THEO
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Dimensionality effects on transition state resonances for H + DH and D + HD reactive collisions

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Abstract

The transition state resonances of the title reactions have been studied on the accurate double many-body expansion (DMBE) potential energy surface for H_3 using two-dimensional (2D) and three-dimensional (3D) time-dependent wave packet propagation methods. It is shown that the resonance energies are strongly associated with the vibrational threshold states of the molecular fragment obtained upon dissociation, both in the 2D and 3D calculations. However, although the two systems have the same threshold states, the resonance widths for the 2D D + HD collisions are found to be considerably narrower than for the 3D ones, while no such phenomenon is observed for H + DH. As a result, we have concluded that there is an apparent dimensional effect on the resonance widths of the heavy–light–heavy (HLH) reaction. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Transition state resonances; Reactive collisions; Isotope effects; Time-dependent quantum dynamics

1. Introduction

Over the past two decades numerous theoretical and experimental efforts have been made to study transition state resonances (energies and lifetimes) in bimolecular reactive dynamics [1–16]. Such resonances appear as sharp peaks in reaction probability versus collision-energy plots and represent quasi-bound states on the potential energy surface. They may be probed experimentally in terms of transition state spectroscopy by using real time photochemistry techniques such as the photodetachment procedure $FHF^- \rightarrow [FHF]^* + e^-$. However, at present, most detailed studies of transition state resonances have been carried out theoretically. Some of the methods used to calculate resonances in exchange reactions are direct search of S-matrix complex poles [17], classical calculations [18], stabilization calculations [19], time-independent scattering calculations [20–26], semi-classical calculations [4,9,10,18], time-dependent [27] and time-independent [28–31] spectral intensity calculations, sensitivity analysis [32], and recently by complex scaling [14,33–35] methods. Being a fundamental prototypical exchange reaction, $H + H_2$ and its isotopic variants have therefore been extensively studied [22,27,36–38] by using most of the above listed methods. Among them, the time-dependent wavepacket method shows good advantages for studying high-energy resonances where dissociative events become important. For this system, the resonance energies have been calculated up to the dissociation limit [36]. Furthermore, the nonadiabatic and geometric phase effects [39,40]

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can easily be implemented in the time-dependent method.

It is well known that resonance energies can be linked to the reactant's and product's channel threshold states [41]. For the Mu + H_2 and Mu + D_2 collisions, it has been shown ([15,42], and references therein) that resonance energies are near the vibrational threshold states of the H_2/D_2 molecule in two-dimensional (2D) dynamics, and most resonance energies in three-dimensional (3D) can be consistently related to the collinear resonance energies by adding to the latter the nearly separable degenerate bends. In addition, although their resonance widths show a non-RRKM behavior, the lifetimes in 3D are slightly shorter than those in 2D. These results have implied that collinear calculations could give good predictions for the resonances in full-dimensional dynamics for this type of exchange reaction. On the contrary, Nakamura and co-workers [43] have carried out full-dimensional accurate quantum dynamics studies of the H + H_2 reaction and its isotopic variants. They have observed apparent mass effects on the reaction probability, which indicated that the corresponding resonances might also show differences. Based on the above evidence, we have chosen the two exchange reactions H + DH and D + HD to study the resonance widths and lifetimes in 3D dynamics as well as in the collinear 2D case; note that the same dissociation threshold states of HD apply to both reactions. As it will be shown in this paper, there are pronounced dimensionality effects on the resonance widths of the heavy–light–heavy (HLH) reaction.

The structure of this work is as follows. After a brief description of the methodology in Section 2, the results and discussion are presented in Section 3. Summary is in Section 4.

2. Methodology

Following our previous work [15,42], we seek a description of the transition state dynamics in terms of a quantum-mechanical wavepacket $\psi(t)$, which is calculated by solving the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \psi(t)}{\partial t} = H\psi(t) \tag{1}$$

with

$$H = T + V \tag{2}$$

where H is the system Hamiltonian, T the kinetic energy operator which has been written in the usual Jacobi coordinates, and V the H_3 double many-body expansion (DMBE) potential energy surface [44] including a proper negative imaginary absorbing potential to prevent reflections of the wavepacket from the edges of the grids [45].

