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Controlling Rotational Quenching Rates in Cold Molecular Collisions

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ABSTRACT

The relative orientation and alignment of colliding molecules plays a key role in determining the rates of chemical processes. Here, we examine in detail a prototypical example: rotational quenching of HD in cold collisions with H_2. We show that the rotational quenching rate from $j = 2 \rightarrow 0$, in the $v = 1$ vibrational level, can be maximized by aligning the HD along the collision axis and can be minimized by aligning the HD at the so called magic angle. This follows from quite general helicity considerations and suggests that quenching rates for other similar systems can also be controlled in this manner.

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I. INTRODUCTION

Across many areas of chemistry, the dynamics of collision processes are determined to a large extent by the relative orientation and alignment of colliding molecules.[1–9] In the cold and ultracold regime, we can study such dynamical effects with exquisite precision.[10–18]

In a recent series of papers, Perreault *et al.* have examined how changing the relative alignment of HD molecules in cold collisions with H_2 and D_2 affects the angular distribution of inelastically scattered HD.[12,19] In the experiments, HD molecules were prepared in the $v = 1$, $j = 2$ state and the angular distribution of the scattered HD for the $v = 1$, $j = 0$ final state was measured. The low collision energy and light masses of the collision partners combined with the choice of the initial and final states limit the number of partial waves involved in the collision process. This was confirmed by subsequent theoretical studies which revealed that the angular distribution of the scattered HD in collisions with H_2 was dominated by a single ($l = 2$) partial-wave shape resonance at around 1 K.[20] Collisions of HD with H_2 are also of current astrophysical interest as the HD molecule is believed to have played an important role in the cooling of the primordial gas in the formation of the first stars and galaxies.[21–23]

Here, we examine how rotational quenching rates for HD in cold collisions with *para*-H_2 in $j = 0$ and *ortho*-H_2 in $j = 1$ can be controlled by changing the relative alignment of the HD. We show that in order to maximize the rate of rotational quenching of HD from $j = 2 \rightarrow 0$, the HD should be aligned along the collision axis, whereas to minimize the quenching rate, the HD should be aligned at the so called magic angle.

II. METHODOLOGY

The H_4 system and its isotopologues contain just 4 electrons as such high quality *ab initio* potential energy surfaces are available. In this work, we have used the full-dimensional H_2–H_2 potential of Hinde,[24] which is in good agreement with other available surfaces.[25,26] Collisions of H_2 dimers and their isotopologues are also amenable to quantum scattering calculations due to the relatively shallow interaction potential and low density of states of their energy level structure.[27–31]

Scattering calculations for collisions of HD with H_2 were performed in full-dimensionality using a modified version of the TwoBC code.[32] This methodology has been applied to many other similar systems[20,33–36] and is outlined in detail elsewhere.[31,37,38] Here, we briefly review the methodology in order to define notation. The scattering calculations are performed within the time-independent close-coupling formalism which yields the scattering S matrix.[39] For convenience, we label each asymptotic channel by the combined molecular state $\alpha = v_1 j_1 v_2 j_2$, where v and j are

vibrational and rotational quantum numbers, respectively, and the subscript 1 refers to HD and 2 to H_2. The integral cross section for state-to-state rovibrationally inelastic scattering is given by

$$\sigma_{\alpha \to \alpha'} = \frac{\pi}{(2j_1+1)(2j_2+1)k_\alpha^2} \sum_{J, j_{12}, j'_{12}, l, l'} (2J+1) |T^J_{\alpha l j_{12}, \alpha' l' j'_{12}}|^2, \quad (1)$$

where $k^2 = 2\mu E/\hbar^2$ is the square of the wave vector, E is the collision energy, μ is the reduced mass, $T^J = 1 - S^J$, $\mathbf{j}_{12} = \mathbf{j}_1 + \mathbf{j}_2$, l is the orbital angular momentum quantum number, and J is the quantum number for the total angular momentum, $\mathbf{J} = \mathbf{l} + \mathbf{j}_{12}$. To compute differential cross sections, we also need the scattering amplitude as a function of the scattering angle θ, which has previously been given by Schaefer and Meyer[27] in the helicity representation

