

## ARTICLE

# Theoretical Research on Scattering Resonance States of Reaction $I+HI(v=0)\rightarrow IH(v'=0)+I$ : Partial Potential Energy Surface and One-dimensional Quantum Reactive Scattering Calculation

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(Dated: Received on November 11, 2005; Accepted on March 14, 2006)

Based on the vibrational potential curves coupled with the minimum energy reaction path, the partial potential energy surface of the reaction  $I+HI\rightarrow IH+I$  was constructed at the QCISD(T)//MP4SDQ level with pseudo potential method. And the formation mechanism of the scattering resonance states of this reaction was well interpreted with the partial potential energy surface. The scattering resonance states of this reaction should belong to Feshbach resonance because of the coupling of the vibrational mode and the translational mode. With the one-dimensional square potential well model, the resonance width and lifetime of the  $I+HI(v=0)\rightarrow IH(v'=0)+I$  state-to-state reaction were calculated, which preferably explained the high-resolved threshold photodetachment spectroscopy of the  $IHI^-$  anion performed by Neumark *et al.*

**Key words:** Partial potential energy surface, Scattering resonance states, Scattering resonance width and lifetime, One-dimensional square potential well model

## I. INTRODUCTION

Chemical reactions in which a light atom (like hydrogen atom) is transferred between two heavy atoms (or groups of atoms) are called heavy-light-heavy (HLH) reactions [1-3]. The reaction  $I+HI\rightarrow IH+I$  is a typical model of the HLH reactions. Over the past 30 years, the research on the scattering resonance states are always the frontier subject, which draws great attention of the experimental and theoretical chemists [4-25], for the HLH reactions have some remarkable characters, for example, (i) the reaction-probability oscillating with the collision energy is not a monotone function; (ii) scattering resonance states with long lifetime are produced by the vibrational excited states normally; (iii) the system passes through the transition region many times which is called the transition state recrossing effects; (iv) the tunneling effect of the light atom is remarkable in the strong interaction region.

Neumark *et al.* discussed the transition state of the reaction  $I+HI\rightarrow IH+I$ , the width and the lifetime of the scattering resonance states with the photodetachment spectroscopy of the  $IHI^-$  anion [4-8]. This research, which is high evaluated by Schatz [9], is regarded as a "direct" measurement on the scattering resonance states of the  $I+HI(v=0)\rightarrow IH(v'=0)+I$  state-to-state reaction. And in recent years, Liu *et al.* developed more rigorous instrument for studying the cross-molecular beams [10-14], by which they measured the excited functions of the reactive systems,  $H+D_2$ ,  $F+H_2$ ,

etc. Furthermore, Yang *et al.* achieved much remarkable work in this aspect [15-17]. All the above experimental work show the direct evidence of the existence of the resonance states in these reactions indubitably. On the other hand, the cross molecular beam experiment is an "indirect" method, which speculates the existence of the scattering resonance states by the space symmetric property of the differential cross section (or the angular distribution of the products). For the reaction  $F+HD(v)\rightarrow FH(v')+D$ , Lee *et al.* obtained the space distribution of the product FH and concluded the existence of the resonance state on the  $v'=2$  state of the system [26]. So they predicate the existence of the resonance state not by observing the scattering resonance states directly, but by analyzing the angular distribution of the products.

In the theoretical aspect, Römelt *et al.* brought forward the LEPS (London-Eyring-Polanyi-Sato) potential energy surface (PES) of the  $I+HI$  reaction system and performed the quantum scattering dynamics calculation on the collinear reaction [24]. More detailed and thorough three-dimensional reaction quantum scattering calculations were carried out on the LEPS PES and the PES proposed by Schatz *et al.* [18-20]. These theoretical research [18-24] can explain the result of the cross molecular beam experiment perfectly and give us more profound explanation for the formation mechanism of the scattering resonance states. However, the results of these studies can not be used directly to interpret the photodetachment spectroscopy of the  $IHI^-$  anion performed by Neumark *et al.* [4-8]. The PES of the target system is necessary to the theoretical study on the scattering resonance states and the PES can be predigested to a great extend. That is to say, the partial potential energy surface (PPES) [27-29] with fewer dimensions is

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a good substitution of the complete PES for the analysis of the scattering resonance states. These PPESs can be constructed by the *ab initio* methods with one or several of the dimensions ignored.

