Resonances at very low temperature for the reaction D$_2$ + H

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Abstract
We present numerical results for rate coefficients of reaction and vibrational quenching in the collision of H with D$_2$(v, j) at cold and ultracold temperatures. We explore both ortho-D$_2$(j = 0) and para-D$_2$(j = 1) for several initial vibrational states (v ≤ 5), and find resonant structures in the energy range 0.01–10 K, which are sensitive to the initial rovibrational state (v, j). We compare the reaction rates for D$_2$ + H with our previously obtained results for the isotopologue reaction H$_2$ + D, and discuss the implications of our detailed study of this benchmark system for ultracold chemistry.

Keywords: ultracold chemistry, molecular hydrogen, deuterium, resonances

(Some figures may appear in colour only in the online journal)

1. Introduction
Research on cold molecules has been growing steadily since they were first predicted [1, 2] and observed experimentally [3, 4]. Indeed, there is now a vast literature on cold molecules, including numerous reviews of certain specialized topics [5–12] and several books [13–15] dedicated to the physics and chemistry of cold molecules. A variety of methods have been developed to produce cold molecules, thus opening the door for studying cold and ultracold chemistry, now a rapidly expanding field. In this article we explore in detail the reaction D$_2$ + H for energies below 100 K, including the ultracold regime (T ~ 10$^{-6}$ K) which corresponds approximately to energies from 10$^{-10}$ to 10$^{-2}$ eV. We published recently a similar study [16] for the isotopologue reaction H$_2$ + D, and in this paper we compare and contrast the results for the two reactions. In both cases we find resonant features in the energy range 0.01–10 K, which we identify as shape resonances in the entrance channel. We remark that these resonances are very close to the entrance channel threshold, and thus even small shifts in their positions can have strong effects on their lineshapes. Indeed, our detailed comparison shows that the positions of the resonances for D$_2$ + H are shifted to slightly higher energy than the resonances for H$_2$ + D, which is primarily due to the different value of the reduced mass in the entrance arrangement. Nevertheless, the lineshapes of the resonances found for these two reactions are very different. Moreover, we also find that the results are strongly dependent on the initial rovibrational state of the dimer.

The reaction we study in this work, together with its isotopologues, is of fundamental importance in quantum chemistry, and is also relevant to astrophysics, especially for the astrochemistry in the early universe [17] and for the evolution of cold molecular clouds in the earliest stages of star formation [18]. Recent experiments with slow collisions between metastable He and H$_2$ [19–22] have detected similar resonances, and studies of this benchmark reaction should lead to a better understanding of the energy surface and of the relevant scattering processes. In section 2 we give a brief description of the theoretical and numerical tools used, as well as the properties of this benchmark system. We present and analyze the results in section 3, and conclude in section 4.

2. Theoretical and computational details
We consider the benchmark reaction D$_2$ + H at low temperatures and pay special attention to the effect of the nuclear spin symmetry, since D$_2$ is a homonuclear molecule. As is well known, the nuclei of D$_2$ are spin $i = 1$ bosons, with possible values of total nuclear spin $I$ of 0, 1, and 2, and the
symmetrization requirements for the nuclear wave function of $D_2$ restricts its rotational states. Specifically, for total nuclear spin $I = 2$ (maximal value) and also for $I = 0$, the nuclear spinor part of the wave function is symmetric, and thus only rotational states $j = 0, 2, 4, \ldots$ are allowed, which one customarily refers to as ortho-$D_2$, while for $I = 1$, the spinor is antisymmetric and the corresponding rotational states are $j = 1, 3, 5, \ldots$ referred to as para-$D_2$. The coupling of the nuclear spins to the other degrees of freedom is negligible, and thus ortho- and para-$D_2$ are treated separately. As in our previous study of $H_2 + D$, hyperfine interactions are neglected [16].

