

A model study of intramolecular energy transfer in polyatomic molecular reactions

Meishan Zhao

¹ The James Franck Institute and Department of Chemistry, The University of Chicago, Chicago, IL 60637, USA

Received April 8 1996/Final revision received June 18, 1996/Accepted June 25, 1996

Summary. This paper reports a model study of intramolecular energy transfer in unimolecular isomerization reaction of cyclobutanone. The calculations of intramolecular energy flow were carried out using the theory of Gray and Rice as extended by Zhao and Rice. The results of the calculations are compared to those of local Lyapunov function analysis, and the agreement is found to be uniformly good.

Key words: Nonlinear Dynamics – Intramolecular energy transfer – Isomerization – Lyapunov exponent – Cyclobutanone

1 Introduction

In the last decade, Davis and Gray [1–5] introduced the theory of nonlinear dynamics [6] and the theory of nonlinear mappings [7–9] into unimolecular reaction rate theory. These ideas were first applied by Gray and Rice [10] to the rate theory of unimolecular isomerization. Besides the introduction of the nonlinear dynamics, the topology of Gray–Rice theory differs fundamentally from that of the RRKM theory [11–13]. Gray–Rice theory shows that it is necessary to have a third state in the phase space rather than the conventional two state representations. The necessity for this classification of the regions of phase space follows from the following observation: besides the states identified with isomers A and B, as long as the molecule remains intact there must be a third state of the system, which is neither A nor B, with energy more than the barrier to isomerization. The existence of these three system states was clearly seen in trajectory studies [10].

Gray–Rice theory is plausible but still ignores the dynamics of intramolecular energy transfer as conventional RRKM theory does. Zhao and Rice [14, 15] extended Gray–Rice theory by developing a useful approximation to the rate of intramolecular energy exchange. This approximation takes advantage of the identification of the barrier to intramolecular energy flow with the remnants of the loci of periodic motion associated with the most irrational frequency ratio in the system (the cantorus), which they replace with a curve defined by analogy with the analytic approximation to the separatrix. As shown already, the inclusion of the intramolecular energy transfer dynamics in the analysis of the isomerization rate qualitatively improves the prediction of the reaction rate constant.

In this paper we study the intramolecular energy transfer in a model polyatomic molecular system, specifically the rate of isomerization of cyclobutanone. We examine the intramolecular energy transfer and compare the rate generated by the Zhao–Rice approximation to those of local Lyapunov function analysis [16].

2 System model

The potential energy surface for the model study is derived by Zhang, Chiang and Laane [17] from the fluorescence excitation spectra of cyclobutanone (C_4H_6O). The kinetic energy and potential parameters are obtained by fitting to the spectroscopic data. The structure of this molecule is shown in Fig. 1.

This model assumes that by ignoring the minor corrections from other degrees of freedom of the molecule, the dynamics of the isomerization process is dominated by the coupling of C=O wagging and ring-puckering motions, without need for consideration of the other degrees of freedom of the molecule. Let s be the coordinate representing the out-of-plane carbonyl C=O wagging, and x the coordinate representing the ring-puckering motion, then the system Hamiltonian for the model cyclobutanone has the form

$$H(x, s) = \frac{1}{2} g_1(s) p_s^2 + \frac{1}{2} g_2(x) p_x^2 + V(x, s) \quad (1)$$

with the kinetic energy coefficients expanded as

$$\begin{aligned} g_1(s) &= g_1^{(0)} + g_1^{(2)} s^2 + g_1^{(4)} s^4 + g_1^{(6)} s^6, \\ g_2(x) &= g_2^{(0)} + g_2^{(2)} x^2 + g_2^{(4)} x^4 + g_2^{(6)} x^6, \end{aligned} \quad (2)$$

and the potential energy surface

$$V(x, s) = V_1(s) + V_2(x) + U(x, s) \quad (3)$$

with

$$V_1(s) = a_1 s^4 + b_1 s^2, \quad V_2(x) = a_2 x^4 + b_2 x^2, \quad U(x, s) = csx^3, \quad (4)$$

where p_s and p_x are the conjugate momenta to the s and x coordinates. Specifically, the numerical parameters of the Hamiltonian function are chosen to be

