Coherent control of reactive scattering at low temperatures: Signatures of quantum interference in the differential cross sections for $F + H_2$ and $F + HD$

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Fundamental entanglement related challenges have prevented quantum interference-based control (i.e., coherent control) of collisional cross sections from being implemented in the laboratory. Here, differential cross sections for reactive scattering at low temperatures are shown to provide a unique opportunity to display such interference-based control by forming coherent superpositions of degenerate rotational states of reactant molecules $|jm\rangle$ with different $m$. In particular, we identify and quantify a unique signature of coherent control in reactive scattering with applications to $F + H_2 \rightarrow H + HF$ and $HF + D \leftrightarrow F + HD \rightarrow HD + F$ at 11 K. Control is shown to be extensive.

Coherent control of atomic and molecular processes (for a review until 2012, see [1]), i.e., the use of quantum interference to effect molecular outcomes, has proven enormously successful for certain classes of processes. These include assorted processes, such as light-induced control of unimolecular processes such as photodissociation [2], photoionization [3], control of currents in live systems [4], control of population transfer between system eigenstates [5], control of internal conversion [6], etc. By preparing multiple interfering pathways as initial states, primarily by laser excitation, quantum-interference-based control over various processes, has been demonstrated both computationally (e.g., [1, 7–9]) and experimentally (e.g., [10, 11]). However, control over the wide class of collision processes such as chemical reactions requires, in general, entanglement between the translation motion of the colliding partners and their internal degrees of freedom [1, 12–14], a non-trivial experimental challenge for molecular collisional systems of interest. While this requirement can be relaxed for coherent control over the differential cross section (DCS) for $A + BC$ collisions by forming coherent superpositions of energetically degenerate states of BC, coherent control of reactive scattering is yet to be demonstrated experimentally.

Such a demonstration would be particularly valuable for cold and ultracold chemical reactions in the quantum regime [15], which have become amenable to experimental studies owing to recent advances in cooling, trapping, and manipulating molecular gases [16]. These studies have revealed a number of fascinating phenomena, such as resonant scattering in cold He$^+$ $+$ $H_2$ [17, 18] and He $+$ NO [19] collisions, stereodynamics of $H_2$ $+$ HD collisions at 1 K [20, 21], quantum tunneling in the chemical reaction $F + H_2 \rightarrow HF + H$ at cold temperatures [22], and electric field control of the chemical reaction $2KrB \rightarrow K_2 + Rb_2$ at 50 mK [23, 24]. Several theoretical studies explored the effects of molecular polarization [25] and alignment [26, 27] on ultracold collision dynamics.

There are three primary motivations for using coherent control to manipulate cold molecular collisions. First, in the low-temperature regime, the number of quantum states of the reactants (including partial waves for the relative motion) is dramatically reduced [15, 16], minimizing thermal fluctuations and decoherence, and thereby enhancing quantum controllability of molecular processes. Second, because coherent control relies on the very general phenomenon of quantum interference, it could potentially be applied to a much wider range of molecular species than dc field control, which typically employs, e.g., Feshbach resonances to tune the scattering properties of ultracold atoms and molecules [28]. Thus, coherent control may prove advantageous in experimental settings, where the presence of dc fields can cause undesirable perturbations, such as in precision measurements using atomic and molecular clocks [29, 30]. Third, recent experimental studies of low-temperature collisions of molecules in single rotational states [19, 22, 24] and in superpositions thereof [20, 21] now provide an experimental platform where such quantum interference-based control of reactive scattering can be carried out.

Here we computationally demonstrate that (a) extensive control can be achieved over the DCS for reactive $F + H_2 \rightarrow HF + H$, and $F + HD \rightarrow HF + D$ or $DF + H$ in cold (11 K) scattering, by preparing a superposition of magnetic sublevels of ortho-$H_2$ and HD, and (b) that such control displays a unique measurable signature, readily identifying quantum interference as the basis for control. Computational results are obtained within a scenario that can be realized in modern experiments using merged beams of $H_2$ molecules created in superpositions of rotational states using, e.g., Stark-induced adiabatic Raman passage (SARP) [20, 21]. The results also provide motivation for the extension to systems of particular interest in ultracold chemistry, such as those involving alkali-metal dimers KRB, NaK, and NaLi [23, 31, 33], and $^2\Sigma$ molecular radicals CaF, SrF, and SrOH [34, 35].

