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I. INTRODUCTION

Detailed knowledge of molecular interactions is crucial for the understanding of a wide variety of environments, ranging from combustion to regions of star formation. The study of rotationally inelastic collisions is a powerful method to probe molecular interactions and the potential energy surfaces (PESs) that represent these interactions. An accurate method to test the quality of PESs is to compare the integral cross sections (ICSs) and differential cross sections (DCSs) obtained from molecular scattering calculations with the cross sections measured in advanced scattering experiments.

In recent years, a variety of scattering experiments between a molecule and rare gas (Rg) atoms have been performed with very high precision. For benchmark systems such as NO–Rg, exceptional levels of detail have been accomplished experimentally, resulting in an advanced understanding of energy transfer in these systems. These include alignment and orientation effects, non-adiabatic dynamics, and quantum phenomena at low energies.

Energy transfer in atom–molecule inelastic scattering mainly manifests itself as a transformation from kinetic to molecular rotational energy. By contrast, molecule–molecule interactions offer additional possibilities for energy transfer, such as vibration–vibration and rotation–rotation energy transfer. The additional internal degrees of freedom of the molecular scattering partner makes theoretical descriptions of bimolecular collisions far more complex than atom–molecule collisions. Experimentally, molecule–molecule collisions are also challenging, as it is difficult to prepare both molecules state selectively and to probe excitation in both products. To date, a detailed understanding of energy transfer in bimolecular systems is therefore lacking in most cases.

A number of state-to-state inelastic scattering experiments have been performed that involve collisions between two molecular partners. Again, the NO radical was often used in these studies because of its high relevance, its open-shell character, and experimental ease in production and detection. Westley et al. measured the angular distributions for rotationally inelastic collisions of NO with D₂ and He in a crossed molecular beam setup combined with velocity map imaging (VMI) techniques. The DCSs of rotationally...
excited NO for both spin–orbit (SO) conserving and SO-changing collisions were extracted from the experimental data. Rotational rainbows were observed, and the rainbow angle was found to be independent of the SO-state for a given $\Delta j$. Compared to the rainbow position in NO–He collisions, the rainbow angle in NO–D$_2$ collisions was smaller for a given $\Delta j$. Using a hexapole state selector, Gijsbertsen et al. determined the DCSs for inelastic collisions of D$_2$ with fully state-selected NO. The effect of parity changing and conserving collisions on the DCSs was investigated. The rotational rainbow angle for parity changing transitions was found to be larger than the one for parity conserving transitions. Molecular collision experiments between electronically excited NO ($A^2\Sigma^+$) and D$_2$ have been reported as well, focusing on DCSs and rotational angular momentum polarization moments. In general, experimentally obtained ICSs and DCSs for NO–H$_2$ inelastic collisions are in good agreement with the calculated cross sections based on $ab initio$ NO–H$_2$ PESs. Several experiments were performed to study collisions of NO with the molecular collision partners N$_2$ and O$_2$ as well.

The resolution in this type of experiments can be significantly enhanced using the Stark deceleration technique, which has also been recently applied to studies of bimolecular scattering, de Jongh et al. observed differences in diffraction oscillations in the DCS between NO + He and NO + ortho-D$_2$ collisions, reflecting the larger size of D$_2$ compared to He as a scattering target. Gao et al. resolved rotational product–pair correlations for inelastic collisions between NO and O$_2$ molecules. The correlated cross sections showed surprisingly good agreement with quantum scattering calculations using $ab initio$ NO–O$_2$ potential energy surfaces. The observations showed that the well-known energy-gap law that governs atom–molecule collisions does not generally apply to bimolecular excitation processes. They also revealed a propensity rule for the vector correlation of the product angular momenta. A similar experimental approach was used to study pair-correlations in collisions between D$_2$ molecules and Stark decelerated ND$_3$ molecules. Rotational excitation of D$_2$ from $j = 0$ to $j = 2$ and rotational quenching of D$_2$ from $j = 2$ to $j = 0$ were observed simultaneously.