Similarly, the initial wave function $\psi(t = 0)$ has been taken as a symmetric Gaussian wavepacket and placed near the saddle point of the H_3 potential energy surface using a discrete grid representation as in our previous collinear and 3D studies [15,42]; the reader is referred to the original papers for details. We also note that the initial wave packet has been placed on the A–B–A channel in order to calculate the corresponding resonances in the 3D case. Moreover, the mean energy of this wave packet has been obtained from

$$\langle E \rangle = \langle \psi(0)|H|\psi(0) \rangle \tag{3}$$

Once the wave functions have been chosen, they can be propagated using a variety of methods such as the split-operator [46], short-iterative Lanczos [47,48], sympletic integrator [49], Chebyshev [50–52] and hybrid [53,54] methods; for discussions on the relative advantages of variants of the time dependent quantum mechanical wavepacket evolution methods, the reader is referred to papers by Leforestier et al. [48] and Truong et al. [55]. In this work, we have used the split-operator algorithm described by Feit and Fleck [46,48,56] via a fast Fourier transform (FFT) algorithm, which has been well documented. Therefore, no more details will be given here.

The autocorrelation function $C(t)$ is computed at each time step by

$$C(t) = \langle \psi(0)|\psi(t) \rangle \tag{4}$$

Then the pseudo-spectral intensity can be generated through the Lorentzian–Fourier transform of $C(t)$

$$I(E) \sim \int_{-\infty}^{+\infty} C(t)\, e^{-\alpha|t|/\hbar}\, e^{iEt/\hbar}\, dt \tag{5}$$

The resonance energies E_n and the lifetimes τ_n can be extracted from the strong peak positions and widths in the spectrum by using a nonlinear least squares fitting
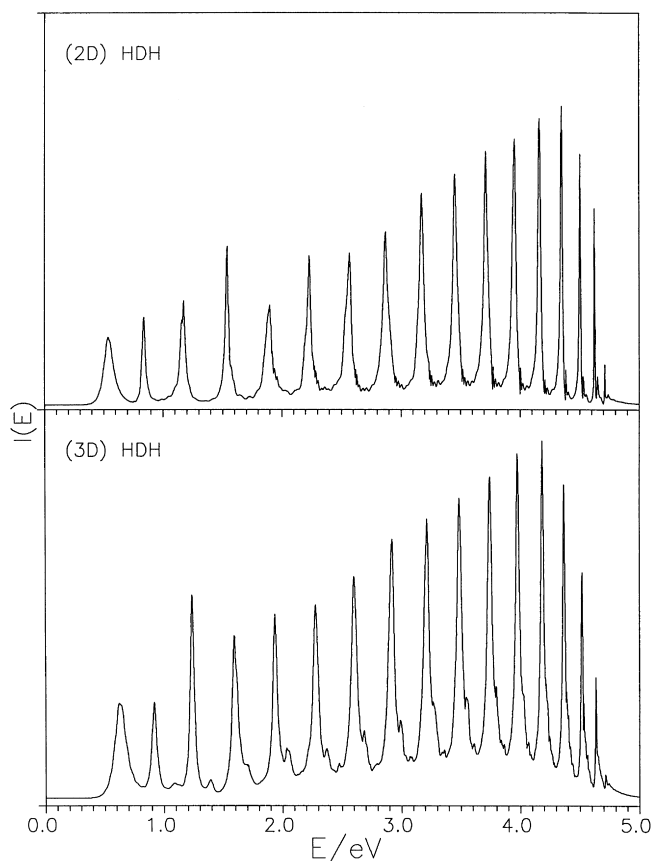
Fig. 1. Transition state resonance spectra for the H + DH reaction:2D results; and 3D results at total angular momentum $J = 0$. Arbitrary units are used for $I(E)$.

of $I(E)$ to a Lorentzian (L_n) function

$$L_n(E) = \frac{L_n^{\max}(\alpha + \Gamma_n/2)^2}{(\alpha + \Gamma_n/2)^2 + (E - E_n)^2} + B(E) \qquad (6)$$

where $L_n^{\max}$ is the height of the resonance at $E = E_n$, and $B(E)$ the background. The widths Γ_n give as usual, the lifetimes through the relation $\tau_n = \hbar/\Gamma_n$. Further, for time-independent Hamiltonian operators and real initial wave packets, the autocorrelation function for time $2t$ can be constructed from the intermediate wave packet at time t as [57]

$$C(2t) = \langle \psi^*(t)|\psi(t)\rangle \qquad (7)$$

which leads to savings of 50% on the computational time.

Once the stationary state with energy E_n has been assigned, its eigenfunction has been computed by Fourier transforming the time evolved wave function as follows [4]

$$\psi_n \sim \lim_{T\to\infty} \left(\frac{1}{2T}\right) \int_{-T}^{+T} \psi(t)\, e^{iE_n t/\hbar}\, dt \qquad (8)$$

From this eigenfunction, we can identify a variety of states such as conventional and barrier (also called box state [28]) resonances. The resonance wave functions can, in turn be used as initial wavepackets, and the corresponding lifetimes extracted from their exponential decay.