We propose to control a reactive atom-molecule collision $A + BC \rightarrow AB + C$ by preparing an initial state $|\psi_\alpha\rangle$ as a superposition of two $m$-states of a diatomic molecule, a procedure that has been experimen-
tally demonstrated using SARP [20 23 30]

\[ |\psi_s\rangle = \cos(\eta) |1,v,j,m_1\rangle + \sin(\eta) \exp(i\beta) |1,v,j,m_2\rangle \]  

(1)

Here \( v \) and \( j \) are the vibrational and rotational quantum numbers, respectively, and the first quantum number \( \alpha \) corresponds to the chemical arrangement (i.e. A + BC, B + A C or C + AB) with \( \alpha = 1 \) denoting the initial A + BC arrangement. The parameter \( \eta \) sets the relative population of the two states in the superposition with relative phase \( \beta \).

Given this initial superposition state [1], the DCS to a final state \( (\alpha', v', j', m'_j) \) can be written as the sum of two terms:

\[ \sigma_{s\rightarrow\alpha'v'j'm_j}(\theta,\phi) = \sigma_{s\rightarrow\alpha'v'j'm_j}^{\text{coh}}(\theta,\phi) + \sigma_{s\rightarrow\alpha'v'j'm_j}^{\text{int}}(\theta,\phi), \]  

where the subscript \( s \) denotes the initial superposition state [Eq. (4)]. The first of these terms, \( \sigma_{s\rightarrow\alpha'v'j'm_j}^{\text{coh}}(\theta,\phi) \) is an incoherent contribution equivalent to the DCS from a mixture of \( m \) states with probabilities \( \cos^2(\eta) \) and \( \sin^2(\eta) \):

\[ \sigma_{s\rightarrow\alpha'v'j'm_j}^{\text{coh}}(\theta,\phi) = \cos^2(\eta) |f_{1vjm_1\rightarrow\alpha'v'j'm_j}(\theta,\phi)|^2 + \sin^2(\eta) |f_{1vjm_2\rightarrow\alpha'v'j'm_j}(\theta,\phi)|^2 \]  

(3)

where \( f_{1vjm_1\rightarrow\alpha'v'j'm_j}(\theta,\phi) \) (i = 1, 2) are the scattering amplitudes into product states \( (\alpha'v', j', m'_j) \) that are the key quantities to compute:

\[ f_{1vjm_1\rightarrow\alpha'v'j'm_j}(\theta,\phi) = \frac{\pi^{1/2}}{(k_{avj}k_{avj'})^{1/2}} \times \sum_{J,M} \sum_{\ell,M} \sum_{\ell',m'_j} [j,\ell,J][j',\ell',J'] [j,0,M][m'_j,m'_j,M] \]  

\[ \times \delta_{\alpha\alpha'}|\delta_{v'v}\delta_{j'j}\delta_{\ell'\ell'} - S_{avjm_1\rightarrow\alpha'v'j'm_j}(E)| Y_{\ell'M}(\theta,\phi). \]  

(4)

Here, \( \ell(\ell') \) is the initial (final) partial wave and \( m'_j(m_j) \) is the initial (final) projection of \( \ell \) on the space-fixed quantization axis \( Z \). \( E \) is the collision energy, \( k_{avj}(k_{avj'}) \) are the initial (final) relative momenta. The symbols in brackets are the Clebsch-Gordan (CG) coefficients, \( Y_{\ell'M}(\theta,\phi) \) are the spherical harmonics and \( S_{avjm_1\rightarrow\alpha'v'j'm_j}(E) \) are the S-matrix elements.

The second term in Eq. (2), \( \sigma_{s\rightarrow\alpha'v'j'm_j}^{\text{int}}(\theta,\phi) \), is the interference contribution, in which coherent control is manifest. Specifically, coherent control occurs via the quantum interference between the two scattering pathways arising from the initial \( m \)-superposition [1]. The interference term is then given by:

\[ \sigma_{s\rightarrow\alpha'v'j'm_j}^{\text{int}}(\theta,\phi) = \cos(\eta) \sin(\eta) \times [e^{-i\beta} f_{1vjm_1\rightarrow\alpha'v'j'm_j}(\theta,\phi) f_{1vjm_2\rightarrow\alpha'v'j'm_j}(\theta,\phi) + e^{i\beta} f_{1vjm_1\rightarrow\alpha'v'j'm_j}(\theta,\phi) f_{1vjm_2\rightarrow\alpha'v'j'm_j}(\theta,\phi)]. \]  