The expression for the state-to-state cross sections, integrated over all scattering directions, averaged over the initial rotational states of the reactant dimer, and summed over the final rotational states of the product, reads

$$
\sigma_{a'\rightarrow a}(E) = \frac{\pi}{k_a^2} \sum_{J=0}^{\infty} \left( \frac{2J+1}{2j+1} \right) \sum_{J'=j}^{J} \delta_{a'a} \delta_{J'J} \times \sum_{\ell'=-|J'-J|}^{\ell'} |S_{a'a'}_{\ell'\ell}(E)|^2.
$$

The generic notation $n = (avj)$ stands for the arrangement label $'a'$ and quantum numbers $(vj)$ of the rovibrational states of $D_2$, and $k_a = \sqrt{2\mu_a E_a^{\text{kin}}}$ is the initial momentum ($\hbar = 1$, atomic units are used), with $\mu_a = (m_{D_2} + m_H)^{-1}$ the reduced mass of the binary system $D_2$–$H$ in the initial arrangement $a = 1$, $E_a^{\text{kin}} = E - \varepsilon_a$ the initial kinetic energy for relative motion, and $\varepsilon_a$ the rovibrational energies. $E$ is the (total) collision energy, $J$ is the total angular momentum, and $\ell$ is orbital angular momentum for the relative motion. The primed symbols indicate the corresponding quantities in the exit channel, with $a' = (a'v'j')$ and orbital angular momentum $\ell'$. Here, $a' = a = 1$ implies that the system remains in the same arrangement HD–$D$, while $a' = 2$ means that it evolved into the other possible arrangement HD + $D$, with reduced mass $\mu_{a'v'j} = (m_{\text{HD}} + m_{D})^{-1}$. The conservation of the total angular momentum $J$ ensures that the $S$-matrix is block diagonal with respect to $J$, and thus the matrices $S'$ are obtained separately for each $J$.

The state-to-state energy dependent rate constants are simply obtained by multiplying the corresponding cross sections with the relative velocity $v_{\text{rel}}$ in the initial channel, with $v_{\text{rel}} = \sqrt{2E_{a}^{\text{kin}}/\mu_a}$. The total rate constants for quenching ($a' = a$) and reaction ($a' \neq a$) are obtained by summing over the appropriate final states $n'$,

$$
K_{a'\rightarrow a}^Q(E) = \sum_{(v',j')}(v,j) K_{a'v'j'\rightarrow avj}(E),
$$
\begin{align}
K_{avj}^R(E) = \sum_{a'=a} K_{a'v'j'\rightarrow avj}(E).
\end{align}

The case $(a'v'j') = (avj)$ corresponds to elastic scattering, which is discussed in section 3.4. The numerical results were obtained using the ABC reactive scattering code developed by Manolopoulos and coworkers [23]. To ensure fully converged results, a sufficiently large number of closed channels were included, and the propagation of the coupled radial equations was monitored for adequate accuracy. The propagation along the hyper radius $\rho$ was initialized at $\rho_{\text{ini}} = 0.01$ and matching was performed at $\rho_{\text{max}} = 40$, which proved sufficient even for the lowest energies considered; note that the hyper-radius $\rho$ is defined in terms of the mass-scaled Jacobi coordinates [24]; the length unit is the Bohr radius. The basis set was controlled by the truncation energy parameter $E_{\text{max}} = 3$ eV, such that the number of closed channels included was adequately large for all initial rovibrational states presented here. The size of the basis set depends on the total angular momentum $J$ and the overall parity $P = \pm 1$. Thus, for ortho-$D_2(J=0)$, the number of coupled channels varied between 237 (for $J=0$, $P = +1$) and 669 (for $J=2$, $P = +1$), while for para-$D_2(J=1)$, the number of coupled channels was between 227 (for $J=1$, $P = +1$) and 672 (for $J=2$ and $P = +1$). Technical details of our computational approach were published elsewhere [16, 25].

3. Results and discussion

The benchmark system $H_2 + D$ has already been studied in the ultracold regime [25] and also at higher temperatures [26], while the isotopologue reaction $D_2 + H$ has only recently been explored in the ultracold regime [27]. We also note that geometric phase effects have been studied recently for the various isotopologues of this reaction [27–30]. Accurate ab initio potential energy surfaces exist [26, 31] for $H_2$, and we adopt here the electronic ground state surface of [31], as we did in our previous studies [16, 25, 32]. Figure 1 shows the rovibrational energy levels for $v = 0, 1$ and $j \leq 3$, for the reactants $H_2$ and $D_2$, and also for the product HD. Note that the reaction $D_2(v, j) + H \rightarrow HD + D$ cannot take place at vanishing energies for $v = 0$ and $j \leq 2$, while $H_2(0, j) + D \rightarrow HD + H$ does take place.

