Vol 18 No 1, January 2009
1674-1056/2009/18(01)/0130-06

Chinese Physics B

© 2009 Chin. Phys. Soc.
and IOP Publishing Ltd

Dynamical potential approach to dissociation of H–C bond in HCO highly excited vibration*

Fang Chao(房 超) and Wu Guo-Zhen(吴国祯)†

Molecular and Nano Sciences Laboratory, Department of Physics, Tsinghua University, Beijing 100084, *China*

(Received 17 July 2008; revised manuscript received 10 September 2008)

The highly excited vibrational levels of HCO in the electronic ground state, $\tilde{X}^1A'$, are employed to determine the coefficients of an algebraic Hamiltonian, by which the dynamical potential is derived and shown to be very useful for interpreting the intramolecular vibrational relaxation (IVR) which operates via the HCO bending motion. The IVR inhibits the dissociation of H atom and enhances the stochastic degree of dynamical character. This approach is from a global viewpoint on a series of levels classified by the polyad number which is a constant of motion in a certain dynamical domain. In this way, the seemingly complicated level structure shows very regular picture, dynamically.

Keywords: HCO dissociation, dynamical potential, stochastic dynamics
PACC: 0545M, 3115Q

1. Introduction

The highly excited vibrational dynamics of triatomic molecules is of much interest since it involves the simplest cases of molecular dissociation and internal rotation. Typical examples are DCO,[1−5] HCO[6−8] and HCP.[9,10] The first two examples involve the dissociation of D/H atoms and the latter involves the internal bending/rotation of the H atom. In our previous work[11] on DCO, the dissociation of D atom was explored based not on the quantal wavefunctions, but on the classical concepts of nonlinear dynamics,[12] such as the Lyapunov analysis. In our work, the adopted algebraic (spectroscopic) Hamiltonian[3] was converted into the coset representation by using the Heisenberg correspondence,[13] and so the derived dynamical potential was shown to be very useful for interpreting the intramolecular vibrational relaxation (IVR) which operates via the DCO bending motion. The IVR inhibits the dissociation of D atom and enhances the stochastic degree of dynamical character. This approach can be appreciated since it is from a global viewpoint on a series of levels classified by the polyad number which is a constant of motion, at least, in a certain dynamical domain. In this way, the seemingly complicated level structure shows a very regular picture for this dissociation dynamics.

In the present study, we pay attention to the HCO case. In Ref.[7], there is a collection of levels with their spectral resonance widths. However, the physical picture behind those data is unclear so far. Hence, this is an appropriate case for the test and the confirmation of our above-mentioned approach. Above all, we elucidate the spectroscopic Hamiltonian by fitting to the levels as shown in Ref.[7], which, to our knowledge, has not been reported previously in the literature. And then, the dynamical simulation, Lyapunov analysis and dynamical potential approach are used to reveal the essence of the H dissociation of HCO. Our analyses are demonstrated to be able to explain the level behaviour as far as the spectral resonance width is concerned. Finally, a concluding remark is given for the evaluation of this semiclassical approach.

2. The determination of algebraic Hamiltonian

Assume this HCO system to have form of the algebraic (spectroscopic) Hamiltonian with nonlinearities and couplings for DCO. This algebraic Hamiltonian is based on the coupled Morse oscillators for the H–C stretching, HCO bending and C–O stretching mo-

*Project supported by the Research Foundation from Ministry of Education of China (Grant No 306020), the Specialized Research Fund for the Doctoral Program of Higher Education, China (Grant No 20060003050), and the National Natural Science Foundation of China (Grant No 20773073).

†Corresponding author. E-mail: wgz-dmp@tsinghua.edu.cn

tions. In the following, subscripts 1, 2 and 3 denote, respectively, the variables for the H–C stretching, the HCO bending and the C–O stretching motions. The couplings (resonances) are 1:1 and 2:2 between the H–C and C–O stretching motions, and Fermi resonance between the stretching and bending motions. This algebraic Hamiltonian reads