(5)

Note the characteristic difference between the direct terms [Eq. (4)] and the interference term [Eq. (5)]. Specifically, the latter shows a dependence of scattering on the azimuthal angle \( \phi \) whereas the direct terms are \( \phi \)-independent. Hence, \( \phi \)-dependent scattering is a unique signature of interfering quantum pathways in the differential scattering cross section. Previous experimental studies [20 21] on scattering with this type of superposition state did not measure this dependence insofar as detection included averaging over \( \phi \).

The \( \phi \)-dependence in Eq. (5) originates from the \( e^{im'\phi} \) term in the spherical harmonics contribution to the scattering amplitudes [see Eq. (4)]. The two CG coefficients in Eq. (4) ensure that \( m'_j = m_j - m' \). Consequently, the scattering amplitudes can be written as \( e^{im'_j\phi} \) times a \( \theta \)-dependent part:

\[ f_{avjm_1\rightarrow\alpha'v'j'm_j}(\theta,\phi) = e^{i(m_j-m'_j)\phi} f_{avjm_1\rightarrow\alpha'v'j'm_j}(\theta)| \times e^{i\xi_{avjm_1\rightarrow\alpha'v'j'm_j}(\theta)} \]  

(6)

The products of the two scattering amplitudes in Eq. (5) are then proportional to \( e^{i(m_j-m'_j)\phi} \). Inserting Eq. (6) into Eq. (5) gives the DCS for a final state as:

\[ \sigma_{s\rightarrow\alpha'v'j'm_j}(\theta,\phi) = \sigma_{s\rightarrow\alpha'v'j'm_j}^{\text{coh}}(\theta,\phi) + 2 \cos(\eta) \sin(\eta) \times |f_{avjm_1\rightarrow\alpha'v'j'm_j}(\theta)| \times |f_{avjm_2\rightarrow\alpha'v'j'm_j}(\theta)| \times \cos((m_1-m_2)\phi + \Delta\xi(\theta) + \beta) \]  

(7)

where \( \Delta\xi(\theta) = \xi_{avjm_1\rightarrow\alpha'v'j'm_j}(\theta) - \xi_{avjm_2\rightarrow\alpha'v'j'm_j}(\theta) \) is the difference in the phase of the scattering amplitudes. The DCS for a specific final arrangement \( \alpha' \), discussed below, is obtained by summing over all vibrational states in this arrangement:

\[ \sigma_{s\rightarrow\alpha'}(\theta,\phi) = \sigma_{s\rightarrow\alpha'}^{\text{coh}}(\theta) + 2 \cos(\eta) \sin(\eta) F_{s\rightarrow\alpha'}(\theta) \times \cos((m_1-m_2)\phi + \xi_{s\rightarrow\alpha'}(\theta) + \beta). \]  

(8)

where \( F_{s\rightarrow\alpha'}(\theta) \) and \( \xi_{s\rightarrow\alpha'} \) are, respectively, the magnitude and the phase of \( \sum_{\alpha'v'j'm_j} f_{avjm_1\rightarrow\alpha'v'j'm_j}(\theta,\phi) f_{avjm_2\rightarrow\alpha'v'j'm_j}(\theta,\phi) \).

Equation (8) provides the central result of this work, which gives the DCS in terms of the scattering amplitude and the control parameters \( \eta \) and \( \beta \) of the initial coherent superposition of the reactant molecule’s rotational states [1]. Below, we expose the \( \theta \) dependence of the cross section via the amplitude \( A \), defined as

\[ A(\eta,\theta) = 2 \cos(\eta) \sin(\eta) F_{s\rightarrow\alpha'}(\theta) \]  

(9)

