\text{CF}_3\text{CF}_2\text{O}$ radical is the steadiest, while the configuration of the CF_3CFHO radical is the least stable. The reactants, which have good symmetry, are more stable and less anharmonic effect given.

4. Conclusions

In this paper, the C-C bond scission of three fluorinated ethoxy radicals $\text{CF}_3\text{CF}_2\text{O}$, CF_3CFHO , $\text{CF}_3\text{CH}_2\text{O}$ has been investigated using YL method. The anharmonic and harmonic rate constants have been calculated for the three reactions in both canonical and microcanonical cases using the YL method. The anharmonic effects on the three decomposition reactions has been also examined at MP2/6-311G(d,p) level.

For the reaction $\text{CF}_3\text{CF}_2\text{O} \rightarrow \text{CF}_3 + \text{CF}_2\text{O}$, we obtain the barrier height of 8.28 kcal/mol. The anharmonic and the harmonic rate constants are:

$$k(300\text{K}) = 6.35 \times 10^6 \text{ s}^{-1} \text{ and } k(300\text{K}) = 7.05 \times 10^6 \text{ s}^{-1}, \text{ respectively.}$$

which are in reasonable agreement with the earlier theoretical ($5.3 \times 10^6 \text{ s}^{-1}$) work by H. Somnitz and R. Zellner [11]. In both canonical and microcanonical cases, on one hand, the rate constants increase with the increasing total energy basically, on the other hand, the harmonic and anharmonic rate constants give similar results at all range of the energy. In other words, the difference between the two kinds of rate constants is quite small at all energies. Therefore we can draw the conclusion that the anharmonic effect is not obvious in either canonical or microcanonical systems.

For the reaction $\text{CF}_3\text{CFHO} \rightarrow \text{CF}_3 + \text{CFHO}$, we obtain the barrier height of 12.34 kcal/mol. The anharmonic and the harmonic rate constants are:

$$k(300\text{K}) = 3.79 \times 10^3 \text{ s}^{-1} \text{ and } k(300\text{K}) = 3.88 \times 10^3 \text{ s}^{-1}, \text{ respectively.}$$

which are different from the earlier theoretical ($5.3 \times 10^6 \text{ s}^{-1}$) work by H. Somnitz and R. Zellner [11]. The main reason is that the value of the energy barrier used in the rate constants calculation is different from that obtained by H. Somnitz and R. Zellner [11]. In both canonical and microcanonical cases, on one hand, the rate constants increase with the increasing total energy basically, on the other hand, the harmonic and anharmonic rate constants give similar results when the temperature and energy are low. However, the difference between the two kinds of rate constants is quite large at higher energy and temperature. Moreover, the difference increases with the increasing of total energy. This can lead to an conclusion that the anharmonic effect is so significant that it is not

negligible in either canonical or microcanonical systems.

For the reaction $\text{CF}_3\text{CH}_2\text{O} \rightarrow \text{CF}_3 + \text{CH}_2\text{O}$, we obtain the barrier height of 20.07 kcal/mol. The anharmonic and the harmonic rate constants are:

$$k(300\text{K}) = 6.34 \times 10^{-2} \text{ s}^{-1} \text{ and}$$

$$k(300\text{K}) = 4.29 \times 10^{-2} \text{ s}^{-1}, \text{ respectively.}$$

which are different from the earlier theoretical ($5.3 \times 10^6 \text{ s}^{-1}$) work by H. Somnitz and R. Zellner [11]. The main reason is that the value of the energy barrier used in the rate constants' calculation is lower than that obtained by H. Somnitz and R. Zellner [11]. In both canonical and microcanonical cases, on one hand, the rate constants increase with the increasing total energy basically, on the other hand, the anharmonic rate constants are higher than those in harmonic cases, especially in the cases of high total energy and temperature. This indicates that anharmonic effect shown in the reaction is significant. The findings of this study suggest that the anharmonic effect is so significant that it is not negligible in either canonical or microcanonical systems.