$$\begin{aligned} H =&\omega_1\left(n_1+\frac{1}{2}\right)+\omega_2\left(n_2+\frac{1}{2}\right)+\omega_3\left(n_3+\frac{1}{2}\right)\\ &+X_{11}\left(n_1+\frac{1}{2}\right)^2+X_{12}\left(n_1+\frac{1}{2}\right)\left(n_2+\frac{1}{2}\right)\\ &+X_{13}\left(n_1+\frac{1}{2}\right)\left(n_3+\frac{1}{2}\right)\\ &+X_{22}\left(n_2+\frac{1}{2}\right)^2+X_{23}\left(n_2+\frac{1}{2}\right)\left(n_3+\frac{1}{2}\right)\\ &+X_{33}\left(n_3+\frac{1}{2}\right)^2\\ &+K_{1,0,-1}[1+\lambda_1(n_1a_1^+a_3+a_3^+a_1n_1)\\ &+\lambda_2(n_3a_1^+a_3+a_3^+a_1n_3)]\\ &+K_{1,-2,0}(a_1^+a_2a_2+a_2^+a_2^+a_1)\\ &+K_{0,-2,1}(a_3^+a_2a_2+a_2^+a_2^+a_3)\\ &+K_{2,0,-2}(a_1^+a_1^+a_3a_3+a_3^+a_3^+a_1a_1), \end{aligned} \tag{1}$$

where ω and X are the parameters for the coupled Morse oscillators; n is the action for the three coordinates; Ks are the coefficients for the resonances; a and a^+ are the destruction and the creation operators, respectively; λs are the additional parameters for the 1:1 resonance between H–C and C–O stretching motions. These coefficients are determined by fitting the eigenenergies of this algebraic Hamiltonian to the experimentally observed data (totally, 77 levels) as collected in Refs.[7,8]. The eigenenergies were obtained by diagonalizing the matrix Hamiltonian constructed from this algebraic Hamiltonian with basis vectors $|n_1,n_2,n_3\rangle$. The standard deviation is $7.4\,\mathrm{cm}^{-1}$. The determined coefficients are ω_1=2858.5 cm^{-1}, ω_2=1118.8 cm^{-1}, ω_3=1892.8 cm^{-1}, X_{11}=–194.1 cm^{-1}, X_{12}=– 46.3 cm^{-1}, X_{13}=4.2 cm^{-1}, X_{22}=–8.2 cm^{-1}, X_{23}=–4.9 cm^{-1}, X_{33}=–11.9 cm^{-1}, K_{101}=38.7 cm^{-1}, K_{120}=10.7 cm^{-1}, K_{021}=–3.3 cm^{-1}, K_{202}=9.4 cm^{-1}, λ_1=0.2, and λ_2=–0.3. This is a first report on the HCO system, to our knowledge. Compared with those in the DCO system,[11] these parameters are reasonable. For instance, ω_1 for HCO is 1.4 times that of DCO due to the isotope effect. ω_2 for HCO is also larger than that for DCO. The values of ω_3 for the two systems are quite similar. The values of X_{11} and X_{22} for HCO are larger. Furthermore, the Fermi resonance strength for HCO is smaller since its $\omega_1-2\omega_2$ is larger than that for the DCO system.

For this Hamiltonian, the action $P=(n_1+n_2/2+n_3)$ is a constant of motion. This is due to the fact that the 1:1 and 2:2 resonances between the two stretches and the Fermi resonance between the two stretching and bending motions conserve the quantized action P by their second quantization operators though individual n_1, n_2 and n_3 are no more conserved. P is called the polyad number and can be used for classifying the quantal levels, for it is a good quantum number which can block-diagonalize the algebraic Hamiltonian. We may obtain the quantum levels belonging to a specified polyad number P by simply diagonalizing the matrix Hamiltonian constructed from the algebraic Hamiltonian with bases $\{|n_1,n_2,n_3\rangle\}$ satisfying $P=n_1+n_2/2+n_3$. There are $(P+1)(P+2)/2$ levels for a given P.

This algebraic Hamiltonian can be cast into the coset space which is a classical dynamical phase space for its quantum levels.[12] A point in this space, corresponding to an eigenstate, represents a vibrational configuration. The transformation is performed by using the Heisenberg correspondence,[13] and the Hamiltonian in the coset space (q_1, p_1, q_2, p_2) is (for its detailed derivation, see Ref.[12])