$$\begin{aligned} g_1^{(0)} &= 135.00 \times 10^3 u^{-1}, & g_1^{(2)} &= -17.69 \times 10^3 u^{-1} \text{ \AA}^{-2}, \\ g_1^{(4)} &= 2.562 \times 10^3 u^{-1} \text{ \AA}^{-4}, & g_1^{(6)} &= -0.237 \times 10^3 u^{-1} \text{ \AA}^{-6}, \\ g_2^{(0)} &= 5.24 \times 10^3 u^{-1}, & g_2^{(2)} &= -4.16 \times 10^3 u^{-1} \text{ \AA}^{-2}, \\ g_2^{(4)} &= -27.76 \times 10^3 u^{-1} \text{ \AA}^{-4}, & g_2^{(6)} &= 34.69 \times 10^3 u^{-1} \text{ \AA}^{-6}, \\ a_1 &= 3.34 \times 10^3 \text{ cm}^{-1} \text{ \AA}^{-4}, & a_2 &= 1.3 \times 10^7 \text{ cm}^{-1} \text{ \AA}^{-4}, \\ b_1 &= -5.26 \times 10^3 \text{ cm}^{-1} \text{ \AA}^{-2}, & b_2 &= -2.65 \times 10^4 \text{ cm}^{-1} \text{ \AA}^{-2}, \\ c &= -5.0 \times 10^5 \text{ cm}^{-1} \text{ \AA}^{-4}. \end{aligned}$$

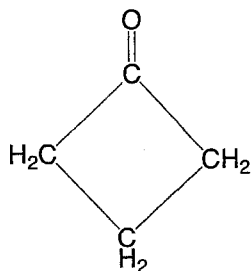


Fig. 1. Chemical structure of cyclobutanone (C_4H_6O)

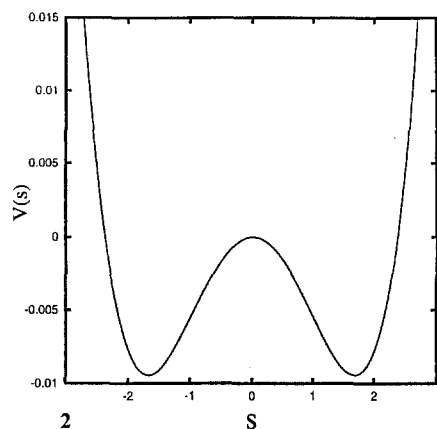
The potential function $V_1(s)$ along the reaction coordinate is plotted in Fig. 2. It has a 0.00094 a.u. barrier height energy. Fig. 3 gives the contours of the potential energy surface along C=O wagging (s) and ring-puckering (x) motions.

The classical dynamics for this model system is governed by the Hamilton equations

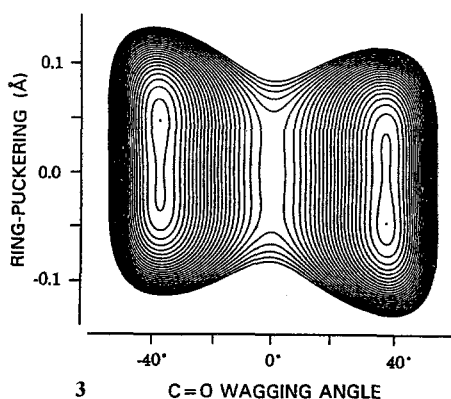
$$\dot{s} = \frac{\partial H}{\partial p_s}, \quad \dot{p}_s = -\frac{\partial H}{\partial s}, \quad \dot{x} = \frac{\partial H}{\partial p_x}, \quad \dot{p}_x = -\frac{\partial H}{\partial x}. \quad (5)$$

To display the dynamics structure of the system we use the Poincaré surface of section representation. The surface of the section is chosen as the plane where the x -coordinate is equal to zero when its conjugate momentum p_x is positive [18]. Since the potential surface $V(x, s)$ in the present study is not homogeneous, the energy can be a control parameter for the system dynamics. For a different system energy the dynamic structure may vary. Figure 4 shows the Poincaré surface of the section for energy $E = 0.0075$ a.u.. The surface of the section for system energy $E = 0.01$ a.u. is displayed in Fig. 5.