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Figure 1. Rovibrational energy levels for $v = 0, 1$ and $j \leq 3$.  

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I Simbotin and R Côté

J. Phys. B: At. Mol. Opt. Phys. 50 (2017) 104001
3.1. Reaction and quenching rates for $j = 0$

In figure 2 we compare the results we obtained previously [16] for $H_2(v, j = 0) + D$ with the newly computed results for $D_2(v, j = 0) + H$. We remark that the initial channels $n = (a = 1, v, j = 0)$ correspond to para-$H_2$ and ortho-$D_2$, respectively. Rate coefficients for initial vibrational levels $v \leq 5$ are presented; note that $v = 0$ appears only in figure 2(a) for $D + H_2(0, 0) \rightarrow HD + H$, which is an exoergic reaction and will thus occur even at vanishing energies, see figure 1. $K_{v=0}^R$ is absent in figures 2(b), (d) because the ground rovibrational level ($v = 0, j = 0$) cannot be quenched any further, while $K_{v=0}^Q$ is absent in figure 2(c) because $H + D_2(0, 0) \rightarrow HD + D$ is endoergic, and all reaction channels are closed at the low energies considered here, see figure 1.

Significant resonant features are readily apparent in figure 2 in the energy range 0.01–10 K, for all initial vibrational states for both isotopologue systems. The most striking case is the resonant peak for $D + H_2(v = 1, j = 0)$, which stems from a shape resonance at $E \approx 15$ mK, just above the zero energy threshold. In the case of $D_2 + H$, this $p$-wave resonance has shifted to $E \approx 1$ K and is much less pronounced. Note that for each initial vibrational channel, the quenching and reaction rates are resonantly enhanced in identical fashion, which is due to the fact that all resonances displayed in figure 2 reside in the entrance channel, near the zero energy threshold, and they will thus imprint nearly identically on all final channels [33, 34]. The reaction rate we obtained for $H + D_2(4, 0) \rightarrow D + HD$ is in excellent agreement with the results obtained by Kendrick et al [27] using a different quantum scattering method.

Figure 3 shows the single-channel potential $V(R)$ for initial rovibrational state $(v, j) = (1, 0)$, which was computed using unperturbed eigenstates of $H_2$ and $D_2$ respectively; note that $V(R)$ is not used directly in the hyperspherical coordinate formulation of the scattering problem. The radial coordinate $R$ is not the hyper radius, but rather the distance between the center of mass of the target and the projectile. Also included in figure 3 is the centrifugal term corresponding to partial waves $\ell \leq 4$. For $\ell = 1$, the height of the centrifugal barrier is less than one kelvin, and thus a possible shape resonance may only appear in the sub-kelvin regime. Indeed, a shape resonance for $p$-wave does exist, as indicated in figure 3, and is
confirmed by the full results in figure 2 for both reactions. For \( \ell = 2 \), the height of the centrifugal barrier is approximately 4 K, but the potential well for \( \text{D}_2 + \text{H} \) is too shallow and the \( d \)-wave contribution gives small bumps corresponding to above-barrier resonances in the energy range 6–8 K. However, for \( \text{H}_2 + \text{D} \), the effective potential for \( \ell = 2 \) is deep enough (due to the larger reduced mass, which diminishes the centrifugal term) to allow shape resonances in the energy range 1–4 K. Figure 2 also shows that the resonant features move towards lower energy as the initial vibrational quantum number \( v \) increases. In fact, in the case of \( \text{H}_2 + \text{D} \), the \( p \)-wave resonance becomes quasi-bound for \( v = 2 \) and higher, and the binding energy of the newly formed van der Waals complex increases slightly with \( v \); thus, the corresponding rounded feature in figures 2(a), (b) moves gradually from the sub-kelvin regime towards higher energy. We remark that although the potential in figure 3 proved useful for making the estimates given above regarding the effect of the centrifugal term, it cannot be relied on to provide accurate predictions for the positions of the resonances. Indeed, in terms of a coupled channel formulation, the single-channel potential is insufficient, as the couplings play an important role, especially for higher vibrational states.