$$\begin{aligned} H(q_1,p_1,q_2,p_2) =&\omega_1\left(\frac{p_1^2+q_1^2}{2}+\frac{1}{2}\right)+X_{11}\left(\frac{p_1^2+q_1^2}{2}+\frac{1}{2}\right)^2+\omega_2\left(\frac{p_2^2+q_2^2}{2}+\frac{1}{2}\right)\\ &+X_{22}\left(\frac{p_2^2+q_2^2}{2}+\frac{1}{2}\right)^2+\omega_3\left(P-\frac{p_1^2+q_1^2}{2}-\frac{p_2^2+q_2^2}{4}+\frac{1}{2}\right)\\ &+X_{33}\left(P-\frac{p_1^2+q_1^2}{2}-\frac{p_2^2+q_2^2}{4}+\frac{1}{2}\right)^2+X_{12}\left(\frac{p_1^2+q_1^2}{2}+\frac{1}{2}\right)\left(\frac{p_2^2+q_2^2}{2}+\frac{1}{2}\right) \end{aligned}$$

$$
\begin{aligned}
&+ X_{13}\left(\frac{p_1^2+q_1^2}{2}+\frac{1}{2}\right)\left(P-\frac{p_1^2+q_1^2}{2}-\frac{p_2^2+q_2^2}{4}+\frac{1}{2}\right)\\
&+ X_{23}\left(P-\frac{p_1^2+q_1^2}{2}-\frac{p_2^2+q_2^2}{4}+\frac{1}{2}\right)\left(\frac{p_2^2+q_2^2}{2}+\frac{1}{2}\right)\\
&+ K_{1,0,-1}q_1\sqrt{2\left(P-\frac{p_1^2+q_1^2}{2}-\frac{p_2^2+q_2^2}{4}\right)}\left[1+\lambda_1\left(\frac{p_1^2+q_1^2}{2}\right)+\lambda_2\left(P-\frac{p_1^2+q_1^2}{2}-\frac{p_2^2+q_2^2}{4}\right)\right]\\
&+ K_{1,-2,0}\frac{1}{\sqrt{2}}(q_1q_2^2-q_1p_2^2+2p_1p_2q_2)+K_{0,2,-1}\sqrt{P-\frac{p_1^2+q_1^2}{2}-\frac{p_2^2+q_2^2}{4}}(q_2^2-p_2^2)\\
&+ K_{2,0,-2}(q_1^2-p_1^2)\left(P-\frac{p_1^2+q_1^2}{2}-\frac{p_2^2+q_2^2}{4}\right) \qquad (2)
\end{aligned}
$$

with $n_3 = P - n_1 - n_2/2$, $n_1 = (q_1^2 + p_1^2)/2$, and $n_2 = (q_2^2 + p_2^2)/2$.

With these preparations, we are able to interpret each quantal level in terms of the classical dynamical concepts. This is realized via Hamilton's equations

$$
\begin{aligned}
&\partial H/\partial p_i = \mathrm{d}q_i/\mathrm{d}t,\\
&\partial H/\partial q_i = -\mathrm{d}p_i/\mathrm{d}t \quad (i=1,2) \qquad (3)
\end{aligned}
$$

on condition that $H(q_i, p_i)$=eigenenergy.

Similarly, we can make the dynamical analysis with $H(q_1,\ p_1,\ q_3,\ p_3)$, if necessary.

3. The Lyapunov analysis

For this (semi)classical approach, the Lyapunov exponent which shows the changing rate of the separation divergence of two neighbouring trajectories in the phase (coset) space corresponding to a level, can be used to characterize the nonlinearity associated with that level. Thus, the Lyapunov exponent is an appropriate parameter to characterize the degree of dynamical stochasticity/chaos for a level. In calculation, we may choose a point together with its neighbouring point in the phase (coset) space and then follow their corresponding trajectories determined by Hamilton's equations of motion. The details of this calculation can be found in Refs.[12, 14, 15]. In calculation, the convergence of the exponent is checked. What we calculated is, in fact, the maximal Lyapunov exponent. In calculation, two hundred such Lyapunov exponents with randomly chosen initial points in the phase space are computed and averaged. This is because different initial points in the phase space may lead to different (maximal) Lyapunov exponents. Averaging the exponents avoids this problem. We call it the average Lyapunov exponent.