3. Results and discussion

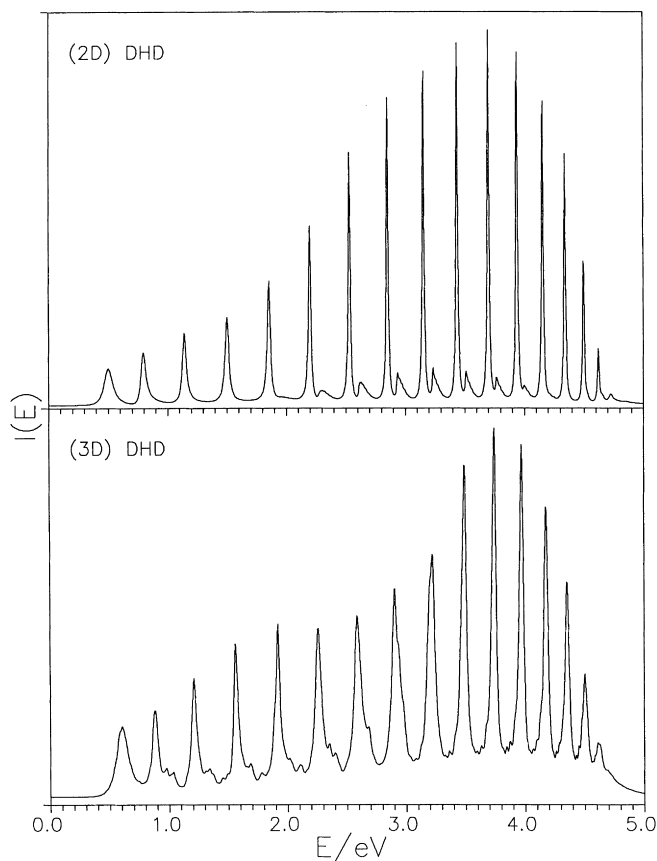Figs. 1 and 2 show the spectra for the collinear (2D)

Fig. 2. Transition state resonance spectra for the D + HD reaction using a Lorentzian window function with $\alpha_L = 7.0$ meV [see Eq.(5)]. The symbols have the same meaning as in Fig. 1. Units are as in Fig. 1.

and 3D cases of H + DH and D + HD exchange reactions, respectively, which were obtained by propagating the broad symmetric stretch wavepackets for 800 fs. From these figures, resonances have been extracted by fitting to the Lorentzian function of Eq. (6). The results are given in Table 1, where ν is the quantum number of asymmetric bond stretch. The lowest one in each spectrum is the barrier resonance state and the others are conventional resonances. We can see that resonance energies in 3D can be associated with those in 2D by introducing a small shift in frequency towards high energies due to the bend zero-point energy. Note that we have prepared the initial wavepacket such that only these zero-bend resonances can be produced in 3D calculations. The energy shift tends to decrease with increasing energy for both systems. In addition, the resonance energies

in H + DH are slightly higher than those in D + HD, which can be attributed to mass effects. However, their differences in 3D become smaller than in 2D because the bend zero-point energy of DHD system gives them some compensation. Further, the resonance energies may be well linked to the vibrational threshold states of DH molecule. For the collinear collision, the resonance energies are higher than their corresponding threshold states (the number of nodes of the eigenvectors is the same as that of the resonance states in the reactant or product channel; see also Ref. [15]) at lower collision energies while they are slightly smaller at higher collision energies for both systems. Indeed, such a rule has been well understood from the plots of the diagonal corrected vibrational adiabatic hyperspherical model (DIVAH) potentials derived by Römelt [41]. Although this

Table 1
Calculated energies E_n (eV) and lifetimes τ_n (fs) of the transition state resonances for the H + DH and D + HD collisions in 2D and 3D cases; ν is the quantum number of asymmetric stretch, while the bending quantum number in 3D is zero