The comparison of the three reactions shows that the anharmonic effect on the decomposition reaction of CF_3CFHO radical is most obvious, while the anharmonic effect is least in the case of $\text{CF}_3\text{CF}_2\text{O}$ radical. The higher symmetry the reactants have, the less anharmonic effects are shown in the reaction. The energies are used to break the good symmetry of the whole molecules firstly, and then the energies left are used to break the C-C bond to form the products.

The present results indicate that in both microcanonical and canonical cases, the YL method works well for investigating the rate constants of such unimolecular decomposition. Moreover, the anharmonic effects in the title reactions and the unimolecular decomposition reactions of CF_3CFHO and $\text{CF}_3\text{CH}_2\text{O}$ radicals cannot be neglected.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (11047110, 11105022), The Natural Science Foundation of Liaoning Province (Grant Nos. L2010055, L2010057, 201102016). The Fundamental Research Funds for the Central Universities (2011QN060, 2011QN062, 2011JC021, 2011QN151).

References

- [1] M. J. Molina, F. S. Rowland, *Nature*. 1974, 249, 810. <http://dx.doi.org/10.1038/249810a0>
- [2] D. J. Weubles, *J. Geophys. Res.* 1983, 88, 1433. <http://dx.doi.org/10.1029/JC088iC02p01433>
- [3] J. D. Farman, B. G. Gardiner, J. D. Shanklin,

Nature 1985, 315, 207.

<http://dx.doi.org/10.1038/315207a0>

- [4] S. Solomon, *Nature. Lond.* 1990, 6291, 347. <http://dx.doi.org/10.1038/347347a0>
- [5] F. S. Rowland, M. J. Molina, *Chem. Eng. News.* 1994, 8, 72.
- [6] R. Zellner, *Global Aspects of Atmospheric Chemistry*, Steinkopff, Darmstadt, 1999.
- [7] A. McCulloch, *J. Fluorine Chem.*, 1999, 100, 163. [http://dx.doi.org/10.1016/S0022-1139\(99\)00198-0](http://dx.doi.org/10.1016/S0022-1139(99)00198-0)
- [8] A. Bhatnagar, R. W. Carr, *Chem. Phys. Lett.*, 1995, 238, 9. [http://dx.doi.org/10.1016/0009-2614\(95\)00360-6](http://dx.doi.org/10.1016/0009-2614(95)00360-6)
- [9] T. J. Wallington, M. D. Hurley, J. M. Fracheboud, J. J. Orlando, G. S. Tyndall, J. Sehested, T. E. Møgelberg, O. J. Nielsen, *J. Phys. Chem.*, 1996, 100, 18116. <http://dx.doi.org/10.1021/jp9624764>
- [10] H. Hou, B. S. Wang, Y. S. Gu, *Phys. Chem. Chem. Phys.*, 2000, 2, 61. <http://dx.doi.org/10.1039/a907481c>
- [11] H. Somnitz R. Zellner, *Phys. Chem. Chem. Phys.*, 2001, 3, 2352. <http://dx.doi.org/10.1039/b009498f>
- [12] F. X. Wu, R. W. Carr, *J. Phys. Chem. A*, 2003, 107, 10733. <http://dx.doi.org/10.1021/jp030566k>
- [13] H. J. Singh, B. K. Mishra, *Indian J. Chem.*, 2010, 49, 1167.
- [14] S. P. Li, T. S. Chwee, W. Y. Fan, *Chem. Phys.*, 2006, 320, 259. <http://dx.doi.org/10.1016/j.chemphys.2005.07.020>
- [15] S. A. C. McDowell, *J. Mol. Struct. Theomchem.* 770 (2006) 119; L. B. Bhuiyan, W. L. Hase, *J. Chem. Phys.* 1983, 78, 5052; G. H. Peslherbe, W. L. Hase, *J. Chem. Phys.* 1996, 105, 7432.
- [16] E. W. Schlag, R. A. Sandmark, *J. Chem. Phys.* 1962, 37, 168. <http://dx.doi.org/10.1063/1.1732944>
- [17] P. C. Haarhoff, *Mol. Phys.* 1964, 7, 101. <http://dx.doi.org/10.1080/00268976300100871>
- [18] R. Krems, S. Nordholm, *Z. Phys. Chem.* 2000, 214, 1467; <http://dx.doi.org/10.1524/zpch.2000.214.11.1467>
D. Shen, H. O. Pritchard, *J. Chem. Soc. Faraday Trans.* 1996, 92, 1297. <http://dx.doi.org/10.1039/f9969201297>
- [19] G. H. Peslherbe, W. L. Hase, *J. Chem. Phys.* 1996, 105, 7432. <http://dx.doi.org/10.1063/1.472571>
- [20] S. S. Mitra, S. S. Bhattacharyya, *J. Phys. B: At. Mol. Opt. Phys.* 1994, 27, 1773. <http://dx.doi.org/10.1088/0953-4075/27/9/015>
- [21] P. Hobza, Z. Havlas, *Chem. Rev.* 2000, 100, 4253. <http://dx.doi.org/10.1021/cr990050q>
- [22] K. Song, W. L. Hase, *J. Chem. Phys.* 1999, 110, 6198. <http://dx.doi.org/10.1063/1.478525>
- [23] W. L. Hase, *Acc. Chem. Res.* 1998, 31, 659. <http://dx.doi.org/10.1021/ar970156c>