4. Dynamical potential

For a better exploration of the HCO vibrational dynamics, we need to calculate the dynamical potentials,[16,17] which are the effective potentials that the H–C stretching, the bending and the C–O stretching motions experience dynamically. This is done by varying $(p_1,\ p_2)$ to obtain extreme energies E_+ (maximal) and E_- (minimal) for each $(q_1,\ q_2)$ under the constraint $p_1^2+q_1^2+(p_2^2+q_2^2)/2 \le 2P$ to ensure positive n_3. Thus $E_+(q_1,\ q_2)$ and $E_-(q_1,\ q_2)$ determine the dynamical potential where reside the levels sharing a common P. We will see how important $E_+(q_1 = 0,\ q_2)$ and $E_-(q_1 = 0,\ q_2)$ are. These dynamical potentials for P=6, 8 and 10 are shown in Figs.1(a), 1(b), and 1(c).

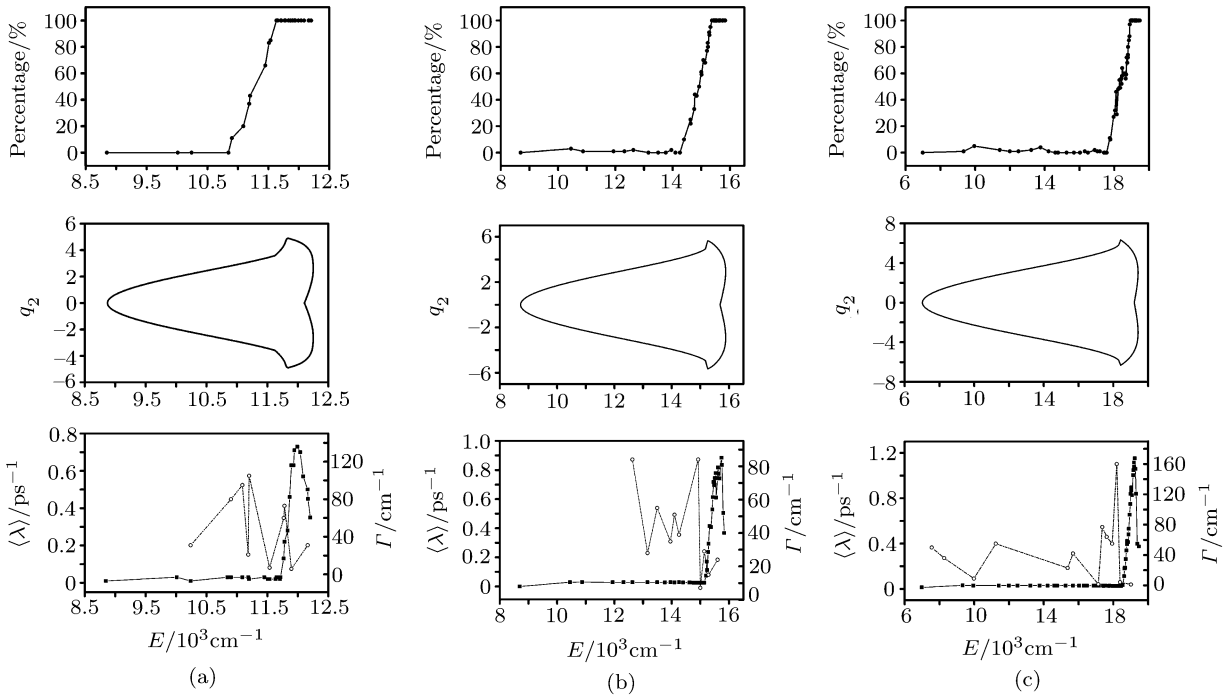


Fig.1. For the states with polyad number P=6 (a), 8 (b), and 10 (c), the percentages of nondissociation cases, the dynamical potentials along the bending coordinate (q_2) and the average Lyapunov exponent $\langle\lambda\rangle$ denoted by (■) versus energy, where also shown is the band width Γ versus energy (denoted by ◯) available from Ref.[7]. See its text for details.

5. The state dynamics under a polyad number

We find that the dynamic states under a polyad number are very similar. In the following, we perform the following analyses.