ν	HDH				DHD			
	E_n^{2D}	τ_n^{2D}	E_n^{3D}	τ_n^{3D}	E_n^{2D}	τ_n^{2D}	E_n^{3D}	τ_n^{3D}
0	0.538	8.6	0.622	5.7	0.501	8.6	0.605	5.4
2	0.839	18.9	0.921	13.7	0.796	14.5	0.881	10.6
4	1.173	13.4	1.237	16.4	1.140	26.4	1.210	21.6
6	1.538	22.2	1.592	11.7	1.500	24.9	1.562	24.6
8	1.897	9.5	1.936	16.5	1.856	41.4	1.920	36.8
10	2.231	26.2	2.278	11.9	2.198	80.0	2.258	14.6
12	2.570	18.2	2.602	11.9	2.530	163.2	2.586	14.4
14	2.868	18.3	2.921	12.3	2.850	281.5	2.903	29.7
16	3.173	19.0	3.215	12.3	3.153	431.7	3.222	32.8
18	3.454	18.9	3.487	14.6	3.437	385.9	3.492	38.5
20	3.714	18.5	3.744	15.0	3.699	401.9	3.744	31.2
22	3.955	20.0	3.977	18.6	3.938	432.2	3.972	25.5
24	4.164	24.6	4.185	25.2	4.153	474.7	4.177	22.6
26	4.349	36.4	4.367	33.6	4.340	488.9	4.352	23.6
28	4.504	56.1	4.518	42.5	4.497	732.9	4.500	16.1
30	4.625	120.6	4.636	66.9	4.621	>353.6	4.622	17.3
32	4.709	293.0						

model is not always correct [58], Römelt and Manz [41,59,60] have successfully used it to elucidate the resonance positions of some collinear reactions such as H + H$_2$, H + MuH, I + HI and F + H$_2$. Again, by comparing with the 2D resonance energies of both reactions, one can notice the mass effects on them although they have the same threshold states. The relative diagram of those energies is clearly shown in Fig. 3.

Compared with the resonance energies, the resonance widths (or lifetimes) show a non-RRKM behavior, reflected in the fact that the lifetimes fluctuate as a function of energy. However, the lifetimes tend to be short in the 3D case. However, they are surprisingly long in 2D collisions for the D + HD exchange reaction while no such phenomenon occurred for the H + DH one. This is also demonstrated in the upper panel of Fig. 2, i.e. the resonance peaks are much narrower (there, we have broaded about 14 meV in the plot by using a Lorentzian window function). Thus, for the HLH reaction, we have observed an apparent dimensional effect on the widths of the transition state resonances.

When the resonance energies have been obtained from the spectra, one can calculate the resonance wavefunctions by using Eq. (8), and then identify the resonance states according to their node structures. Figs. 4 and 5 display the probability densities of the stationary wavefunctions of two conventional resonance states for the collinear H + DH and D + HD collisions, respectively. The resonance energies are indicated in boxes. As we can see, both have the same quantum number $\nu = 12$ that is equal to the number of their nodes around the asymmetric bond stretch. Therefore, those resonances are associated with the threshold state of HD ($\nu = 6$) whose energy is calculated to be 2.6135 eV. Obviously, the resonance energies are below it. In addition, due to the symmetry of systems, the probability densities are even distributed and symmetric in both reactant and product channels. However, the patterns of the probability densities show some differences in the reactant or product valleys. They are relatively higher but more localized for H + DH than for D + HD. Such a localization of the resonance state in the valley implies that the resonance state of HDH has a higher probability in the unsymmetric bond-stretch configuration as the heavy middle atom moves slowly. For such geometries, it can easily lead to dissociation, and hence such a resonance is unstable. Conversely, for the DHD system, such a resonance state is mainly trapped above the saddle point at the high-energy regions of the potential energy surface, with a smaller localization in the valley. The middle hydrogen atom has therefore a small coupling to the terminal atoms due to its fast transfer between them. These profiles of wavefunctions may rationalize the big discrepancy in their lifetimes (from 18.2 fs for HDH to 163.2 fs for DHD). On the contrary, such phenomena can also be explained on the basis of the DIVAH model by Römelt [41] as follows: the widths of Feshbach resonances are proportional to the off-diagonal potential term $U_{\nu'\nu}$ which couples the different channels together [41, Eq. (21)]. This term is found to decrease with the decreasing skew angle of the system. As expected, the skew angle for DHD system is smaller than that for HDH. Therefore, the Feshbach-type resonances are narrower (i.e. they have longer lifetimes) for the HLH system.
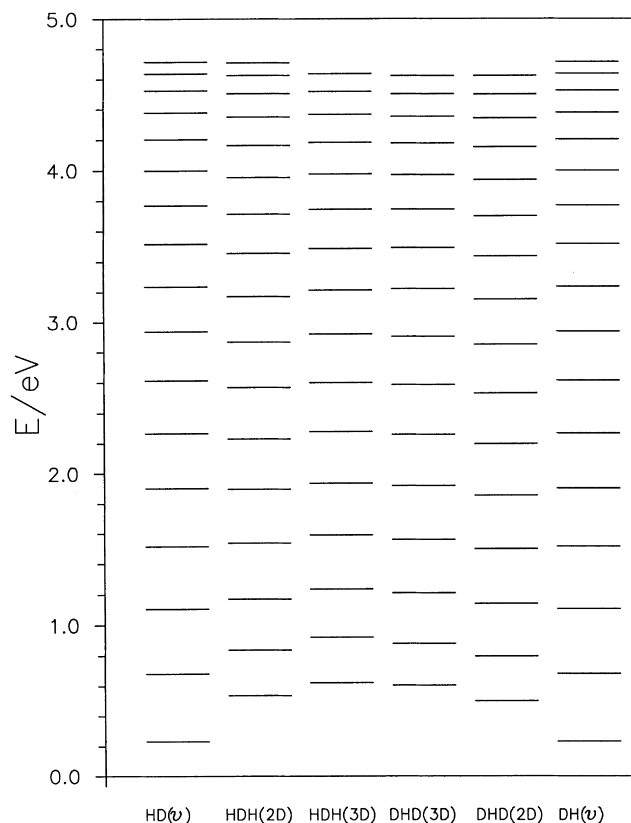
Fig. 3. Energy level correlation diagram for the threshold states of HD and the resonance states of H + DH and D + HD collisions: 2D results; and 3D results.