$$q(\theta) = \frac{1}{2k_\alpha} \sum_J (2J+1) \sum_{j_{12}, j'_{12}, l, l'} i^{l-l'+1} T^J_{\alpha l j_{12}, \alpha' l' j'_{12}} d^J_{m_{12}, m'_{12}}(\theta)$$
$$\times \langle j'_{12} m'_{12} J - m'_{12}|l'0 \rangle \langle j_{12} m_{12} J - m_{12}|l0 \rangle$$
$$\times \langle j'_1 m'_1 j'_2 m'_2 | j'_{12} m'_{12} \rangle \langle j_1 m_1 j_2 m_2 | j_{12} m_{12} \rangle, \quad (2)$$

where $d^J_{m_{12}, m'_{12}}(\theta)$ is Wigner's reduced rotation matrix. The rovibrational helicity resolved differential cross section is then obtained by summing over m'_1 and m'_2 and averaging over m_1 and m_2

$$\frac{d\sigma_{\alpha m_{12} \to \alpha' m'_{12}}}{d\Omega} = \frac{1}{(2j_1+1)(2j_2+1)}$$
$$\times \sum_{m_1, m_2, m'_1, m'_2} |q_{\alpha, m_1, m_2, m_{12} \to \alpha', m'_1, m'_2, m'_{12}}|^2, \quad (3)$$

where $d\Omega$ is the infinitesimal solid angle $\sin\theta d\theta d\phi$. Helicity resolved cross sections are useful as $m_{12} \to m_{12}$ transitions conserve j_z in the body-fixed frame. This is the assumption made in the coupled-states approximation[40–42] where the differential cross section is given by

$$\frac{d\sigma_{\alpha \to \alpha'}}{d\Omega} = \sum_{m_{12}} \frac{d\sigma_{\alpha m_{12} \to \alpha' m_{12}}}{d\Omega}. \quad (4)$$

The coupled-states approximation has been shown to be generally valid for inelastic and reactive collisions away from resonances.[27,43,44]

The cross section formulas presented so far are derived assuming that the relative alignment of the colliding molecules is uncontrolled—by averaging over initial projection quantum numbers (m_1, m_2, and m_{12}) and summing over final projection quantum numbers (m'_1, m'_2, and m'_{12}). Here, however, we are interested in the cross section when the relative alignment of the collision partners is controlled in the manner described in the experiments of Perreault et al. on rotational quenching of HD in cold collisions with H_2 and D_2.[12,19,45] In those experiments, the HD molecule was prepared using the Stark-induced adiabatic Raman passage (SARP) which polarizes the angular momentum vector $\mathbf{j}$. In this way, the HD can be prepared in a state $|j = 2, \tilde{m} = 0\rangle$ with the quantization axis of $\tilde{m}$ determined by the alignment of the linear polarization of the SARP laser.[46,47] Choosing β as the angle between the linear

polarization of the SARP laser and the beam velocity in the laboratory frame, the state of a molecule prepared in a rotational state $|j, \tilde{m}\rangle$ can be expressed as

$$\sum_{m=-j}^{j} d^j_{\tilde{m}, m}(\beta) |j, m\rangle \quad (5)$$

in terms of projections m onto the relative velocity axis. In the work of Perreault et al., the HD was prepared in the $v = 1$, $j = 2$ level with two different alignments, $\beta = 0$ and $\frac{\pi}{2}$ referred to as HSARP and VSARP, respectively, where the H and V preceding SARP refer to the horizontal and vertical alignment of the laser polarization. HSARP therefore corresponds to the initial state $|j_1 = 2, m_1 = 0\rangle$ with the molecular bond axis preferentially parallel to the relative velocity axis, while VSARP corresponds to