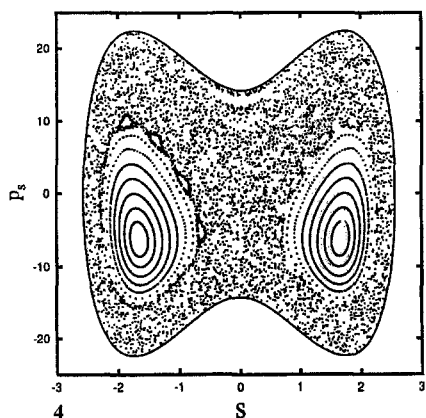
Figures 4 and 5 show clearly that in the Poincaré surface of section representation a considerable portion of the surface is taken by quasi-periodic motion. The two elliptic fixed points are separated by the point ($s = 0, p_s = 0$). Trajectories started on any of the closed curves evolve forever on the surfaces of the corresponding KAM tori [16]. Such a stable quasi-periodic motion gives no contribution to the isomerization reaction; only the chaotic trajectories, which wander over the entire energy hypersurface can lead to isomerization. More interesting is the fact that the region of the surface of the section with irregular motion can be separated into distinct subregions [19], and an irregular trajectory remains in that subregion in which it starts. These subregions are intimately intermingled with each other. The quasiperiodic motion covers about 36% of the available phase space region for $E = 0.007$ a.u. and it is about 33% for $E = 0.01$ a.u. Figures 4 and 5 also show a chain of islands between the regions of quasi-periodic and chaotic motion; these correspond to nonlinear resonances in the system. In the case of $E = 0.0075$ a.u. shown in Fig. 4, it shows the 4:1 resonance corresponding to the frequency ratio of ring-puckering to C=O wagging motions. For the case of $E = 0.01$ a.u. this ratio turns out to be 3:1 as shown in Fig. 5. In the neighbourhoods of the resonance islands there are remnants of broken KAM torus (the cantorus). The cantorus may be thought of as a torus with an infinite number of deleted gaps caused by the overlapping of nearby resonance island chains. Phase space trajectories can leak through the holes in the cantorus and thereby escape to cover the remainder of the surface of the section. The leakage can be very slow, in which case the cantorus serves as a substantial barrier to large scale diffusion of the trajectories [20].



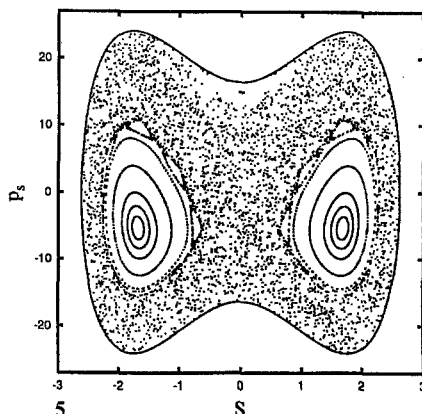
2



3



4



5

Fig. 2. The double well potential function for the model cyclobutanone system, along the reaction coordinate

Fig. 3. The contours of the potential surface of cyclobutanone, ring-puckering (x) versus the C=O wagging angle ϕ . The C=O wagging coordinate s defined in the text is given by the C=O bond distance (r) times the C=O wagging angle $s = r\phi$

Fig. 4. The Poincaré surface of the section for the model of cyclobutanone at $E = 0.0075$ a.u.

Fig. 5. The Poincaré surface of the section for the model of cyclobutanone at $E = 0.010$ a.u.

3 Gray–Zhao–Rice rate theory of isomerization

The Gray–Rice analysis of the rate of isomerization divides the energy surface into three regions in phase space by use of a redefined transition state – the dynamical separatrix. The two closed regions inside the separatrix, which represent the two isomers, are denoted A and B; the exterior region between the separatrix and energy boundary is denoted C.

The elementary rate constants describing phase point transfer amongst the states A, B and C are given

$$k_{AC} = \frac{F_{AC}}{N_A}, \quad k_{CA} = \frac{F_{CA}}{N_C}, \quad k_{BC} = \frac{F_{BC}}{N_B}, \quad k_{CB} = \frac{F_{CB}}{N_C}, \quad (6)$$

where F_{AC} is the forward flux from region A to region C; N_A is the phase space volume of region A. $F_{AC} = F_{CA}$ is obtained by consideration of the microscopic reversibility.