5.1. The classical simulation of the dissociation of H–C bond

For each level, we simulate the stability of H–C bond by choosing randomly 200 initial points (The choice of 500 points has been tried but a similar result is obtained.) in its phase space and by following their trajectories for a duration of 10 ps. The H–C bond is considered to be stable (nondissociative), if $n_{\mathrm{H-C}} < 4$ in this time interval. The dissociation can be understood in the sense that once crossing the dividing surface in the direction of products, a trajectory will not return to the reactant region in phase space any more.[18] The criterion that $n_{\mathrm{H-C}} > 4$ is set for H dissociation is based on the consideration that this action coincides with the threshold region of the dissociation of D atom in the DCO case.[3] With this action, the H–C bond has a displacement over 72% of its equilibrium bond length. This is large enough for the dissociation of H atom. The results for the percentages of nondissociation cases for $P = 6$, 8 and 10 are shown in Figs.1(a), 1(b), and 1(c). In the figures, also shown are the spectral widths for some levels which are available from Ref.[7]. The larger the spectral width is for a level, the larger the probability that the H–C bond is dissociative. Clearly, the general trend, where for the levels sharing a polyad number the lower levels are scattering (dissociative) states and those higher levels are resonance (stable) states, is well reproduced by this classical simulation. Quantum effect like tunnelling, which can be crucial in the dissociation of H–C bond, is expected. This implies that we just could not expect our result to be in agreement with that implied by the spectral width quantitatively.

5.2. The significance of the dynamical potential and the Lyapunov exponents

It is noted that for the levels sharing a common polyad number, the energy at which the bending coordinate (q_2) of the dynamical potential comprised of

$E_+(q_1 = 0,\ q_2)$ and $E_-(q_1 = 0,\ q_2)$ reaches its full range, corresponds well to the level which possesses a significantly dropping spectral width. Significantly, this is also the region where the average Lyapunov exponent is enhanced greatly. This demonstrates that the forming of the resonance states with smaller spectral widths and the appearing of nonzero (average) Lyapunov exponent are well correlated with the mediation by the bending motion in IVR. This is logical in the sense that the bending motion often plays a pumping role in the energy exchange between the two stretching motions in this three-body dynamics.[19,20] The energy flow mediated by the bending motion between the H–C and C–O stretches facilitates the relaxation of energy accumulated in the H–C bond and thus reduces the chance of its dissociation. This leads to a narrower spectral width. This mediation by the bending motion is also favourable for the IVR, thereby enhancing the degree of dynamical stochasticity. This leads to a larger Lyapunov exponent. For the higher levels, we can image that due to stronger couplings among the three modes, the dynamics turns out to be more stable and regular, instead. This leads to a reduction in the average Lyapunov exponent as expected.

6. The comparison among dynamical potentials

Shown in Fig.2 are the dynamical potentials along q_1 (the H–C stretching), q_2 (the H–C–O bending) and q_3 (the C–O stretching) coordinates for HCO with P=6. The horizontal segments are the corresponding levels.

It is shown that all the levels are enclosed in the dynamical potentials. Furthermore, it is interesting to note the inverse Morse type for the dynamical potential along the H–C stretching coordinate as contrasted to those along the bending and the C–O stretching coordinates which are of Morse type. We note that for a Morse potential, the lowest point is stable and the highest point is unstable, which is corresponding to the dissociation while for an inverse Morse potential, the situation is just reversed, i.e. the highest point is stable and the lowest point is unstable, which is corresponding to the dissociation. Apparently, this is related to the dissociative nature of the H–C bond. In summary, it is seen that dynamical potentials do exhibit the dynamical nature of this many-body problem.