$$\sqrt{\frac{3}{8}} |j_1 = 2, m_1 = -2\rangle - \frac{1}{2}|j_1 = 2, m_1 = 0\rangle + \sqrt{\frac{3}{8}} |j_1 = 2, m_1 = 2\rangle \quad (6)$$

with the molecular bond axis preferentially perpendicular to the relative velocity axis. The helicity-resolved differential cross section for collisions of molecules prepared using the SARP method is therefore given by

$$\frac{d\sigma_{\alpha, m_{12} \to \alpha', m'_{12}}}{d\Omega} = \frac{1}{(2j_2+1)} \sum_{m_2, m'_1, m'_2} \left| \sum_{m_1} d^{j_1}_{0, m_1}(\beta) \right.$$
$$\left. \times q_{\alpha, m_1, m_2, m_{12} \to \alpha', m'_1, m'_2, m'_{12}} \right|^2. \quad (7)$$

Integrating over ϕ and taking advantage of the cylindrical symmetry of the problem, we obtain the cross section as a function of the scattering angle θ

$$\frac{d\sigma_{\alpha, m_{12} \to \alpha', m'_{12}}}{d\theta} = \frac{2\pi \sin\theta}{(2j_2+1)} \sum_{m_1, m_2, m'_1, m'_2} |d^{j_1}_{0, m_1}(\beta)|^2$$
$$\times |q_{\alpha, m_1, m_2, m_{12} \to \alpha', m'_1, m'_2, m'_{12}}|^2. \quad (8)$$

We can now see that the effect of aligning the collision partners is to change the relative weighting of the helicity resolved cross sections.

III. RESULTS

We first consider off resonant collisions between HD and para-H_2 in its $j = 0$ rotational state due to its relative simplicity. At the low collision energies considered here, rotational excitation of para-H_2 is not possible which simplifies the angular momentum algebra as $m_{12} = m_1$, and as discussed, helicity is approximately conserved for off resonant collisions. Figure 1 shows the helicity resolved differential rate for collisions of HD ($v = 1$, $j = 2$) with para-H_2 at 1 K which is off-resonant.[20] As expected, the dominant contribution is from $0 \to 0$ which conserves helicity. In this case, Eq. (8) is simplified as $m_2 = 0$ and so $m_{12} = m_1$ and $m'_1 = m'_2 = m'_{12} = 0$

$$\frac{d\sigma_{\alpha \to \alpha'}}{d\theta} = 2\pi \sin\theta \sum_{m_{12}=-2}^{2} |d^2_{0, m_{12}}(\beta)|^2$$
$$\times |q_{\alpha, m_1 = m_{12}, m_2 = 0, m_{12} \to \alpha', m'_1 = 0, m'_2 = 0, m'_{12} = 0}|^2. \quad (9)$$
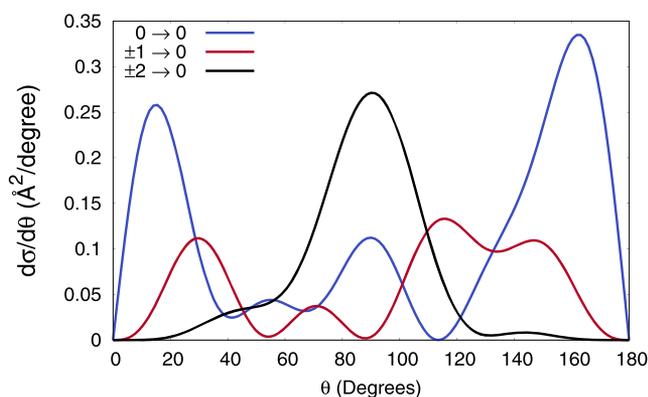
FIG. 1. Helicity resolved ($m_{12} \rightarrow m'_{12}$) differential cross sections for rotational quenching from HD ($v = 1$, $j = 2$) to HD ($v = 1$, $j = 0$) in collisions with *para*-H_2 at 1 K.