Given an initial superposition state [Eq. (1)], control can be affected by varying the \( \eta \) and \( \beta \) parameters. Note that several structural features of the interference term are universal, i.e. independent of the system under consideration. These include the \( e^{i(m_j-m'_j)\phi} \) dependence on \( \phi \), the role of \( \beta \) as a phase in the DCS, and the dependence on \( \eta \) through \( \cos(\eta) \sin(\eta) \). Below, we examine the case of a symmetric superposition (\( \eta = \pi/4 \),
which gives the maximum value of $\cos(\eta)\sin(\eta)$, and set $\beta = 0$ since variations in $\beta$ just correspond to a shift in phase of the interference term. We emphasize below the $\phi$ dependence of the cross sections because it is a unique signature of quantum interference contribution to the scattering. The extent of this contribution can be quantified via the visibility $V(\theta)$ manifest here as the difference between the maximum and minimum DCSs as a function of $\phi$, scaled by the sum of both

$$V(\theta) = \frac{\sigma_{s=a'v''m''}^{\max}(\theta, \phi) - \sigma_{s=a'v''m''}^{\min}(\theta, \phi)}{\sigma_{s=a'v''m''}^{\max}(\theta, \phi) + \sigma_{s=a'v''m''}^{\min}(\theta, \phi)}. \quad (10)$$

From Eqs. (8) and (9), we obtain the visibility as the ratio $A(\theta)/\sigma_{s=a''v''m''}^{\alpha \rightarrow \alpha}(\theta)$. Indeed, the extent to which coherent control is significant is dictated by the relative magnitude of the amplitude $A$ and the incoherent contributions, i.e. by the visibility $V$ of the interference fringes. For the case of two pathways, $V$ satisfies \[\|\mathcal{P}(\theta)\|^2 + V(\theta)^2 \leq 1, \quad (11)\]
an expression of wave-particle duality, with $V$ measuring the wave-like behavior and $\mathcal{P}(\theta)$ is the path distinguishability. The highest value for the visibility $V$ is then 1, corresponding to a situation where the two pathways are completely indistinguishable. The closer it is to unity, the greater the contribution of the interfering indistinguishable pathways to the scattering.

Note that the positivity of the DCS implies that $A \leq \sigma_{s=a''v''m''}^{\alpha \rightarrow \alpha}(\theta)$, which is consistent with the unitary limit for the visibility.

We now apply the methodology developed above to explore the possibility of controlling cold chemical reactions $F + H_2 \rightarrow HF + H$ and $F + HD \rightarrow H + DF$ and $D + HF$. Recent experimental advances in preparing coherent superpositions of rotational states of $H_2$ and in reactive scattering of $F + H_2$ at 11 K indicate the feasibility of an experiment (the first coherent control experiment of reactive scattering) of the kind motivated by the results below. The reaction DCSs are computed using Eqs. (9) parametrized by the $S$-matrix elements obtained via a numerically exact time-independent quantum reactive scattering approach (see the Supplemental Material for further details). After, for a specific arrangement, we summed over all rovibrational states in this arrangement. Similar control results were obtained at 1 K. We note that while the Stark-Werner PES used here is known to overestimate the true $F + H_2$ reaction rate by a factor of $\leq 3$ at 11 K, it does provide a qualitatively correct picture of this tunneling-dominated reaction, and can therefore be used to establish qualitative trends in controlling low-temperature reaction rates, the main goal of this work.

We consider two different $m$-superpositions of the magnetic sublevels of the first excited rotational state ($j = 1$) of the vibrational ground state ($v = 0$) of either ortho-$H_2$ or HD. The first superposition, between $m_1 = -1$ and $m_2 = 0$, is denoted -1/0 and the second, between $m_1 = -1$ and $m_2 = +1$, is denoted -1/+1.

The calculated DCS for the $F + H_2(-1/0) \rightarrow HF + H$ reaction is shown in Fig. (a) as a function of $\theta$ and $\phi$. Although the interference contribution affects both the dependence on $\theta$ and $\phi$, the explicit $\phi$ dependent signature of interference at the $\theta$ value, for which the DCS is maximal, (here, $\theta = 0.65 \pi$), is shown in Fig. (b). The $\phi$ dependence of the DCS is seen to oscillate about the direct term, with a frequency equal to the difference of the projections of magnetic sublevels in the superposition, as anticipated from Eq. (8). A simple computation gives $V = 0.54$, whose square, $\approx 0.33$, constitutes a considerable interference contribution.

Whereas the functional form (albeit not the magnitude) of the $\phi$ dependence of the DCS given by $\exp[i(m - m')\phi]$ is universal, the $\theta$ dependence of the amplitude $A(\theta)$, of the incoherent contribution (8) and therefore of the visibility (10) are system dependent. Figure 2(a) shows the $\theta$ dependence of the visibility for the $F + H_2$ superpositions -1/0 and -1/+1. No clear advantage of one superposition over the other appears, with the maximal visibility $V_{\max} = 0.54$. The interference clearly vanishes in the forward and backward directions, where the scattering amplitudes are zero.