It is necessary to be indicated that the precision of the semi-empirical LEPS PES depends on the choice of the adjustable parameters greatly. It can not give us the correct formation mechanism of the reactive scattering resonance states if the choice is incorrect. Just like what Wyatt *et al.* said [30], by adjusting the parameters of the Muckerman #5 PES of the F+H<sub>2</sub> reaction, the dynamic potential well of the vibrational potential energy vanished, and then the resonance states can not be seen on this PES curve.

In this work, QCISD(T)//MP4SDQ method with pseudo potential is employed to construct the PPES of the I+HI reactive system. And the width and lifetime of the scattering resonance states in the I+HI(*v*=0)→IH(*v*'=0)+I state-to-state reaction are calculated with the one-dimensional square potential well model (see Fig.1). We hope to present the theoretical explanation for the photodetachment spectroscopy of the IHI<sup>-</sup> anion performed by Neumark *et al.* [4-8], and to comprehend the scattering resonance states of the reaction more profoundly.

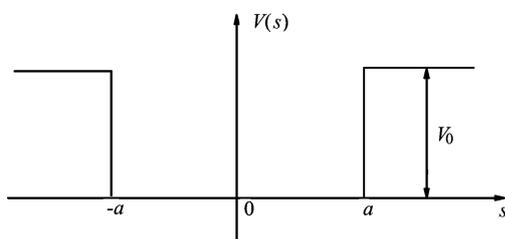


FIG. 1 The sketch map of the one-dimensional square potential well.

## II. THEORETICAL CALCULATION METHODS

### A. Construction of the partial potential energy surface

The translational and vibrational degrees of freedom and their nonadiabatic coupling are necessary to the theoretical explanation of the photodetachment spectroscopy of the IHI<sup>-</sup> anion performed by Neumark *et al.* [4-8], except the rotational mode. Then, the Hamiltonian of the nuclear motion of the system in the natural collision coordinate (*s*,  $\rho$ ) can be written as:

$$\hat{H} = -\frac{\hbar^2}{2\mu} \left[ \eta^{-1} \frac{\partial}{\partial s} \eta^{-1} \frac{\partial}{\partial s} + \eta^{-1} \frac{\partial}{\partial \rho} \eta \frac{\partial}{\partial \rho} \right] + V(s, \rho) \quad (1)$$

where  $V(s, \rho)$  is the PES of the system, shown as follows:

$$V(s, \rho) = V_1(s) + V_2(\rho; s) \quad (2)$$

and the factor  $\eta = 1 + \kappa(s)\rho^2$ , which can be treated as  $\eta = 1$  when the curvature of the reaction path  $\kappa(s)$  is small. This has been proved to be a good approximation in the former work [31].  $V_1(s)$  is the minimum energy path (MEP), and  $V_2(\rho; s)$  is the vibrational potential energy along the reaction coordinate. The  $V_1(s)$  varies only with the reaction coordinate, so it can be represented by the intrinsic reaction coordinate (IRC) calculation.

$V_2(\rho; s)$  can be represented in its Taylor series as:

$$V_2(\rho; s) = V_2^0(s) + \frac{1}{2!} \frac{\partial^2 V(\rho; s)}{\partial \rho^2} \Big|_s \rho^2 + \frac{1}{3!} \frac{\partial^3 V(\rho; s)}{\partial \rho^3} \Big|_s \rho^3 + \dots \quad (3)$$

where  $V_2^0(s)$  is the zero-point correction to the potential energy which can be obtained in the Gaussian program calculation. In Eq.(3), the third term and the terms behind it are the nonadiabatic correction, which can be neglected for it is assumed to be small in most cases [32]. It can be seen from our calculation results that the value of the third term is no more than 1% of that of the second term and the latter terms are even smaller than the third.

So the vibrational potential energy along the reaction coordinate can be calculated if the vibrational coordinate is averaged to the reaction path at each *s* point. And then the vibrational angular frequency can be shown by the following equation:

$$\omega^2(s) = \frac{1}{\mu} \frac{\partial^2 V(\rho; s)}{\partial \rho^2} \Big|_s \quad (4)$$

As the harmonic model is adopted, the eigenvalue of the vibration energy is given in terms of  $\omega(s)$  by

$$\varepsilon_n(s) = \left( n + \frac{1}{2} \right) \hbar \omega(s) \quad (5)$$

Therefore, the PPES only including the reaction coordinate *s* can be represented as

$$V(s) = V_1(s) + V_2^0(s) + \varepsilon_n(s) \quad (6)$$

Eqs.(4)-(6) provide us an effective method to construct the PPES, in which the  $V \sim s$  curves can describe the detailed process (from the reactants to the products) of the system, which involves translational and vibrational motions. In the following text, it can be seen that the PPES is different from the equipotential curves including the two degrees of freedom of the translational and vibrational motions. The PPES represented by the Eq.(6) is very convenient and helpful to analyze the mechanism of the chemical reaction, especially for the investigation on the reactive scattering resonance states.

