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Prediction of a Feshbach resonance in the below-the-barrier reactive scattering of vibrational excited HD with H

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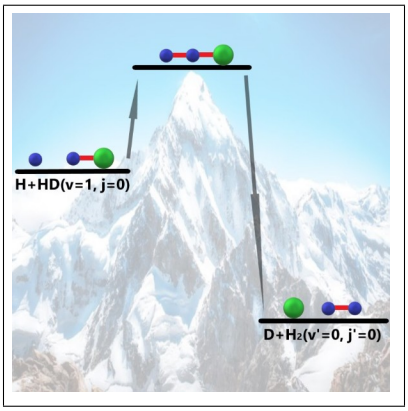
Abstract

Quantum reactive scattering calculations of the vibrational quenching of HD due to H collisions are carried out employing an accurate potential energy surface. The state-to-state cross sections for collision energies between 1 cm^{-1} and 10,000 cm^{-1} of the HD $(v = 1,\ j = 0) + H \rightarrow D + H_2\ (v' = 0,\ j')$ chemical reaction are presented and a Feshbach resonance in the low-energy regime, below the reaction barrier, is observed for the first time. The resonance is attributed to coupling with the vibrationally adiabatic potential correlating to the $v = 1,\ j = 1$ level of the HD molecule and it is dominated by contribution from a single partial wave. The properties of the resonance, such as its dynamic behavior, phase behavior, and lifetime, are discussed.

Graphical TOC Entry



The study of reactive collisions in atom-diatom systems is a very effective way to probe the interaction and reaction dynamics between atoms and molecules. Therefore, triatomic collision processes have played an important role in quantum dynamics as they can give valuable insight into the chemical reaction mechanism.[1,2] Due to their light mass and the availability of high accuracy molecular potentials, H_2, HD, and D_2 are the most commonly studied molecular species and they serve as benchmark systems for state-to-state chemistry. Due to their high abundance in the interstellar medium, collisions of H_2 and HD with atomic hydrogen have attracted significant interest. For practical reasons, the reactions of D + H_2[3–6] and H + D_2[7–11] have been studied rather extensively. HD, as the singly deuterated form of molecular hydrogen, is one of the products in these reactions. Because of the relatively large abundance of HD in space and its finite dipole moment, the observable properties of the collisional reaction of HD with H, such as cross sections and rate coefficients, are of particular interest.

Much attention has been devoted to the study of the H + HD reaction recently, stimulated by geometric phase effects in this system and the crucial role of HD in astrophysics.[12–18] However, most of these studies, in particular those relevant to astrophysics, have only investigated rotational excitation of HD in its ground vibrational state. Vibrationally excited HD can be produced by a variety of processes in space, thus it is of interest to study their interaction with atomic hydrogen.[19] Inspired by this point, we focus on the study of the reaction between vibrationally excited HD molecules and atomic hydrogen. Stereodynamics of rotational quenching of state-prepared HD in the $v = 1$ vibrational level in collisions with H_2, D_2 and He have also been reported recently.[20–24] In this paper, we aim to present the results of cross sections of the reactive processes for the H-HD collisional system when HD is in its first excited vibrational state $v = 1$ and discuss the behavior of vibrational quenching of HD molecules due to collisions with H atoms. In particular, we report the presence of a narrow Feshbach resonance in HD + H → D + H_2 reaction at energies below the reaction barrier with its origin traced to coupling with the adiabatic potential correlating with the

$v = 1, j = 1$ level of the HD molecule.

A reliable PES for the H-HD system ensures the accuracy of the quantum dynamics calculations. Thus an accurate description of the potential energy surface (PES) is required to obtain the cross sections for the reaction of H with HD. There have been several PESs for the H_3 system that are widely used in quantum mechanical calculations. The best known are the LSTH,[25–27] BKMP2,[28] and CCI[29] potentials. Among them, the BKMP2 and CCI potentials are considered the most accurate, and they reproduce most available experimental data. In our scattering calculation, we employ the CCI PES, but some comparisons are also provided on the BKMP2 PES. The CCI PES was developed with *ab initio* calculations of near full configuration interaction quality using a highly accurate many-body basis set extrapolation. There is a large barrier of about 3500 cm^{-1} on this PES for the hydrogen exchange reaction with ground state reactants, and the well depth of the global minimum is about 20 cm^{-1}.