For higher partial waves, the centrifugal term becomes dominant and the effective potential in figure 3 is almost entirely repulsive and thus it cannot bind a van der Waals complex; consequently, shape resonances cannot appear at energies above 10 K. Nevertheless, with increasing energy, the contribution of higher partial waves will gradually become significant. For a quantitative estimation, figure 4 shows the partial rates for \( J = 3 \) for \( \text{H} + \text{D}_2(v = 1, j = 0) \rightarrow \text{HD} + \text{D} \) and one can see that the contributions for \( J \leq 2 \) dominate for energies below \( E_{\text{kin}} = 10 \text{ K} \). Indeed, the \( J = 3 \) contribution amounts to 4% at \( E_{\text{kin}} = 10 \text{ K} \), and it only increases to 19% at \( E_{\text{kin}} = 20 \text{ K} \). The contributions of higher partial waves will be smaller still, as indicated by the dominance of the centrifugal term in figure 3(b). Thus, in this work we only include contributions from \( J \leq 2 \), which ensure a level of accuracy of a few percent or better for the kelvin (and sub-kelvin) regime, where the shape resonance are found.

The dependence of the reaction rates on the initial vibrational excitation is not surprising for this system, and was analyzed in our previous work [16, 25]. Although in this work we only focus on the prominent shape resonances found at low energy, we remark that the overall magnitude of the rate coefficients reveals an anomaly; namely, the results for \( \text{D}_2(v = 1) + \text{H} \) are surprisingly large. For \( v \geq 2 \), the reaction rates for \( \text{D}_2 + \text{H} \) are lower than the rates for \( \text{H}_2 + \text{D} \), as expected due to the lower internal vibrational energy of \( \text{D}_2(v) \) compared to \( \text{H}_2(v) \). However, for \( v = 1 \), the background
values of the reaction rates are nearly the same for both reactions. Moreover, the rate coefficient for the vibrational quenching of $v_{D_2} = 1$ is larger than that of $v_{H_2} = 1$, if we ignore the shape resonance (which only affects a limited energy range). Figure 2 also shows that the quenching rate for $v_{D_2} = 1$ is nearly as large as that of $D_2 v_{j} = 2$. We remark that a simple explanation in terms of Feshbach resonances due to closed channels, as discussed for example in [35] for $H_2 + F$ scattering, is ruled out, as there are no nearby channels (open or closed) to affect the results significantly. We also eliminated the possibility of numerical artifacts by performing convergence tests with respect to the size of the basis set and the radial propagation, as described in our previous work [25]. Thus, the $v = 1$ anomaly for $D_2 + H$ remains an open question which deserves further study.

We now discuss briefly the individual contributions for total angular momentum $J$. In the case of ortho-$D_2 (j = 0)$, the orbital angular momentum in the entrance channel is restricted to $\ell = J$, and the corresponding sum over $\ell$ in equation (1) reduces to a single term, yielding

$$\sigma_{v_i \rightarrow n}(E) = \frac{\pi}{k_n^2} \sum_{J=0}^{\infty} (2J + 1) \sum_{\ell'=|J-j'|} S_{\ell' \rightarrow J}^j(E).$$

For the low energies explored here, only the partial waves $\ell = J \leq 2$ give significant contributions, which are shown in figure 5 for $D_2(v = 0) + H$. At the very lowest energies, the rate coefficient is dominated by $s$-wave ($\ell = 0$). However, for energies above 100 mK, the $s$-wave contribution decreases towards a minimum located at $E \approx 30$ K, as seen in figure 5. Thus, higher partial waves become dominant even in the kelvin regime; in fact, the resonantly enhanced $p$-wave contribution is already dominant in the sub-kelvin regime.

