Controlling rotational quenching rates in cold molecular collisions

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The relative orientation 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.

I. INTRODUCTION

Across many areas of chemistry the dynamics of collision processes are determined to a large extent by the relative orientation of colliding molecules. In the cold and ultracold regime we can study such dynamical effects with exquisite precision.

In a recent series of papers Perreault et al. have examined how changing the relative orientation of HD molecules in cold collisions with H$_2$ and D$_2$ affects the angular distribution of inelastically scattered HD. 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 as around 1 K. 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.

Here we examine how rotational quenching rates in cold molecular collisions can be controlled by changing the relative alignment of one of the collisions partners, taking collisions of HD with H$_2$ as a prototypical example. 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 $ab\text{ initio}$ potential energy surfaces are available. In this work we have used the full-dimensional H$_2$-H$_2$ potential of Hinde, which is in good agreement with other available surfaces. 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.

Scattering calculations for collisions of HD with H$_2$ were performed in full-dimensionality using a modified version of the TwoBC code. This methodology has been applied to many other similar systems and is outlined in detail elsewhere. 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. For convenience, we label each asymptotic channel by the combined molecular state $\alpha = v1j1j2j2$, where $v$ and $j$ are vibrational and rotational quantum numbers respectively, in this work 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,

$$
\sigma_{\alpha \rightarrow \alpha'} = \frac{\pi}{(2j_1+1)(2j_2+1)k^2} \times \sum_{j,j_1,j_2,l,l'} (2J+1)|T_{\alpha j_1 j_2 \alpha' j_1' j_2'}|^2.
$$

where $k^2 = 2\mu E/\hbar^2$ is the square of the wave vector, $E$ is the collision energy, $\mu$ is the reduced mass, $T^{J} = 1 - S^{J}$, $j_{12} = j_1 + j_2$, $l$ is the orbital angular momentum quantum number, and $J$ the total angular momentum quantum number $J = 1 + j_{12}$. To compute differential cross sections we also need the scattering amplitude as a function of the scattering angle $\theta$, which has previously been given by Schafer et al. in the helicity representation:

$$
q(\theta) = \frac{1}{2k_{\alpha}} \sum_{J} (2J+1) \sum_{j_{12} j_{12}' l l'} j_{l}^{-l'} + T^{J}_{\alpha j_1 j_2 \alpha' j_1' j_2'} \\
\times \langle j_{12} m_{12} | J - m_{12}' | 0 \rangle \langle j_{12} m_{12} J - m_{12}' | 0 \rangle \\
\times \langle j_{1}' m_{1}' J_{2} | J_{12} m_{12} j_{12} m_{12} | 0 \rangle \\
\times \langle j_{1}' m_{1}' J_{2} j_{12} m_{12} | 0 \rangle \\
\times \langle j_{1}' m_{1}' J_{2} j_{12} m_{12} | 0 \rangle
$$

where $d_{m_{12},m_{12}'}^{J}(\theta)$ 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
In the work of Perreault et al., the laboratory frame, the state of a molecule prepared in polarization of the SARP laser and the beam velocity in $v = 1$ HD in cold collisions with H$_2$ is controlled — 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 orientation 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$_2$. In those experiments the HD molecule was prepared in a state $|j = 2, \hat{m} = 0\rangle$ by Stark-induced adiabatic Raman passage (SARP) with the quantization axis of $\hat{m}$ determined by the orientation of the linear polarization of the SARP laser. Choosing $\beta$ 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 $|j, \hat{m}\rangle$ can be expressed as

$$
\sum_{m=-j}^{j} d^2_{m,m}(\beta)|j,m\rangle,
$$

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 orientations, $\beta = 0$ and $\pi$ referred to as HSARP and VSARP respectively, where the H and V refer to the horizontal and vertical alignment of the laser polarization respectively. HSARP therefore corresponds to initial state $|j_1 = 2, m_1 = 0\rangle$ while VSARP corresponds to,

$$
\sqrt{\frac{3}{8}}|j_1 = 2, m_1 = -2\rangle - \frac{1}{2}|j_1 = 2, m_1 = 0\rangle + \sqrt{\frac{5}{8}}|j_1 = 2, m_1 = 2\rangle.
$$