In order to describe the reactive scattering of HD with H, the quantum mechanical reactive scattering program ABC[30] is employed. To solve the Schrödinger equation, ABC uses a coupled-channel hyper-spherical coordinate method for the motion of the three nuclei on a Born-Oppenheimer PES. The hyperradius is divided into a large number of sectors and at each sector the wavefunction is expanded in terms of rovibrational eigenfunctions of the diatomic fragments in each atom-diatom arrangement channel. For low collision energies, we used a large maximum hyperradius and a large number of log derivative propagation sectors to ensure the integration step size $\Delta\rho$ was small enough to obtain converged results. With the convergence parameters used in ABC (See Table S1), the calculations were carried out for the total angular momentum J from 0 up to 120 in the range of collision energy from 1 cm^{-1} to 10,000 cm^{-1}. The results of the ABC program are the S-matrix elements in parity-adapted form. To obtain the collision energy variation of the cross sections for reactive processes, the S-matrix elements need to be converted from the parity-adapted form $S^{J,P}_{n'k',nk}(E)$ into standard helicity-representation form $S^{J}_{n'k',nk}(E)$.[30] After the conversion, the

reactive scattering integral cross sections (ICS) can be calculated from,

$$\sigma_{n'k'\leftarrow nk}(E) = \frac{\pi}{k_n^2}\sum_J (2J+1)|S^J_{n'k',nk}(E)|^2, \quad (1)$$

where J is the total angular momentum quantum number, E is the collision energy, n and n' are composite indices for αvj and $\alpha' v' j'$, α and α' are arrangment labels, k and k' are helicity quantum numbers, k_n is the wave vector with $k_n^2 = \frac{2\mu E}{\hbar^2}$, and μ is the reduced mass of the system.

Figure 1 plots the state-to-state cross section as a function of collision energy for the reaction of HD ($v = 1,\ j = 0$) + H $\rightarrow$ D + H_2 ($v' = 0,\ j' = 0$). As can be seen, the cross section at low energies is small and decreases with increasing collision energy, reaching a global minimum at 84.69 cm^{-1}. The broader hump appearing around 750 cm^{-1} can be interpreted as metastable states of the H + HD reaction.[31] The system passes through a transition state region along the reaction coordinate, the maximum value of the minimum energy reaction pathway for the H + HD is about 1036 cm^{-1}, therefore the cross section increases rapidly above a collision energy of 1000 cm^{-1}. Below this barrier, the reactivity can be attributed to quantum tunneling.

A striking feature of the results presented in Figure 1 is a sharp resonance peak appearing at 84.85 cm^{-1} as seen in the inset. To our knowledge, this is the first time a resonance for the H_3 system has been predicted in this energy range and below the reaction barrier. In order to confirm this observation, we performed the calculation of state-to-state cross sections with different final states. Figure 2 presents the collision energy variation of cross sections for the HD ($v = 1,\ j = 0$) + H $\rightarrow$ D + H_2 ($v' = 0,\ j'$) reaction, with j' from 1 to 4. All of the resonance peaks are located at 84.85 cm^{-1}, but they vary in magnitude. The resonance peaks decrease from j' =1 to 4, however, it is worth noting that the peaks for $j' = 1$ and $j' = 2$ are larger than that of $j' = 0$. We also computed the total integral cross sections, summed over all final states. As can be seen in Figure S1, the resonance survives in the total