Gray–Rice theory uses a zero-order analytic approximation to the separatrix with respect to the reaction coordinate [10, 14]. For the model cyclobutanone it is defined by

$$S_{\text{sep}}(p_s, s, \bar{x}) = \frac{1}{2} g_1(s) p_s^2 + V(s) + U(\bar{x}, s) \quad (7)$$

and the time derivative of the separatrix is obtained by the use of Hamiltonian equations,

$$\dot{S} = g_1(s) p_s \frac{\partial [U(\bar{x}, s) - U(x, s)]}{\partial s}, \quad (8)$$

where in Eqs. (7) and (8), \bar{x} is a fixed value of x and is normally chosen to be at the saddle point of the potential energy surface.

The flux going through the separatrix from one phase space region to another can be calculated from

$$F_{AC} = \int dp_s dp_x ds dx \delta(E - H) \delta(S) \theta(\dot{S}) \dot{S}, \quad (9)$$

and the phase space volume for region A is given by

$$N_A = \int dp_s dp_x ds dx \delta(E - H) \delta(S). \quad (10)$$

These integrals can be simplified by the integration over the δ -functions, which yields the flux from A to C,

$$F_{AC} = \int ds dx \frac{2^{1/2} |\partial [U(\bar{x}, s) - U(x, s)] / \partial s|}{g_2(x)^{1/2} [E - \frac{1}{2} g_1(s) \bar{p}_s^2 - V(x, s)]^{1/2}}, \quad (11)$$

with

$$\bar{p}_s = 2^{1/2} [-V(s) - U(\bar{x}, s)]^{1/2} g_1(s)^{-1/2}, \quad (12)$$

and the normalization constant for phase region A,

$$N_A = \int ds dx \frac{4 \sin^{-1} [p_{\min}/p(x, s)]}{[g_1(s) g_2(x)]^{1/2}}, \quad (13)$$

with

$$p(x, s) = 2^{1/2} [E - V(x, s)]^{1/2} g_1(s)^{-1/2},$$

$$p_{\min} = \min [p(x, s), \bar{p}_s]. \quad (14)$$

Since the potential energy surface for the model cyclobutanone has a symmetric double well representing isomers A and B, it has $N_A = N_B$. Finally, the phase space

volume of region C is calculated from

$$\begin{aligned}
 N_C &= \int dp_s dp_x ds dx \delta(E - H) - N_A - N_B \\
 &= 2\pi \int ds dx \frac{\theta(E - V(x, s))}{[g_1(s)g_2(x)]^{1/2}} - 2N_A.
 \end{aligned} \tag{15}$$

If one assumes that A to C and C to B transitions are independent processes, the rate constant k_{AB} of the isomerization $A \rightarrow B$ can be calculated from $k_{AB} = 1/(k_{AC}^{-1} + k_{CB}^{-1})$. For systems with complete chaotic dynamics motions, Gray–Rice theory gives satisfactory prediction of the rate of isomerization.

As mentioned, Gray–Rice theory ignores intramolecular dynamics motion. It may yield misleading numerical factors in the prediction of reaction rate constants for systems with both chaotic and unstable quasi-periodic motions. To improve the Gray–Rice theory, Zhao and Rice introduced a semiclassical approximation for the representation of the intramolecular bottlenecks [14–15, 21–23]. One can imagine that a well-defined dividing surface can be drawn around the region corresponding to quasi-periodic motion of isomer A; this surface splits the lobe of the phase space corresponding to isomer A into an interior region A_1 and an exterior region A_2 . The proposed dividing surface, of course, lies inside the separatrix and is intended to approximate the last broken KAM torus, namely, the torus which corresponds to the most irrational frequency ratio. Zhao and Rice then suggested using the functional form of Eq. (7) for this dividing surface, which implies that the n -th intramolecular bottleneck has the form

$$S_{\text{intra}}(p_s, s, \bar{x}) = \frac{1}{2} g_1(s) p_s^2 + V(s) + \bar{U}(\bar{x}, s) - E_s(n). \tag{16}$$

When the motion in the degree of freedom s is confined to the vicinity of the isomer equilibrium value, a harmonic approximation should be valid. This assumption yields

$$E_s(n) = \left(n + \frac{1}{2} \right) \hbar \omega_s \tag{17}$$

and

$$\omega_s = \left[g_1(s) \frac{\partial^2 V(x, s)}{\partial s^2} \right]_{s=s_0, x=x_0}^{1/2}, \tag{18}$$

where the derivative is evaluated at the potential well minimum. For the system potential of cyclobutanone, the potential minimum appears at $s = s_0 = 1.68$ a.u. and $x = x_0 = 0$.