## B. Quantum scattering calculation of the width and lifetime for the scattering resonance states

In Fig.2 we can see that, in the PPES of the reaction  $I+HI\rightarrow IH+I$ , the  $v=1$  vibrational potential curve and the upper curves, all shape like rectangle. And only one variable  $s$  is involved in the PPES when the vibrational coordinate is averaged. So the one-dimensional square potential well model (see Fig.1) is advisable. Suppose the width of the potential well is  $2a$ , and the depth of it is  $V_0$ , then its wavefunction outside the well can be written as [33]:

$$\Psi(s) = \begin{cases} e^{iks} - R \cdot e^{-iks}, & s < -a \\ -T \cdot e^{iks}, & s > a \end{cases} \quad (7)$$

where  $k = \hbar^{-1}\sqrt{2\mu E}$ ,  $\mu$  is the reduced mass of the system, and  $E$  is the total energy.

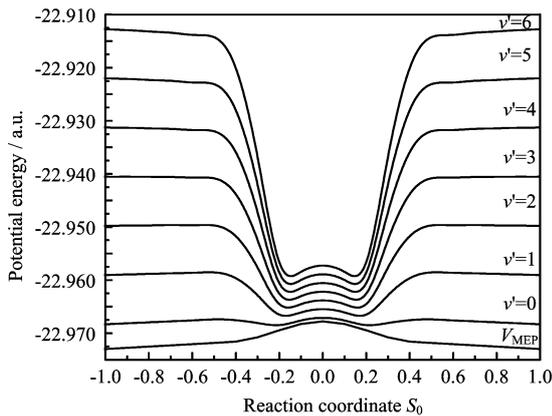


FIG. 2 The PPES of the reaction  $I+HI(v)\rightarrow IH(v')+I$ .

If the scattering matrix model is chosen, then

$$S = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \quad (8)$$

where  $S_{11} = S_{22} = R$  ( $R$  is the reflection amplitude),  $S_{12} = S_{21} = T$  ( $T$  is the transmission amplitude). They depend on the two dimensionless parameters,  $\alpha$  and  $\beta$ :

$$\alpha = \frac{E}{V_0}, \quad \beta = \frac{a}{\hbar} \sqrt{2\mu V_0}$$

The probability of the particle being inside the well reaches its maximum value when the condition  $2k'a = n\pi$  is satisfied, which means that the resonance state is formed. In this formula,  $n$  is a positive integer and  $k' = \hbar^{-1}\sqrt{2\mu(E+V_0)}$ .

The transmission amplitude  $T$  can be written in its complex form as  $T = |T| \cdot e^{i\Phi_T}$  ( $\Phi_T$  is the phase), and the transmission probability is written as:

$$|T|^2 = \frac{(\Gamma/2)^2}{(\Gamma/2)^2 + (E - E_{\text{res}})^2} \quad (9)$$

The time that the particle spends in the well region can be calculated as:

$$\tau_T = \hbar \frac{d\eta_T}{dE} \quad (10)$$

where  $\eta_T = \tan^{-1}[\varepsilon/2 \cdot \tan(2k'a)]$ , or  $\eta_T = \Phi_T + 2ka - \pi$ ,  $\eta_T$  is the contribution of the resonance to the phase, and  $\varepsilon = k/k' + k'/k$ .

The relationship between the resonance lifetime  $(\tau_T)_{\text{res}}$  and the resonance width  $\Gamma$  is

$$(\tau_T)_{\text{res}} = 2\hbar/\Gamma \quad (11)$$

$$\Gamma = \frac{8}{n\pi} \sqrt{E_{\text{res}}(E_{\text{res}} + V_0)} \quad (12)$$

The resonance energy is given by

$$E_{\text{res}} = \frac{n^2\pi^2\hbar^2}{8\mu a^2} - V_0 \quad (13)$$

All these equations are the work equations for investigating the scattering resonance states of the reactions, and the most important ones are the calculations about  $(\tau_T)_{\text{res}}$ ,  $\Gamma$  and  $E_{\text{res}}$ .