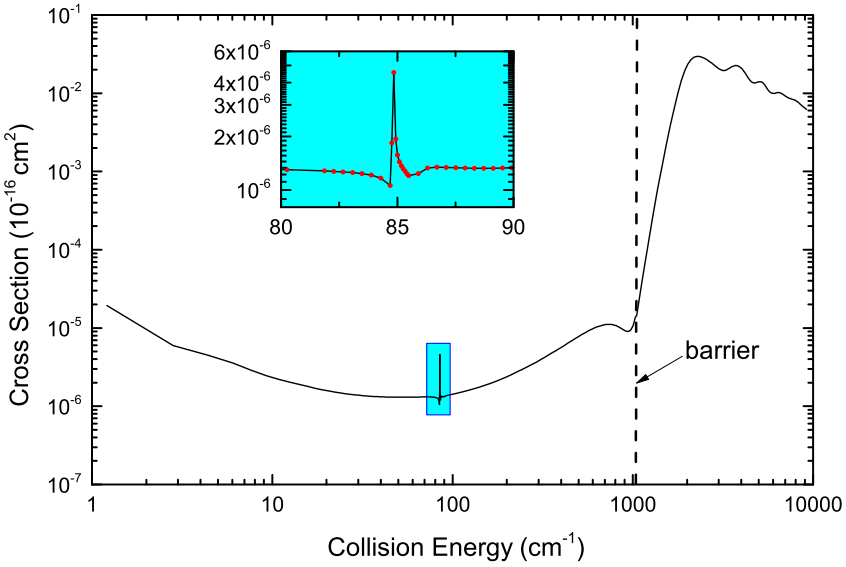


Figure 1: Collision energy variation of cross section for the HD ($v = 1,\ j = 0$) + H $\rightarrow$ D + H_2 ($v' = 0,\ j' = 0$) reaction. Inset: Feshbach resonance region.

vibrationally resolved cross sections.

Because resonance peaks are usually dominated by contributions from a single or narrow range of partial waves, the square of the S-matrix for $J = 0 - 6$ is plotted in Figure 3 (we note that here the partial wave or orbital angular momentum L of H about HD is equal to J since $j = 0$). It is clear that $J = 1$ dominates the peak at 84.85 cm^{-1}. The behavior that $J = 1$ dominates the resonance can also be seen in the cross sections for j' from 1 to 3 (See Figure S2). As can be seen in Figure 3, the broader hump in the region of about 750 cm^{-1} can be attributed to a nearly in-phase sum of J-resolved cross sections. To confirm that this resonance feature is not an artifact of the CCI PES or the ABC code used for the scattering calculations, separate quantum mechanical reactive scattering calculations were also carried out on the BKMP2 potential using the APH3D quantum mechanical reactive scattering program.[32,33] Indeed, the BKMP2 PES also captures this resonance at exactly the same energy though the magnitude of the background cross sections differ from the two calculations at energies below the barrier where tunneling contributions become very sensitive to the details of PESs and the basis sets employed in the ABC and APH codes (See