The rates of transport of phase points across the intramolecular bottlenecks can be calculated as follows. The net flow rate $k_{A_1 A_2}$ characterizes the spreading of phase points from the region with quasi-periodic motion to the region with chaotic motion, hence simulates the intramolecular energy transfer process. In Zhao–Rice theory one takes this net flow rate to be the intramolecular energy exchange rate.

The kinetics of the three state mechanism of isomerization, with inclusion of the rate of intramolecular energy transfer, can be represented by a set of coupled

kinetics differential equations

$$\begin{aligned}
 \frac{dN_{A_1}}{dt} &= -k_{A_1 A_2} N_{A_1} + k_{A_2 A_1} N_{A_2}, \\
 \frac{dN_{B_1}}{dt} &= -k_{B_1 B_2} N_{B_1} + k_{B_2 B_1} N_{B_2}, \\
 \frac{dN_{A_2}}{dt} &= -(k_{A_2 A_1} + k_{A_2 C}) N_{A_2} + k_{A_1 A_2} N_{A_1} + k_{CA_2} N_C, \\
 \frac{dN_{B_2}}{dt} &= -(k_{B_2 B_1} + k_{B_2 C}) N_{B_2} + k_{B_1 B_2} N_{B_1} + k_{CB_2} N_C, \\
 \frac{dN_C}{dt} &= -(k_{CA_2} + k_{CB_2}) N_C + k_{A_2 C} N_{A_2} + k_{B_2 C} N_{B_2}.
 \end{aligned} \tag{19}$$

By solving this set of differential equations one obtains $N_{A_1}(t)$ and $N_{A_2}(t)$ for isomer state A. Since $N_A(t) = N_{A_1}(t) + N_{A_2}(t)$, one can fit the functional form $N_A(t) = N_A(0) \exp(-k_{AC} t)$ to obtain the rate constant k_{AC} for the reaction from state A to state C. The rate between any other two states can be obtained in the same fashion, and finally the reaction rate of isomerization from isomer A to isomer B can be calculated from

$$\frac{1}{k_{AB}} = \frac{1}{k_{AC}} + \frac{1}{k_{CB}}. \tag{20}$$

More detailed discussion on the methodology used for extracting the isomerization rate constant from this set of equations can be found elsewhere [15].

4 Results and conclusions

The integrals in the last section for the fluxes and the volumes of the phase space were evaluated by Monte Carlo integration. Large sets of random numbers (10^7 – 10^8) were used to guarantee good convergence.

It has been shown [24] that for this model system of cyclobutanone the RRKM theory generates about an order of magnitude overestimate of the reaction rate constant. Gray–Zhao–Rice theory rate constants agree within a factor of two with those derived from the trajectory calculations. This discrepancy is largely due to the uncertainty associated with the difference between the rate constants extracted from the three-state Gray–Zhao–Rice model and the two-state RRKM-like trajectory studies. Overall, it shows that the intramolecular energy transfer is a very important factor for the model cyclobutanone. The inclusion of the intramolecular energy exchange process is unavoidable in order to correctly predict the isomerization rate in this model polyatomic molecular reaction.

Table 1 shows the rate constants of intramolecular energy transfer derived from an analysis of Zho–Rice theory, and comparing to Lyapunov relaxation rate generated from a local Lyapunov function analysis. The results of these two theories are in fairly good agreement.

Table 1. The intramolecular energy exchange rate constants from Zhao–Rice theory and the local Lyapunov function analysis (in units of 10^{-4} a.u. for all entries)

Energy	Zhao–Rice	Lyapunov Analysis
25	0.104	0.13
75	0.113	0.18
100	0.132	0.16

As shown in this paper, the RRKM prediction of the isomerization rate constant of cyclobutanone is an order of magnitude too large. It poorly describes the competition between the rates of intramolecular energy transfer and reaction. Davis' nonlinear dynamical turnstile approach gives accurate dynamical description, but generally requires very heavy numerical computation. Although in the present study there is a reasonable agreement between the Zhao–Rice prediction of the intramolecular energy transfer rate and the relaxation rate of local Lyapunov analysis for the model cyclobutanone, it remains to be determined if this kind of agreement is universal. Besides, local Lyapunov analysis for multidimensional polyatomic molecular systems may also lead to uncontrollable numerical computation. For the present, we consider our analysis from the Gray–Zhao–Rice theory as a computationally feasible alternative to Davis' turnstile approach and to the local Lyapunov analysis for the calculation of the rate of intramolecular reaction in a system with both quasi-periodic and chaotic motion.