Up to now, the energy transfer processes studied in bimolecular inelastic collisions primarily originate from the transformation of kinetic energy to molecular rotational energy. The study and observation of other energy transfer processes such as rotation–rotation energy transfer has remained elusive. Here, we present studies of rotational energy transfer processes in collisions between NO ($X^2\Sigma_g^+, j = 1/2$) radicals and D$_2$ molecules with the combination of Stark deceleration and velocity map imaging at collision energies of 750 cm$^{-1}$ and 100 cm$^{-1}$. The state-to-state scattering images of NO radicals for both SO-conserving and SO-changing transitions were accurately measured. Both rotational excitation ($j = 0 \rightarrow 2$) and rotational de-excitation ($j = 2 \rightarrow 0$ and $j = 3 \rightarrow 1$) of D$_2$ molecules was observed, and the dependence of the cross sections on the final rotational and SO-state of NO was studied. At the lowest energy probed, we observe direct rotation–rotation energy transfer, i.e., the released rotational energy of the D$_2$ molecule was directly transferred to the rotational motion of the NO radical. The experimental results are in excellent agreement with the results obtained from quantum coupled-channels calculations based on a high-quality NO–D$_2$ interaction potential. The observed trends in the scattering cross sections are rationalized in terms of the NO–D$_2$ quadrupole–quadrupole interaction.

II. EXPERIMENTAL AND THEORETICAL METHODS

A. Experimental setup

The experiments were performed in two different crossed molecular beam machines to study NO–D$_2$ collisions at two different collision energies. Both machines include a Stark decelerator to manipulate the NO radicals and velocity map imaging (VMI) detector to record the scattered products. They are schematically shown in Figs. 1(a) and 1(b), and we refer to these instruments as the high and low collision energy setup, respectively. The detailed description of the Stark decelerator and VMI detector has been given previously, here, we only give a brief summary.

In the high collision energy setup, a pulsed supersonic beam of 5% NO seeded in Kr at a backing pressure of 1 bar was expanded through a Nijmegen Pulsed Valve (NPV). After passage through a 3 mm diameter skimmer, the beam entered a 2.6-m-long Stark decelerator. A packet of NO ($X^2\Pi_{1/2}, j = 1/2$) radicals was selected by the Stark decelerator with a mean velocity of 440 m/s. Subsequently, the packet of NO was scattered by a pulsed beam of neat D$_2$ at an intersection angle of 90°, which resulted in a collision energy of 750 cm$^{-1}$. The D$_2$ beam was produced using a commercially available jordan valve. After collisions with the D$_2$ beam, NO radicals were state-selectively ionized through a (1 + 1′) resonance-enhanced multi-photon (REMPI) scheme with two dye lasers. The NO ions were subsequently collected by the VMI ion optics, which induced a homogeneous electric field of 35.1 V/cm in the ionization region.

The experiment was repeated in the low collision energy setup. Here, a mixture of 5% NO seeded in 65% Ne and 30% Ar, with a typical backing pressure of 1 bar, was expanded through a NPV to generate a NO supersonic beam. The NO radicals with a mean velocity of 760 m/s were manipulated through the Stark decelerator and then guided by a hexapole toward the interaction region. The neat D$_2$ molecular beam was produced at a 5 bar backing pressure using a commercial Even–Lavie (EL) valve cooled to 180 K. The packet of NO intersected with the D$_2$ molecular beam at a 10° angle of incidence, resulting in a collision energy of 100 cm$^{-1}$.

The design of the VMI optics in the low energy setup is different from the one used in the high energy setup. Consequently, the electric field of the VMI optics in the ionization region amounted to 244.7 V/cm.