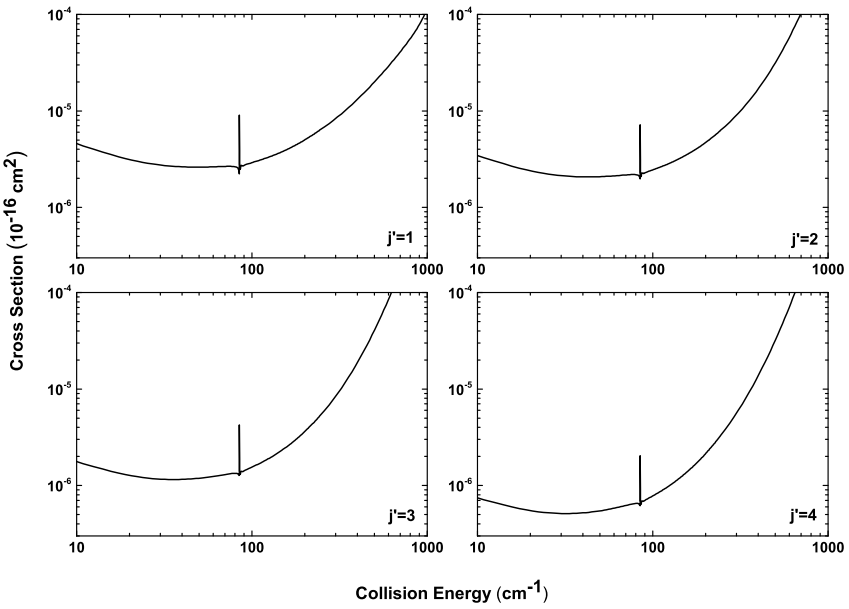


Figure 2: Collision energy variation of cross sections for the HD ($v = 1,\ j = 0$) + H $\rightarrow$ D + H_2 ($v' = 0,\ j'$) reaction, where $j' = 1$, 2, 3, 4.

Figure S3).

To confirm that the resonance exhibits the proper phase behavior, an argand diagram is presented in Figure 4 for the HD ($v = 1,\ j = 0$) + H $\rightarrow$ D + H_2 ($v' = 0,\ j' = 0$) reaction for $J = 1$. The collision energy increases from 1.2 cm^{-1} to 1033.6 cm^{-1}. The points were computed on a fine energy grid near the resonance to display its phase behavior. The background phase behavior corresponds to the smooth counter clock-wise motion of the energy trajectory in the argand plot. Near the resonance peak (blue insert), a kink in the argand plot is observed where the resonance phase shift dominates and the trajectory temporarily reverses direction and exhibits a clockwise motion. The kink and associated clockwise loop in the argand plot is a signature of a quantum resonance. Thus, the observation of the peak in the cross section is reconfirmed from the phase behavior. Specifically, the resonance point we note in the argand diagram corresponds to the sharp peak located at 84.85 cm^{-1}, and the contribution at 84.69 cm^{-1} causes the global minimum of the cross section shown in Figure 1 at the same collision energy.

To gain more insight into the origin of the resonance, we examined the adiabatic potentials

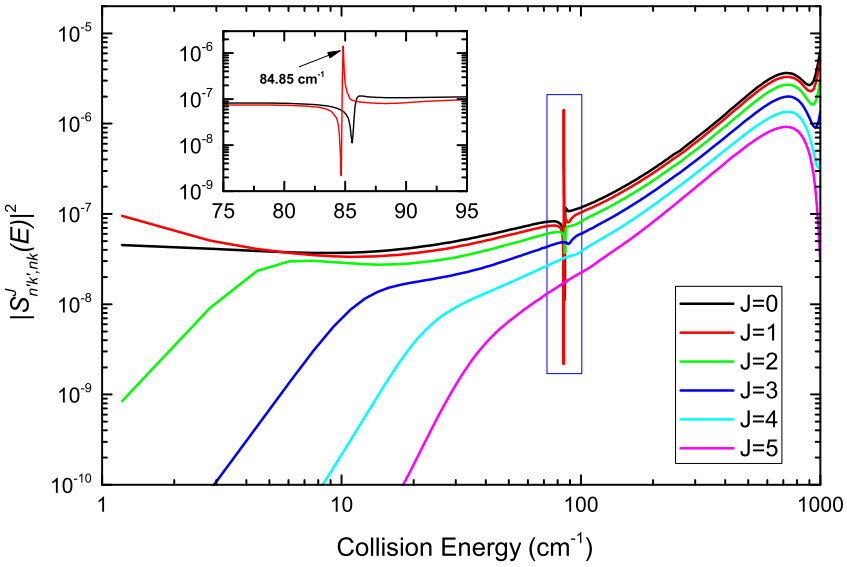


Figure 3: Collision energy variation of $|S^J_{n'k',nk}(E)|^2$ for the HD $(v = 1,\ j = 0)$ + H $\rightarrow$ D + H_2 $(v' = 0,\ j' = 0)$ reaction for different values of the total angular momentum quantum number J.