## III. RESULTS AND DISCUSSION

Based on the Eqs.(1)-(6), the PPES of the reaction  $I+HI\rightarrow IH+I$  is constructed at the QCISD(T)//MP4SDQ level with pseudo potential method, which is shown in Fig.2, the discussion on the PPES is as follows:

(i). In Fig.2, the downmost curve is the minimum energy reaction path, on which there is no intrinsic potential well (also called ‘‘Eyring Lake’’), so the Shape resonance should not appear in this system. But as the vibrational potential energy was added to the minimum energy reaction path, the potential wells with double-well structure emerge on each curve. And according to Eq.(6), we can clearly see that these potential wells are the results that the degrees of freedom of the transitional and vibrational motions are coupled with each other, which are called dynamic Eyring Lakes. By these dynamics Eyring Lakes, the system is trapped to form the scattering resonance states (also called quasi-bound states), which are named with the Feshbach resonance states [34,35].

(ii). It can be seen that more resonance states of the system in the strong interaction region on the PPES come into being when the system energy provided by the outside environment increases. For example, when the collision energy is close to the first excited vibrational state ( $v=1$ ) of the reactant HI, the number of the open resonance states in the transition region is 4 ( $v=0,1,2,3$ ). Consequently, for the  $I+HI(v=0)\rightarrow IH(v'=0)+I$  state-to-state reaction, there will be three different symmetric stretch spectrum peaks ( $3\rightarrow 0$ ,  $2\rightarrow 0$ ,  $1\rightarrow 0$ ). The conclusion is consistent with

the photodetachment spectroscopy of the  $\text{IHI}^-$  anion performed by Neumark *et al.* [4-8]. In the strong interaction region, the vibrational energy levels of the activated complex  $[\text{IHI}]$  are at intervals of 0.047 eV. Based on this result, the lifetime of the resonance state is estimated at 150 fs by the quantum uncertainty principle. And the result is coincident with the range of 120-180 fs from Neumark's experimental spectrum perfectly.

(iii). The formation mechanism of the double-well structure in the transition region of the PPES for the reaction  $\text{I} + \text{HI} \rightarrow \text{IH} + \text{I}$  is because of the symmetric oscillation of the H atom between the two I atoms and the tunneling effect of the transfer of the H atom. Skodje *et al.* found the double-well structure once [36], but he did not investigate the reactant region and the product region, for he cared only about the transition region and calculated with the quantum mechanics energy minimum method at that time.

Neumark *et al.* studied on the transition state activated complex  $[\text{IHI}]$  and the scattering resonance states in the reaction by the photodetachment spectroscopy of the  $\text{IHI}^-$  anion [4-8]. Therefore, we also construct the PPES of the reaction  $\text{I}^- + \text{HI} \rightarrow \text{IH} + \text{I}^-$  at the QCISD(T)//MP4SDQ level with pseudo potential method and show it in Fig.3.

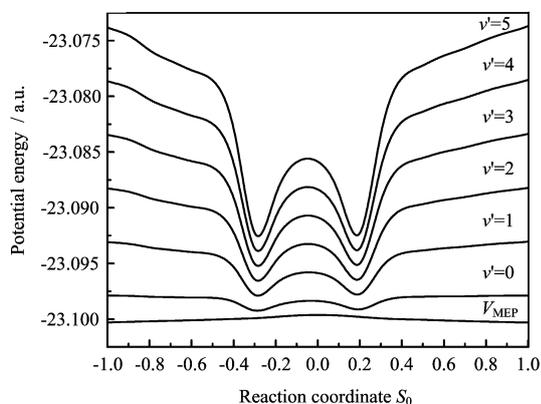


FIG. 3 The PPES of the reaction  $\text{I}^- + \text{HI}(v) \rightarrow \text{IH}(v') + \text{I}^-$ .

Comparing Fig.2 with Fig.3, it can be seen that: (i) the structures of the two figures are similar, which is the theoretical basis for studying on the activated complex  $[\text{IHI}]$  by the photodetachment spectroscopy of the  $\text{IHI}^-$  anion; (ii) in the transition region, the double-well structure of  $\text{IHI}^-$  is deeper than that of  $[\text{IHI}]$ . In another word,  $\text{IHI}^-$  is more stable than  $[\text{IHI}]$ , so it is not strange to study the transition state of this reaction by observing the photodetachment spectroscopy of the  $\text{IHI}^-$  anion, but not by the infrared spectrum of  $[\text{IHI}]$  directly. In Fig.2, the shape of the excited vibrational curves of the system likes rectangular structures. With the hemline averaged to a beeline, the depth of the well can be calculated and the well is changed into a square well structure, just like the model in Fig.2. For example, let  $v=1$  (it is mentioned in the former text that the

collision energy provided by the environment is close to the first vibrational excited state of the reactant molecular HI):  $a=0.365$  (amu) $^{0.5}$  Bohr,  $V_0=0.0078$  a.u.. Then we can get the resonance energy:  $E=0.629$  kJ/mol, the resonance width:  $\Gamma=9.279$  kJ/mol, and the resonance lifetime:  $(\tau_T)_{\text{res}}=13.69$  fs. For the  $v=2$ ,  $v=3$  states, calculated in the same way, the resonance lifetime are 31.24 and 63.96 fs.