Figure 5. Energy dependent rate coefficients $K_{v_j}(E)$ for $H + D_2(v, j)$, for initial rovibrational states $v \leq 5$ (as indicated) and $j = 0$. The panels on the left correspond to reaction, while those on the right to quenching. Each panel shows the total rate (thick gray line) and the individual contributions for different values of the total angular momentum $J = 0, 1, 2$ (black, red, and green lines).
3.2. Reaction and quenching rates for $j = 1$

Figure 6 shows the rate coefficients for initial rotational state $j = 1$. We first remark that the resonant features for $j = 1$ are significantly different than the resonances presented in figure 2 for $j = 0$. Such a strong dependence on the initial rotational state of the dimer stems mostly from the fact that different partial waves $\ell$ in the entrance channel are coupled when both $j \neq 0$ and $J \neq 0$. Hence, if a shape resonance in a certain partial wave $\ell$ appears for a particular value $J$ of the total angular momentum, then it may also manifest for all other possible values: $J = |\ell - j|, \ldots, \ell + j$. We recall that the coupled channel problems for different values of $J$ are separate; thus, if a certain shape resonance appears repeatedly (for different values of $J$), each occurrence can be regarded as a different resonance associated with a particular coupled channel system of equations for a given $J$. Moreover, when a shape resonance is near the entrance channel threshold, it is very sensitive to the details of the coupled channel problem; e.g., small changes in the coupling matrix may cause the resonance to shift significantly, either away from the threshold, or closer to it—even becoming quasi-bound.

To better understand the complicated resonant features of the total rate coefficients for $j = 1$, we show the individual partial ($J$) contributions in figure 7. First, note that for $J = 0$, the relative angular momentum $\ell$ in the entrance channel is restricted to $\ell = j = 1$, corresponding to the black curves in figure 7, which are similar to the results shown previously in figure 5 for $\ell = J = 1$. In both cases ($j = 0$ in figure 5, and $j = 1$ in figure 7) there is a gradual shift of the $p$-wave shape resonance towards lower energy as $v$ increases. However, for $j = 1$, the overall attractive effect of the interaction is slightly stronger than for $j = 0$, most notably for $v = 5$ with the van der Waals complex for $j = 1$ (with $J = 0$ and $\ell = 1$) becoming quasi-bound just below the threshold and producing the rounded resonant feature shown in figure 7 (uppermost panel). Next, for $J = 1$, the partial waves $\ell = 0, 1, 2$ in the entrance channel are coupled together, and their net contribution is shown by the red curves in figure 7. Thus, the $J = 1$ contribution includes $s$-wave ($\ell = 0$, dominant at vanishing energies), $p$-wave, and $d$-wave (responsible for the small bump near $E \approx 6$ K). For $J = 2$, we have $\ell = 1, 2, 3$, whose contribution is shown by the green curves in figure 7. The $p$-wave shape resonances for $J = 0$ and $J = 2$ partly overlap, and thus the sum of all $J$-terms yields a complicated profile for the total rate coefficients.
3.3. Distributions over the product states

At low energy, and for any given initial rovibrational state of D₂, all state-to-state rate coefficients have nearly identical energy dependence (apart from their own overall magnitude) as illustrated in figure 8 for H + D₂(v = 4, j) → D + HD (v', j'). This holds true even in the presence of resonances, which can be understood in terms of the entrance channel Jost function [33, 34], whose energy dependence gets imprinted on all final channels. Consequently, at low energy, the rovibrational distribution of the product is nearly energy independent. In figure 9 we show in detail the distribution over the rovibrational states of the product for the same representative case (v = 4) depicted in figure 8. Note that the rovibrational distributions for ortho-D₂(j = 0) and para-D₂(j = 1) are very similar. Figure 10 shows the vibrational distributions of the product for all initial states considered in this work; apart from their different overall magnitude, ortho-D₂ and para-D₂ have similar distributions. The rovibrational distributions for v = 4 shown in figure 9 were extracted at energies E_{kin}^{ortho} = 0.6 K and E_{kin}^{para} = 0.17 K, which correspond to the locations of the resonances (where the rates are maximal). Similarly, the vibrational distributions in figure 10 were extracted at energies corresponding to the locations of the resonances, which differ slightly for each initial vibrational state.

3.4. Elastic cross sections

For the sake of completeness, we describe very briefly the results for the elastic cross section, σ_{n\rightarrow n}^{elast}(E), which is denoted as σ_{n}^{elast}(E); its expression is obtained by setting n' = n in equation (1),

\[
\sigma_{n}^{elast}(E) = \frac{\pi}{k_{n}^{2}} \sum_{J=0}^{\infty} \left( \frac{2J + 1}{2j + 1} \right) \sum_{I=0}^{J} | \delta_{II} - S_{n', nd}(E)|^2.
\]
Figure 8. State-to-state rate coefficients for H + D$_2$(v = 4, j) → D + HD(v', j').