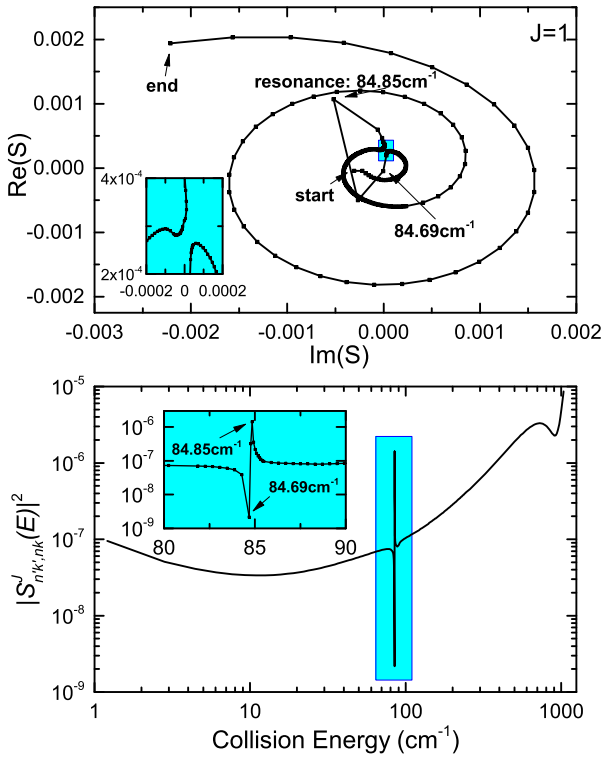


Figure 4: (Top panel) Argand diagram of HD $(v = 1,\ j = 0)$ + H $\rightarrow$ D + H_2 $(v' = 0,\ j' = 0)$ reaction for $J = 1$. (Bottom panel) The corresponding values of $|S^J_{n'k',nk}(E)|^2$.

for the H + HD interaction for $J = 1$. Because the resonance occurs at about 85 cm^{-1} relative to the $v = 1,\ j = 0$ level, it is most likely due to coupling with $v = 1,\ j = 1$ of HD which becomes energetically accessible at a collision energy of 85.37 cm^{-1}. Thus, it is very likely that this is a Feshbach resonance due to coupling with a quasibound state of the adiabatic potential correlating with the $v = 1,\ j = 1$ level of HD. For the initial $v = 1,\ j = 0$ state of HD only $L = 1$ contributes for $J = 1$. Thus, only odd inversion parity, $P = (-1)^{j+L} = -1$ contributes. For the $v = 1,\ j = 1$ level, odd inversion parity states for $J = 1$ that couple to the $v = 1, j = 0, L = 1$ channel are limited to $L = 0$ and 2. The corresponding adiabatic potentials are shown in Figure 5 as functions of the center-of-mass separation R between H and HD. The adiabatic potentials are computed by diagonalizing the interaction potential matrix at each value of R. Since the resonance occurs at the same energy for different j' levels of the product H_2, this is an entrance channel feature and we used reactant Jacobi coordinates and included only ro-vibrational levels of HD in constructing the matrix elements of the interaction potential. It is seen that the adiabatic potential corresponding to $v = 1,\ j = 1,\ L = 0$ potential supports a quasibound state at an energy of 84.82 cm^{-1} which is very close to the energy of the resonance. The $v = 1,\ j = 1,\ L = 2$ potential does not support a bound state. We have carried out similar analysis with the BMKP2 potential which also supports a bound state for the $v = 1,\ j = 1,\ L = 0$ potential at 84.98 cm^{-1} (see Figure S4) consistent with a similar resonance feature at 85.33 cm^{-1} shown in Figure S3.