The change of  $\eta_T$  as a function of the collision energy is shown in Fig.4, and the change of  $|T|^2$  as a function of the collision energy in Fig.5. In the two figures we can see that neither of  $\eta_T$  and  $|T|^2$  varies with the collision energy monotonically, but a maximum (or a minimum) appears at a certain point. That is the evidence for the existence of the scattering resonance states in the  $\text{I} + \text{HI}(v=0) \rightarrow \text{IH}(v'=0) + \text{I}$  state-to-state reaction.

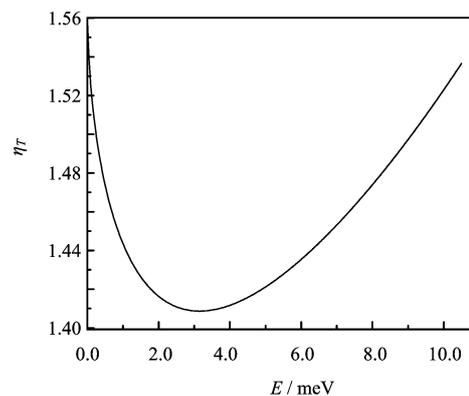


FIG. 4 The curve of  $\eta_T$  as a function of the  $E$ .

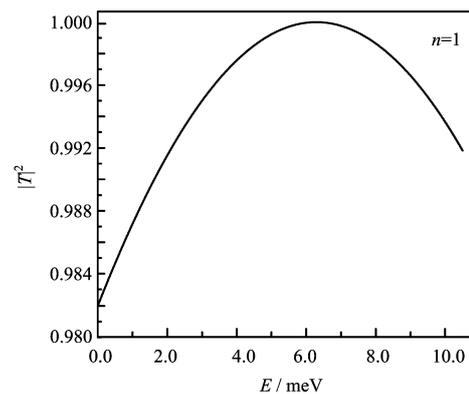


FIG. 5 The curve of the reactive probability as a function of the collision energy  $E$ .

The lifetime of the resonance states can be obtained by another method with Eq.(10). In Fig.4, we can easily calculate the slope of the curve at the point where the energy value equals to the resonance energy, and then the resonance lifetime can be calculated by Eq.(10). The three values of the resonance lifetime calculated in this way are 9.80, 25.89 and 75.49 fs, respectively, which are consistent with the results of the first method commendably.

In addition, it is also a good method to solve the differential section directly with the value of  $a$  and  $V_0$  to estimate the resonance lifetime.

It is obvious that with the one-dimensional square potential well model the results of the resonance width and lifetime, which is calculated by quantum scattering theory, are in good agreement with the results from the estimate based on the PPES. And both of them preferably coincide with the experimental results performed by Neumark *et al.* [4-8]. The lifetime values estimated in this work are smaller than the experimental results, which could be the outcome of the error produced while the reactive potential well is changed into the square model, however, the one-dimensional square potential well model is helpful to calculate the resonance width and lifetime of HLH reaction systems semi-quantificationally.

#### IV. CONCLUSION

The reaction  $I+HI\rightarrow IH+I$  is one of the several reactions in which we can investigate the transition region and the scattering resonance states directly. The experimental result of the photodetachment spectroscopy of the  $IHI^-$  anion performed by Neumark *et al.* [4-8] can be explained by the quantum scattering calculations with the PPES curves and the one-dimensional square potential well model. The results in this work demonstrate that the PPES can elucidate the formation mechanism of the scattering resonance states of the  $I+HI(v=0)\rightarrow IH(v'=0)+I$  state-to-state reaction, classify the scattering resonance states and estimate the lifetime of the resonance states semi-quantificationally. Moreover, the structural character of the PPES determines the feasibility of the adoption of the one-dimensional square potential well model. And the one-dimensional quantum scattering calculation results can not only present the results of the resonance width and lifetime coincident with the experimental results, but also provide more accurate and profoundly dynamic information, such as the resonance energy, the reactive probability, the eigenvalue of the phase and etc.

#### V. ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No.20573064) and Ph. D. Special Research Foundation of Chinese Education Department.

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