The effect of changing the relative alignment of the HD by β is to change the relative contribution from each helicity—which gives us a handle with which to control the outcome. For example, if we were interested in maximizing the cross sections, we would want to maximize the helicity conserving contribution $0 \rightarrow 0$. Figure 2 shows the square of Wigner's reduced rotation matrix $|d^2_{0,m}(\beta)|^2$ as a function of the polar angle β. In order to maximize the cross section, we choose $\beta = 0$ as the only contribution to the integral cross section that conserves helicity ($m_{12} = m_1 = 0 \rightarrow m'_{12} = m'_1 = 0$)—which corresponds to HSARP in the work of Perreault *et al.* Whereas to minimize the integral cross section, we choose $\beta = \beta_m = \arccos\frac{1}{\sqrt{3}} \approx 54.7°$ the so called magic angle, which corresponds to an initial state

$$\frac{1}{\sqrt{6}}|j_1 = 2, m_1 = -2\rangle + \frac{1}{\sqrt{3}}|j_1 = 2, m_1 = -1\rangle - \frac{1}{\sqrt{3}}|j_1 = 2, m_1 = 1\rangle$$

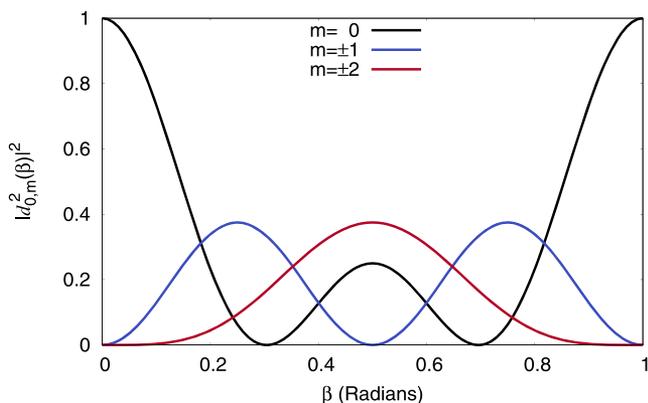$$+ \frac{1}{\sqrt{6}}|j_1 = 2, m_1 = 2\rangle, \qquad (10)$$

as then, none of the contributions to the integral cross section conserve helicity ($m_{12} = m_1 = \pm 1, \pm 2 \rightarrow m'_{12} = m'_1 = 0$).

Figure 3 shows the integral cross section as a function of the collision energy for different values of β for *para*-H_2 collisions. It is seen that as expected, $\beta = 0$ leads to the largest cross section and the magic angle leads to one of the smallest cross sections at any given energy. We would expect this approach to work for rotational quenching quite generally, at least away from resonances, as the contribution from $0 \rightarrow 0$ will always be one of the helicity conserving contributions and to work especially well when quenching to a state where $j'_1 = j'_2 = 0$, as we have here, where it would be the only helicity conserving contribution. The angle β where $|d^j_{0,0}(\beta)|^2 = 0$ would however change depending on the initial rotational state j such that $P_j(\cos \beta) = 0$, where P_j is the Legendre polynomial of degree j.

We now move on to on-resonant collisions of HD with *ortho*-H_2 in its $j = 1$ rotational state. Rotational excitation of H_2 is still not possible at the energies considered here, but the extra angular momentum complicates the analysis as m_2 can change during the collision. Unlike in the off resonance case where we took advantage of the approximation that helicity is conserved we do not expect that to be the case here.[44] Figure 4 shows the dominant helicity resolved cross sections. Unlike in the *para*-H_2 case, there are significant contributions to the cross section from nonhelicity conserving transitions, specifically $1 \rightarrow 0$ and $3 \rightarrow 0$. The contribution from $2 \rightarrow 0$ on the other hand is relatively small. Just as for the *para*-H_2 case, β gives a handle to vary the integral cross section: in this case, however, we take advantage of the relatively small cross section for $2 \rightarrow 0$. To maximize the cross section, we again choose $\beta = 0$ as $m_1 = 0$ can couple with $m_2 = 0, \pm 1$ to make $m_{12} = m_1 + m_2 = \pm 1, 0$ all of which have large cross sections. In order to minimize the cross section, we want to minimize exactly those contributions and maximize the contribution from $2 \rightarrow 0$, so again we choose the magic angle.