Figure 9. Rovibrational distributions for H + D$_2$(v = 4, j) → D + HD(v', j'). The vertical dashed lines mark the threshold energies of the entrance channel for ortho-D$_2$ and para-D$_2$, respectively.

Figure 10. Vibrational distributions for H + D$_2$(v, j) → D + HD(v').
In general, different partial waves \( \ell \) are coupled, and the elastic cross section comprises the double sum \( \sum_{\ell} \sum_{\ell'} \alpha_{\ell \ell'} \beta_{\ell' \ell} \) as well as \( J_{\ell \ell'} \). A much simpler expression for \( \sigma_{\text{elast}}(E) \) only exists for initial rovibrational states \( (v,j) \) with \( j = 0 \), when we have \( \ell = J \) and \( \ell' = J \), and equation (6) reads

\[
\sigma_{\text{elast}}(E) = \frac{\pi}{k_0^2} \sum_{\ell=0}^{\infty} (2\ell + 1) |1 - S_{\ell J, \ell J}(E)|^2.
\]

The results for \( j = 0 \) and \( j = 1 \) are shown in figure 11 for \( 1 \leq v \leq 5 \). Although the elastic cross section shows resonant features in the kelvin and sub-kelvin regimes, they appear less pronounced due to the large value of the s-wave contribution in the Wigner regime (\( E \to 0 \)). The zero energy limit of \( \sigma_{\text{elast}}(E) \) decreases from approximately 5000–3000 a.u., while its maximal resonant value near \( E \approx 1 \) K increases from 5000 to 10⁴ a.u., as \( v \) increases from \( v = 1 \) to \( v = 5 \). Table 1 summarizes the real and imaginary parts of the scattering length.

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### Table 1. Real and imaginary contributions to the scattering length

| \( \alpha_{v,j} \) | \( \beta_{v,j} \) |
|-----------------|-----------------|
| \( H + D_2(v,j = 0) \) | \( H + D_2(v,j = 1) \) |
| \( \alpha \) (a.u.) | \( \beta \) (a.u.) | \( \alpha \) (a.u.) | \( \beta \) (a.u.) |
| 1 | 3.2 × 10⁻⁶ | 19.3 | 19.4 | 4.3 × 10⁻⁶ |
| 2 | 3.3 × 10⁻⁵ | 18.1 | 18.2 | 1.0 × 10⁻⁵ |
| 3 | 3.3 × 10⁻⁴ | 17.2 | 17.3 | 5.2 × 10⁻⁴ |
| 4 | 6.1 × 10⁻³ | 16.3 | 16.6 | 7.6 × 10⁻³ |
| 5 | 3.0 × 10⁻² | 15.2 | 15.4 | 4.5 × 10⁻² |

Figure 11. Elastic cross sections for \( H + D_2(v,j) \) for initial rovibrational states \( (v,j) \) with \( 1 \leq v \leq 5 \) and \( j = 0 \), 1. The panels on the left correspond to \( j = 0 \), while those on the right side to \( j = 1 \). Each panel shows the total elastic cross section, as well as the contributions of individual \( J = 0 \), 1, 2. The atomic unit (Bohr radius squared) is used for the cross section.
4. Conclusion

We presented results for the scattering of H on D₂ for initial vibrational states \( v \leq 5 \), and we found prominent shape resonances at very low energy. We remark that these resonant structures are sensitive to the details of the potential energy surface and they could serve as stringent tests if experimental data were to become available. We have demonstrated that the initial rotational state of D₂ affects the resonant features significantly; indeed, the lineshapes of the resonances for ortho-D₂\((j = 0)\) and para-D₂\((j = 1)\) are very different. Moreover, the initial vibrational state also has a strong effect on the resonant features. Finally, comparing the results presented here for H + D₂ with the results obtained previously for D + H₂, we report a very strong isotopic effect, as the resonant features for the two reactions differ drastically.

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