Acknowledgements. The author thanks Professor Stuart A. Rice for support and contributions to this research. He has also benefited from the use of the facilities for materials research at the University of Chicago.

References

1. Davis MJ, Gray SK (1986) *J Chem Phys* 84:5389
2. Davis MJ (1985) *J Chem Phys* 83:1016
3. Davis MJ (1984) *Chem Phys Lett* 110:491
4. Davis MJ, Wagner AF (1984) In: Truhlar DG (ed.) *Resonances in electron–molecular scattering, van der Waals complexes, and reactive chemical dynamics*, ACS Symp. Series 263, Washington, D.C.
5. Gray SK, Rice SA, Davis MJ (1986) *J Phys Chem* 90:3470
6. See, for example, Lichtenberg AJ, Leiberman MA (1983) *Regular and stochastic motion*. Springer New York; Arrowsmith DK, Place CM (1990) *An introduction to dynamical systems*. Cambridge University Press Cambridge (1990)
7. Mackay RS, Meiss JD, Percival IC (1984) *Physica D* 13:55; (1987) 27:1
8. Bensimon D, Kadanoff LP (1984) *Physica D* 13:65
9. Dana I, Murray NV, Percival IC (1988) *Phys Rev Lett* 62:233
10. Gray SK, Rice SA (1987) *J Chem Phys* 86:2020
11. Rice OK, Ramsperger HC (1927) *J Am Chem Soc* 49:1616; (1928) 50:617; Kassel LS (1928) *J Phys Chem* 32:225 (1932) In: *Kinetics of homogeneous gas reactions*, chap. 5. Reinhold New York
12. Marcus RA, Rice OK (1951) *J Phys Colloid Chem* 55:894; Marcus RA (1952) *J Chem Phys* 20:359; Wieder GM, Marcus RA (1962) *J Chem Phys* 37:1835; Marcus RA (1965) *J Chem Phys* 43:2658

13. See, for example, Robinson PJ, Holbrook KA (1972) Unimolecular reactions. Wiley-Interscience London; (1973) Theory of unimolecular reactions. Academic New York; Laidler KJ (1987) Chemical kinetics, 3rd ed. Harper-Row New York
14. Zhao M, Rice SA (1992) *J Chem Phys* 97:943
15. Zhao M, Rice SA (1993) *J Chem Phys* 98:3827
16. See, for example, Hale J, Kocak H (1991) Dynamics and bifurcations. Springer New York; Zaslavsky GM (1985) Chaos in dynamic systems, Harwood Academic, New York; Zaslavsky GM, Sagdeev RZ, Usikov DA, Chernikov AA (1991) Ott E, Weak chaos and quasi-regular Patterns. Cambridge Press New York; (1993) Chaos in dynamical system. Cambridge New York
17. Zhang J, Chiang W, Laane J (1994) *J Chem Phys* 100:3455; (1993) *bf* 98:6129
18. Henon M (1982) *Physica D* 5:412; Bohigas O, Tomsovic S, Ullmo D (1993) *Phys Rep* 233:43
19. Meyer H (1986) *J Chem Phys* 84:3147
20. Reichl LE (1992) The transition of chaos: in conservative classical system, quantum manifestations. Springer New York
21. Zhao M, Rice SA (1992) *J Chem Phys* 96:3541; Zhao M, Rice SA (1992) *J Chem Phys* 96:6654; Zhao M, Rice SA (1992) *J Chem Phys* 96:7483
22. Jang S, Zhao M, Rice SA (1992) *J Chem Phys* 97:8188; Tang H, Jang S, Zhao M, Rice SA (1994) *J Chem Phys* 101:1; Jang S, Rice SA (1994) *J Chem Phys* 99:9585; Tang H, Jang S, Zhao M, Rice SA, to be published.
23. Zhao M (1993) *Chin J Chem* 11:409; Zhao M (1994) *Chin J Chem Phys* 7:102; Zhao M (1995) *Chin J Chem* 13:40
24. Zhao M (1996) *Int J Mod Phys C*, vol 7; Rice SA, Zhao M (1996) *Int J Quant Chem* 58:593