Figure 5 shows the integral cross section for *ortho*-H_2 collisions as a function of the collision energy for different values of β. Again, it is seen that as expected, $\beta = 0$ leads to the largest cross section
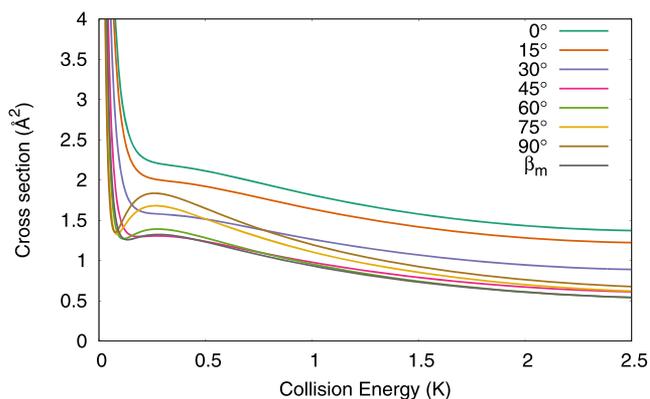

FIG. 2. Wigner's reduced rotation matrix $|d^2_{0,m}(\beta)|^2$ as a function of the polar angle β for $m = \pm 2, \pm 1, 0$.

FIG. 3. Integral state-to-state cross sections for HD ($v = 1$, $j = 2$) $\rightarrow$ HD ($v = 1$, $j = 0$) in collisions with *para*-H_2 for $\beta = 0, 15, 30, 45, 60, 75, 90$ and the magic angle β_m.
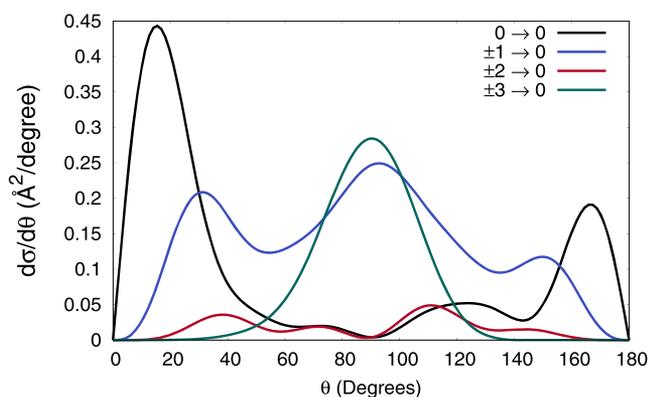
FIG. 4. Dominant helicity resolved ($m_{12} \rightarrow m'_{12}$) differential cross sections for rotational quenching from HD ($v = 1$, $j = 2$) to HD ($v = 1$, $j = 0$) in collisions with *ortho*-H_2 at 1 K.

FIG. 6. Ratio of the integral cross section for $\beta = 0$ to $\beta = \beta_m$ as a function of energy.

and the magic angle leads to the smallest cross section. It is not clear from this case if it is in general true that the magic angle minimizes the cross section on resonance. We do however expect that choosing the magic angle will always reduce the cross section compared to $\beta = 0$ as $0 \rightarrow 0$ is expected to be a significant (even if not dominant) contribution to the total cross section in the on resonant case.