The rotational energy level diagrams of the NO radical and the D$_2$ molecule are shown in Fig. 2. The Stark decelerator ensures that all NO radicals that exit the decelerator are in the upper A-doublet component of the $X^2\Pi_{1/2}, j = 1/2$ rotational ground state. The rotational state distribution of the reagent D$_2$ beam strongly depends on the temperature and type of valve that is used and is therefore different in the two setups. In the high-energy setup, the room-temperature Jordan valve results in a relatively high rotational temperature, and various rotational states are populated that can contribute to the scattering results. The state population of the D$_2$ beam was measured using (2 + 1) REMPI via the $E_1^2 \Sigma_g^+ \rightarrow X^2\Pi_{1/2}$ transition. In order to determine the state distribution as accurately
FIG. 1. Scheme of the experimental setups to reach high (a) and low (b) collision energies. (a) A pulsed supersonic beam of NO radicals was passed through a 2.6 m long Stark decelerator. After exiting the Stark decelerator, NO radicals were scattered with a pulsed neat D$_2$ beam from the Jordan valve at an intersection angle of 90°. The scattered NO radicals were state selectively ionized through a (1 + 1)$'$ REMPI scheme with two dye lasers and then detected with VMI ion optics. (b) A mixture of 5% NO seeded in 65% Ne and 30% Ar was expanded through a Nijmegen pulsed valve. The NO radicals with a mean velocity of 760 m/s were selected by the Stark decelerator and then guided by a hexapole. The neat D$_2$ molecular beam was produced with a cryogenic valve. The packet of NO was scattered with the D$_2$ beam at an intersection angle of 10°. Only the last sections of the Stark decelerators are shown.

as possible, only each REMPI peak around the resonant wavelength was scanned, avoiding the effect of large laser power fluctuations. From the REMPI spectrum (see Fig. 3), we estimate that the population of D$_2$ molecules in the $j = 0$–3 levels approximately amounts to 40%, 28%, 28%, and 4%, respectively. In the low energy setup, the cryogenic Even–Lavie valve resulted in a lower rotational temperature. Here, the population in the $j = 2$ level of D$_2$ amounted to about 20%.

FIG. 2. Rotational energy levels diagram of the NO radical (left) and D$_2$ molecule (right). $F_1$ and $F_2$ represent the different SO-manifolds within the $X'\Sigma^+$ electronic ground state of NO. The $\Lambda$-doublet splitting of each rotational level in NO is exaggerated for clarity. The rotational quantum numbers for ortho-D$_2$ and para-D$_2$ are denoted with $j_{\text{ortho}}$ and $j_{\text{para}}$, respectively.

FIG. 3. Experimentally measured REMPI spectrum of the D$_2$ molecular beam produced from a room-temperature Jordan valve. Only each REMPI peak around the resonant wavelength was scanned.
**B. Scattering calculations**

Coupled-channels scattering calculations were performed to calculate the cross sections for inelastic NO-D₂ collisions at collision energies of 750 cm⁻¹ and 100 cm⁻¹. The technical details of our scattering program can be found elsewhere. The rotational constants of NO and D₂ were taken to be 1.6961 cm⁻¹ and 29.9024 cm⁻¹, respectively. We used a body-fixed (BF) coordinate frame with its z-axis along the vector \( \mathbf{R} \) that connects the centers of mass of NO and D₂. The Hamiltonian expressed in BF Jacobi coordinates is (in atomic units with \( \hbar = 1 \))

\[
\hat{H} = \hat{H}_{\text{NO}} + \hat{H}_{\text{D₂}} = \frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{\hbar^2}{2\mu R^2} \left( \frac{\partial^2}{\partial \phi^2} + \frac{2}{R} \frac{\partial}{\partial R} R \frac{\partial}{\partial \phi} \right) J^2 + \hat{\mathcal{V}}(R, \zeta_{\text{NO}}, \zeta_{\text{D₂}}),
\]

(1)

where \( \hat{H}_{\text{NO}} \) and \( \hat{H}_{\text{D₂}} \) are the monomer Hamiltonians, \( \mu \) is the total mass of the complex, \( R \) is the length of the vector \( \mathbf{R} \), \( J \) is the total angular momentum operator, and \( \hat{\mathcal{V}} \) is the sum of the monomer angular momentum operators. The angles \( \zeta_{\text{NO}} = (\ell_{\text{NO}}, \phi_{\text{NO}}) \) and \( \zeta_{\text{D₂}} = (\ell_{\text{D₂}}, \phi_{\text{D₂}}) \) are the polar angles of the monomers in the BF frame.