4. Summary

We have used a time-dependent wavepacket propagation method to study transition state resonances (energies and lifetimes) in collinear and three-dimensional H + DH and D + HD collisions. For both systems, the 3D resonance energies are well associated with the 2D ones by an approximate bend mode. However, the lifetimes of resonances for the collinear D + HD reaction are much longer than those for the 3D calculation, which may indicate that there exists an apparent dimensional effect on the resonance widths of the HLH reaction. Of course, the present work has been carried out on the lowest adiabatic sheet of the H_3 DMBE potential energy surface in Born-Oppenheimer approximation, although our recent studies with two coupled adiabatic potential energy surfaces [39] or considering the geometric
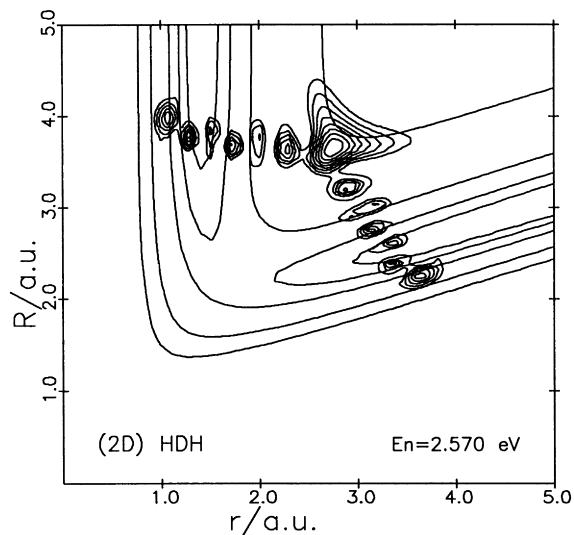

Fig. 4. Probability density for the stationary state $E_n = 2.570$ eV of the H + DH collinear collision.
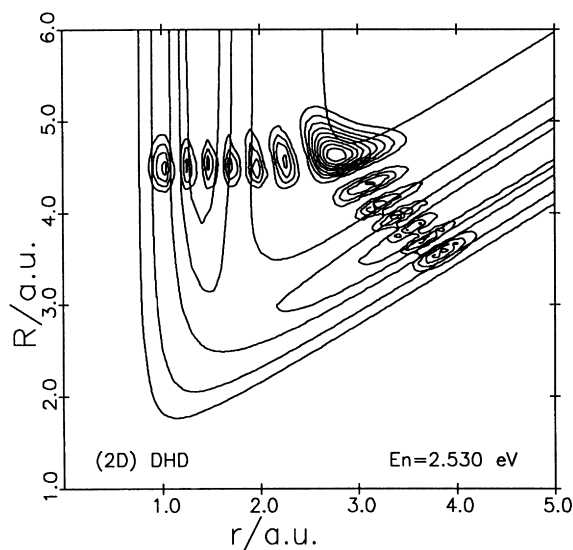
Fig. 5. Probability density for the stationary state $E_n = 2.530$ eV of the D + HD collinear collision.

phase effects [40] have shown that they have only minor influences on transition state resonances of H_3, at least, for zero-bend resonance states.

Acknowledgements

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