The degree of control over the integral cross section can be quantified by the ratio of the integral cross section for $\beta = 0$ to $\beta = \beta_m$, $\frac{\sigma(E, \beta=0)}{\sigma(E, \beta=\beta_m)}$, which is shown in Fig. 6 as a function of collision energy. Away from resonance, it is seen that greater control over the rate of rotational quenching can be exerted for collisions with *para*-H_2 than for *ortho*-H_2. This is because by choosing $\beta = 0$, the only contribution to the total cross section conserves helicity ($m_{12} = m_1 = 0 \rightarrow m'_{12} = m'_1 = 0$), whereas by choosing $\beta = \beta_m$, none of the contributions conserve helicity ($m_{12} = m_1 = \pm1, \pm2 \rightarrow m'_{12} = m'_1 = 0$). In collisions with *ortho*-H_2, however, contributions from helicity conserving transitions are
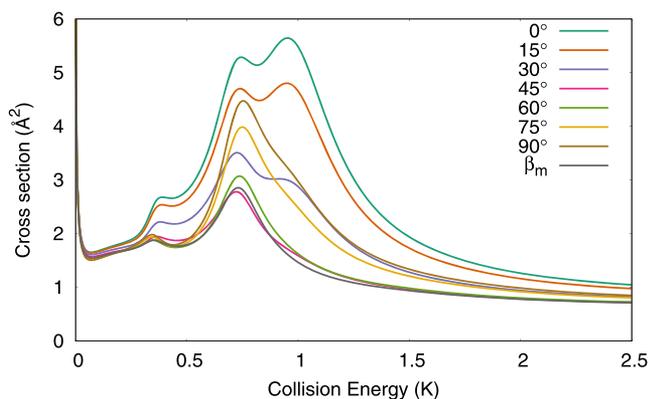
unavoidable. Generally speaking, we therefore expect that choosing $\beta = 0$ as opposed to $\beta = \beta_m$ will have the biggest effect when quenching to a state where $j'_1 = j'_2 = 0$. On the other hand, the biggest effect on the integral cross section is seen on resonance for collisions with *ortho*-H_2 where the integral cross section can be enhanced by up to a factor of 4. It is not clear if choosing $\beta = \beta_m$ will in general be as effective for other resonances or whether this is a consequence of the small contribution from $m_{12} = 2 \rightarrow m'_{12} = 0$ in this case.

IV. CONCLUSION

In this work, we have examined how rotational quenching rates in cold collisions of HD with H_2 can be controlled by changing the relative alignment of the collision partners, showing they can be enhanced by up to a factor of 4. In order to maximize the rotational quenching rate of HD from $j = 2 \rightarrow 0$, the HD should be aligned along the relative collision axis, whereas to minimize the rate, the HD should be aligned at the so called magic angle. This follows from quite general helicity considerations, and as such, we expect that rotational quenching rates for cold collisions of other similar molecules can also be controlled in this way. Control over the alignment of colliding molecules of the kind described in this work has already been experimentally demonstrated using the SARP method.[12] This work therefore further demonstrates the exquisite control that can be achieved in cold molecular collision experiments when the incoming molecules are prepared using the SARP method.[12,19,20] In future work, we intend to examine rotational quenching rates for other initial rotational states as well as other systems.

FIG. 5. Integral state-to-state cross sections for HD ($v = 1$, $j = 2$) → HD ($v = 1$, $j = 0$) in collisions with *ortho*-H_2 for $\beta = 0$, 15, 30, 45, 60, 75, 90 and the magic angle β_m.
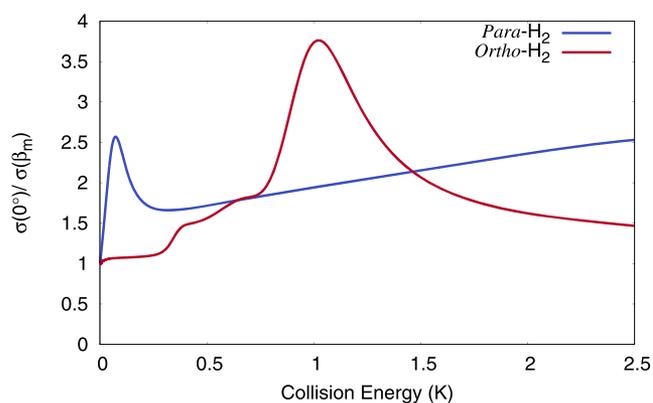
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