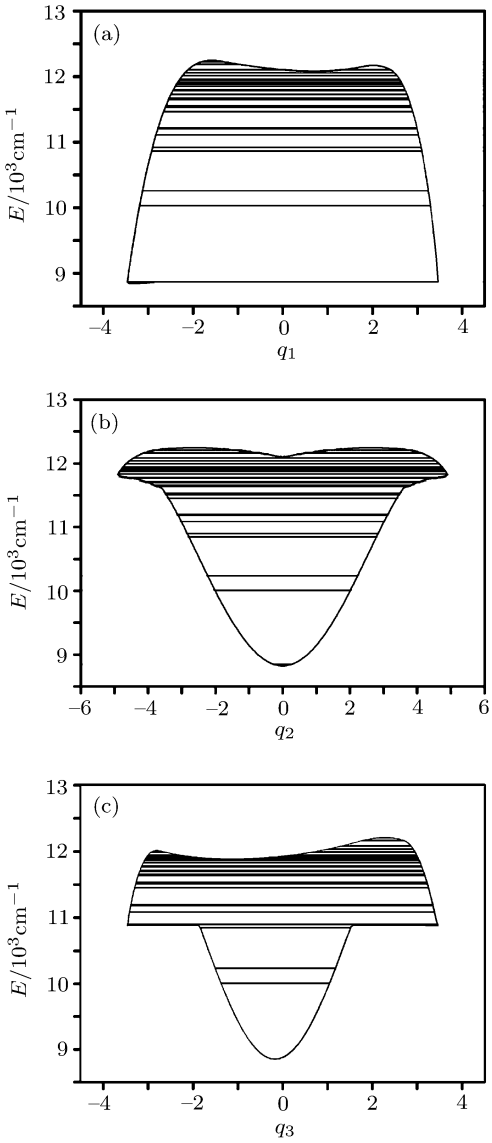


Fig.2. The dynamical potentials along q_1 (the H–C stretch) (a) , q_2 (the H–C–O bend) (b), and q_3 (the C–O stretch) (c) coordinates for HCO with P=6, where the horizontal segments are the corresponding levels.

7. Concluding remark

Highly excited vibration possesses a very complicated structure, spectroscopically. However, if the conserved (or almost conserved) quantum numbers can be identified, then we can classify the states by these quantum numbers. This classification will eminently show up the simple structure embedded therein. The dynamics for each classified group of states of such a kind will show parallelity and similarity. This helps us gain an insight into the essence of the system dynamics. What is important is that

all these observations can be achieved classically by making the nonlinear dynamical analysis via the algebraic/spectroscopic Hamiltonian which is elucidated from the fit with the level spacings. In the present study on the HCO, this idea is well demonstrated. What is deserving of special attention is the employment of dynamical potential in the coset space (via Heisenberg correspondence). Its structure shows up the crucial property of this HCO dynamics that bending motion regulates the IVR dynamics including the dissociation of the H–C bond. Along with the classical Lyapunov analysis, experimental observations such as the band spectral widths can be well understood with deep physical interpretation. This demonstrates the powerfulness of the approach by using the dynamical potential. We will apply this idea to the vibrational dynamical analysis in our future work.

References

[1] Stock C, Li X, Keller M H, Schinke R and Temps F 1997 *J. Chem. Phys.* **106** 5333

[2] Keller M H, Stumpf M, Schroder T, Stock C, Temps F, Schinke R, Werner H J, Bauer C and Rosmus P 1997 *J. Chem. Phys.* **106** 5359

[3] Troellsch A and Temps F 2001 *Z. Phys. Chem.* **215** 207

[4] Stamatiadis S, Faratos S C, Keller H M and Schinke R 2001 *Chem. Phys. Lett.* **344** 565

[5] Jung C, Taylor H and Atilgan E 2002 *J. Phys. Chem.* A **106** 3092

[6] Werner H J, Bauer C, Rosmus P, Keller H M, Stumpf M and Schinke R 1995 *J. Chem. Phys.* **102** 3593

[7] Keller H M, Floethmann H, Dobbyn A J, Schinke R, Werner H J, Bauer C and Rosmus P 1996 *J. Chem. Phys.* **105** 4983

[8] Tobiason J D, Dunlop J R and Rohlfing E A 1995 *J. Chem. Phys.* **103** 1448

[9] Ishikawa H, Field R W, Farantos S C, Joyeux M, Koput J, Beck C and Schinke R 1999 *Annu. Rev. Phys. Chem.* **50** 443

[10] Joyeux M, Sugny D, Tyng V, Kellman M, Ishikawa H, Field R, Beck C and Schinke R 2000 *J. Chem. Phys.* **112** 4162

[11] Huang J and Wu G Z 2007 *Chem. Phys. Lett.* **439** 231

[12] Wu G Z 2005 *Nonlinearity and Chaos in Molecular Vibrations* (Amsterdam: Elsevier)

[13] Heisenberg W 1925 *Z. Physik* **33** 879

[14] Benettin G, Galgani L, Giorgilli A and Strelcyn J M 1980 *Meccanica* **15** 9

[15] Benettin G, Galgani L and Strelcyn J M 1976 *Phys. Rev.* A **14** 2338

[16] Jung C and Taylor H S 2007 *J. Phys. Chem.* A **111** 3047

[17] Kellman M E 1985 *J. Chem. Phys.* **83** 3843

[18] Forst W 2003 *Unimolecular Reactions* (Cambridge: Cambridge University Press)

[19] Wu G Z 1994 *Chem. Phys. Lett.* **227** 682

[20] Ou S Q and Wu G Z 2007 *Chin. Phys.* **16** 2952