Similarly to the amplitude $A(\theta)$, the phase $\xi_{s=a''v''}(\theta)$ of DCS oscillations (5), given by the difference of phases of scattering amplitudes, is system-dependent. The phase is particularly sensitive to the presence of a symmetry between the different components of the superposition (1). For example, the two states of the superposition -1/+1 are related by the time-reversal symmetry and the phase $\xi$ of the DCS oscillations is zero for all $\theta$. Inversely, for the superposition -1/0, we observe a $\theta$-
dependent phase $\xi(\theta)$ of the DCS oscillations [see, e.g., Fig. 1(b)]. Thus, by measuring the angular dependence of the DCS for molecules reacting in quantum superposition states, it is possible to infer information not only about the magnitude, but also about the phase of the scattering amplitudes.

Control over reactive $F + HD$ scattering presents additional challenges and opportunities, insofar as successful control should be able to selectively distinguish between the $H + FD$ and $D + HF$ product channels. Figure 3 shows the results for controlling the individual DCSs for each of the product channels with the initial superposition $-1/+1$. Extensive $\phi$-dependences of the DCSs are evident in a wide range, from 3.6 to 16.5, clearly demonstrating the different product channels are evident with large visibility, $V = 0.81$ for the $H + DF$ channel, and 0.69 for the $H + FD$ channel. Note that the DCS is larger for $D + HF$ than for the $DF + H$ channel, a consequence of larger tunneling for the hydrogen atom.

The vanishing of the phases $\xi(\theta)$ for both of the product channels [see Figs. 3(b) and (d)] due to the time-reversal symmetry implies that the selectivity in the control over these channels can only arise from differences in the $\theta$-dependence of the visibilities $V$ shown in Fig. 2(b). We observe that the best selectivity is expected for $\theta = \pi/4 - \pi/2$ rather than at the maximum of the visibilities, where the $\theta$-dependence is similar for both of the product channels. To further reveal this selectivity, we plot in Fig. 4 the differential branching ratio, the ratio of the DCSs $\sigma(\theta, \phi)$ for the two product channels $HF + D$ and $DF + H$. The $\phi$-dependence of the ratio shown in Fig. 4(b) is seen to vary over a wide range, from 3.6 to 16.5, clearly demonstrating interference-based product channel selectivity with interference quantified at $V = 0.64$. We note that since the $\phi$-dependence of the $HF+D/DF+H$ branching ratio is given by the ratio of two in-phase oscillations, it is not symmetric about the ratio of incoherent contributions shown by the horizontal line in Fig. 4(b).

In summary, we have computationally demonstrated extensive quantum-interference based coherent control over low-temperature differential scattering in the $F + H_2$ and $F + HD$ chemical reactions using an approach that is experimentally feasible. Quantum interference control is manifest explicitly in a signature experimental observable, the non-zero $\phi$ dependence of the DCS. The successful experimental demonstration of this control would open the entire class of scattering processes to coherent control.

The proposed control scenario is completely general and can be extended to all reactive scattering processes of interest to ultracold chemistry. Significantly, this scheme allows for controlling chemical reactions that are not readily susceptible to traditional electric and magnetic field control, such as those involving homonuclear alkali-metal dimers and $H_2$, the most abundant molecule in the Universe and one of the very few molecules, whose reaction dynamics can be studied theoretically with spectroscopic accuracy. Furthermore, because $\phi$-dependent interference is observed only if the atom-molecule PES is anisotropic, this dependence provides direct insight into the angular dependence of the PES. Measuring the $\phi$-dependent DCS in a coherently controlled cold scattering experiment could, therefore, serve as a useful probe of the interaction anisotropy in atom-molecule reactive scattering.

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FIG. 4. Differential branching ratio (HF + D)/DF + H) of the DCS between the reactive channels for F+HD with the initial superposition 1/1. (a) 3D surface plot of the $\theta$- and $\phi$-dependences of the DCS. (b) $\phi$-dependence of the branching ratio at a fixed $\theta = 0.47\pi$. The differential branching ratio is plotted in blue while the incoherent contribution is plotted in red.

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