- [24] V. N. Bagratashvili, V. S. Letokhov, A.A. Makarov, E. A. Ryabov, *Laser. Chem.* 1983, 1, 211.
<http://dx.doi.org/10.1155/LC.1.211>
- [25] S. S. Mitra, S. S. Bhattacharyya, *J. Phys. B: At. Mol. Opt. Phys.* 1994, 27, 1773.
<http://dx.doi.org/10.1088/0953-4075/27/9/015>
- [26] J. Troe, *J. Chem. Phys.* 66 (1977) 4758; J. Troe, *Chem. Phys.* 1995, 190, 381; J. Troe, *J. Phys. Chem.* 83 (1979) 114; J. Troe, *J. Chem. Phys.* 1983, 79, 6017; D. Romanini, K. K. Lehmann, *J. Chem. Phys.* 1993, 98, 6437.
- [27] L. Yao, A. M. Mebel, H. F. Lu, H. J. Neusser, S. H. Lin, *J. Phys. Chem. A* 2007, 111, 6722; L. Yao, S. H. Lin, *Mod. Phys. Lett. B* 2008, 22, 3043; L. Yao, S. H. Lin, *Science in China Series B* 2008, 51, 1146; L. Yao, R. X. He, A. M. Mebel, S. H. Lin, *Chem. Phys. Lett.* 2009, 470, 210; Y. Shao, L. Yao, S. H. Lin, *Chem. Phys. Lett.* 2009, 478, 277; L. Yao, A. M. Mebel, S. H. Lin, *J. Phys. Chem. A* 2009, 113, 14664. <http://dx.doi.org/10.1021/jp9044379>
- [28] M. J. Frisch, et al., *Gaussian 03*, revision C. 02, Gaussian, Inc.: Wallingford, CT, 2004.
- [29] J. I. Steinfeld, J. S. Francisco, W. L. Hase, *Chemical Kinetics and Dynamics*, Prentice-Hall, Englewood-Cliffs, NJ, 1989.
- [30] W. Forst, Z. J. Prasil, *Chem. Phys.* 1970, 53, 3065; W. Forst, *Chem. Rev.* 1971, 71, 339; W. Forst, *Theory of Unimolecular Reactions*, Academic Press, 1973.
- [31] M. R. Hoare, Th. W. Ruijgrok, *J. Chem. Phys.* 1970, 52, 113. <http://dx.doi.org/10.1063/1.1672655>
- [32] H. Eyring, S. H. Lin, S. M. Lin, *Basic Chemical Kinetics*, A Wiley-Interscience Publication, 1980.
- [33] T. Baer, W. L. Hase, *Unimolecular Reaction Dynamics: Theory and Experiments*, Oxford University Press, New York, 1996.
- [34] R. G. Gilbert, S. C. Smith, *Theory of Unimolecular and Recombination Reactions*, Blackwell, Oxford, 1990.