The helicity-resolved differential cross section for molecular collisions of molecules prepared using the SARP method is therefore given by

$$
\frac{d\sigma_{\alpha \rightarrow \alpha'}}{d\Omega} = \frac{1}{(2j_1 + 1)} \sum_{m_1} \sum_{m'_1} |d^2_{m_1,m'_1}(\beta)|^2 |q_{\alpha,m_1,m_2,m_{12} \rightarrow \alpha',m'_1,m'_2,m'_{12}}|^2.
$$

Integrating over $\phi$ and taking advantage of the cylindrical symmetry of the problem we obtain the cross section as a function of the scattering angle $\theta$,

$$
\frac{d\sigma_{\alpha,m_12 \rightarrow \alpha',m'_{12}}}{d\theta} = \frac{2\pi \sin \theta}{(2j_2 + 1)} \sum_{m_1} \sum_{m'_1} |d^2_{m_1,m'_1}(\beta)|^2 |q_{\alpha,m_1,m_2,m_{12} \rightarrow \alpha',m'_1,m'_2,m'_{12}}|^2.
$$

We can now see that the effect of orienting 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$_2$ due to its relative simplicity. As discussed helicity is approximately conserved for off resonant collisions and the angular momentum algebra is simplified since $j_2 = 0$ and so $m_{12} = m_1$. Fig. 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. As expected the dominant contribution is from $0 \rightarrow 0$ which conserves helicity. In this case Eq. (8) is simplified as $m_2 = 0$ and so $m_{12} = m_1$ and $m_1' = m_2' = m_{12}' = 0$

$$\frac{d\sigma_{\alpha \rightarrow \alpha'}}{d\theta} = 2\pi \sin \theta \sum_{m_{12} = -2}^{2} |d_{0,m_{12}}^{m}(\beta)|^2$$

$$\times |q_{m_{1} = m_{12}, m_{2} = 0, m_{1} = m_{1}', m_{1}' = 0, m_{2}' = 0}|^2.$$  

The effect of changing the relative alignment of the HD by $\beta$ 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 $0 \rightarrow 0$. Fig. 2 shows the square of Wigner’s reduced rotation matrix $|d_{0,m}(\beta)|^2$ as a function of the polar angle $\beta$. 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 Perreau et al. Whereas to minimize the integral cross section we choose $\beta = \beta_m = \arccos \frac{m_1}{\sqrt{m_1^2}} \approx 54.7^\circ$ the so called magic angle, which corresponds to an initial state

$$\frac{1}{\sqrt{6}}|j_1 = 2, m_1 = -2\rangle + \frac{1}{\sqrt{3}}|j_1 = 2, m_1 = -1\rangle \quad (10)$$

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

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

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

Fig. 3 shows the integral cross section as a function of the collision energy for different values of $\beta$ para-H$_2$ collisions. It is seen that as expected $\beta = 0$ leads to the largest cross section and the magic angle leads to the 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 $\beta$ where $|d_{0,0}(\beta)|^2 = 0$ 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 the more complicated case of collisions of HD with ortho-H$_2$ on resonance. Unlike in the off resonance case where we took advantage of the approximation that helicity is conserved here we do no expect that to be the case. In addition the extra angular momentum of the H$_2$ complicates the analysis. Fig. 4 shows the dominant helicity resolved cross sections. Unlike in the para-H$_2$ case there are significant contributions to the cross section from non-helicity 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 $\beta$ 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.

Fig. 5 shows the integral cross section for ortho-H$_2$ collisions as a function of the collision energy for different
values of $\beta$. Again it is seen that, as expected, $\beta = 0$ leads to the largest cross section 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 ($m_{12} = m_1 = \pm 1, \pm 2 \rightarrow m_{12}' = m_1' = 0$). 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

Precise stereodynamic control of cold molecular collisions has been experimentally demonstrated by changing the relative alignment of the collision partners using the SARP method. In this work we have examined how rotational quenching rates in cold collisions of HD with H$_2$ can be controlled using this technique, showing they can be enhanced by up to 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 other similar molecules can also be controlled in this way. This work demonstrates the exquisite control that can be achieved in cold molecular collisions when the incoming molecules are prepared using the SARP method. In future work we intend to examine rotational quenching rates for other initial rotational states as well as other systems.

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