Resonances are often associated with metastable states of lifetime $\tau \simeq \hbar/\Gamma$, where Γ is the width of the resonance. For guidance of future experiments, we carried out a Lorentzian fit and extracted the lifetime. A very high resolution energy scan in the resonance region using Smith's collision lifetime matrix formulation[34] was performed using the APH3D program on the CCI (BKMP2) PES. The result shows that the lifetime is about 0.6 s (0.2 s) for this resonance state (See Figures S5 and S6). As can be seen, the lifetime on the two PESs are very similar, and there is a slight shift in resonance energy: 85.37 cm^{-1} for CCI relative to

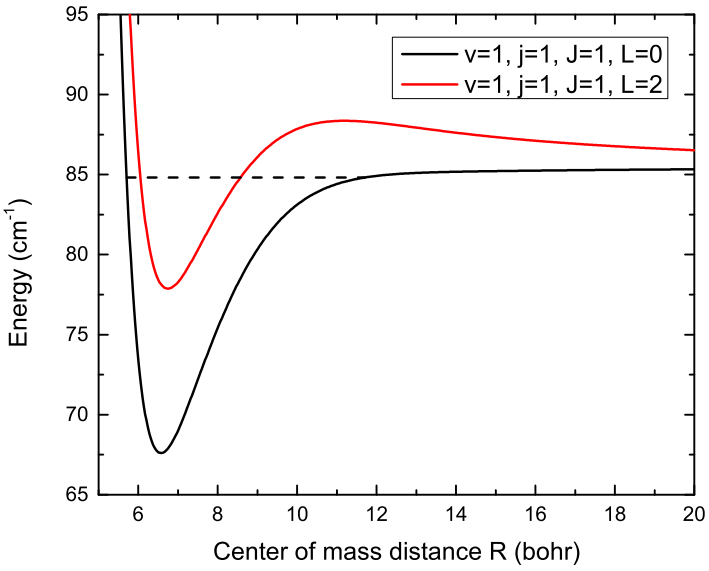


Figure 5: The adiabatic potentials correlating with different $(v,\ j)$ states of HD in H + HD $(v = 1,\ j = 0)$ collisions for $J = 1$ on the CCI PES.

85.33 cm^{-1} for BKMP2.

From an experimental point of view, a crossed-molecular-beam approach may be a good method to verify our theoretical prediction. A variety of experimental techniques were developed over the past decade including, for example, the Stark-induced adiabatic Raman passage (SARP),[35] the H-atom Rydberg tagging technique (HRTOF),[36,37] the photoinitiated reaction method (PHOTOLOC),[11,38,39] the velocity map ion imaging (VMI) technique,[40,41] the resonance enhanced multiphoton ionization (REMPI) with ultraviolet (UV) pulses,[42] and the quantum-state-specific backward scattering spectroscopy (QSSBSS) method.[1] SARP can be used to prepare the HD molecules in a specific internal state. The HRTOF, PHOTOLOG, REMPI with UV pulses, and QSSBSS approaches can be used for detection. The Feshbach resonance is predicted to appear in a low collision energy region, is very narrow, and has a small magnitude. As such an experimental approach will require very fine kinetic energy resolution and sensitivity.

In conclusion, quantum reactive scattering calculations for the H + HD $(v = 1,\ j = 0)$

reaction were performed to obtain the collision energy variation of the cross section. A Feshbach resonance is found at about 85 cm^{-1} due to the coupling with the $v = 1,\ j = 1,\ L = 0$ potential, which is significantly below the $\sim$1000 cm^{-1} reaction barrier. In this reaction, the peak is dominated by the partial wave $L = 1$. The resonance is very long-lived with lifetime close to a tenth of a second. We hope these results stimulate experiment exploration of this resonance and further theoretical in-depth studies of this reaction.

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Supporting Information Available

The SI includes parameters used in the calculations, cross sections summed over all final states, cross sections for different partial waves, comparisons of CCI-ABC and BKMP2-APH3D results, adiabatic potentials, and the lifetime of Feshbach resonance.

This material is available free of charge via the Internet at `http://pubs.acs.org/`.

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