The open-shell molecule NO has a twofold degenerate \( \Pi \) ground state with electronic angular momentum projections \( \Lambda = \pm 1 \) on the N–O bond axis. We use the \( \textit{ab initio} \) diabatic interaction potentials calculated for NO–H₂ in Ref. 26, which can be expanded in functions depending on the BF angles,

\[
\langle \Lambda^j | \mathcal{V}(R, \theta_{\text{NO}}, \theta_{\text{D₂}}, \phi) | \Lambda^j \rangle = \sum_{L_{\text{NO}}, L_{\text{D₂}}} \sum_{M} v_{L^0_{\text{NO}}, L_{\text{D₂}}, L}^{j_0, j} (R) \sum_{L} (-1)^{L_{\text{NO}} + L_{\text{D₂}} + L} \times \frac{L_{\text{NO}} L_{\text{D₂}}}{M} D^L_{M,-M} (\phi_{\text{NO}}, \theta_{\text{NO}}, 0)^* \times c_{L^0_{\text{NO}}, L_{\text{D₂}}, L}^{j_0, j} (\theta_{\text{D₂}}, \phi_{\text{D₂}}). \tag{2}
\]

with the dihedral angle \( \phi = \phi_{\text{NO}} - \phi_{\text{D₂}} \) and the \( R \)-dependent expansion coefficients \( v_{L^0_{\text{NO}}, L_{\text{D₂}}, L}^{j_0, j} (R) \) are Wigner D-matrix elements, \( C^L_\Lambda (\theta, \phi) \) are Racah-normalized spherical harmonics, and the expression in round brackets is a Wigner 3-j symbol. The terms in this expansion for which \( L = L_{\text{NO}} + L_{\text{D₂}} \) correspond to the long range to the electrostatic interactions between the \( 2^\text{ixo} \)-pole of NO and the \( 2^\text{iro} \)-pole of D₂. All the radial expansion coefficients are real-valued, and the diagonal diabatic potentials \( (1 | \mathcal{V} | 1) \) and \( (1 | \mathcal{V} | -1) \) are equal. The off-diagonal diabatic potentials \( (1 | \mathcal{V} | 1) \) and \( (1 | \mathcal{V} | -1) \) are each other’s complex-conjugate so that the \( 2 \times 2 \) matrix of diabatic potentials is Hermitian. The BF diabatic channel basis in the coupled channels calculations for NO–D₂ collisions is described in detail in Ref. 39. The expression for the matrix elements of the potential in the diabatic basis is given in the Appendix of the present paper. In our scattering calculations, which can be carried out independently for each value of the total angular momentum \( J \) and each overall parity, we included total angular momenta up to \( J = 80.5 \). The channel basis contained the rotational states of NO and D₂ up to \( J_{\text{NO}} = 15.5 \) and \( J_{\text{D₂}} = 4 \). The largest number of channel functions amounts to 8130. The radial propagation grid ranges from \( R = 4.0a_0 \) to \( 45a_0 \), with a grid spacing of 0.1\( a_0 \). Scattering calculations were performed at the experimental collision energies of 750 cm⁻¹ and 100 cm⁻¹ for different initial rotational states of NO \([J_{\text{NO}}(1/2, f)]\) and D₂ \([j_{\text{D₂}} = 0, 1, 2, 3]\). For the interpretation of the results, the calculations were repeated with the exclusion of specific coupling terms in the potential in order to find out how they affect the cross sections.

**C. Theoretical discussion**

Figure 4 shows the most important radial expansion coefficients of the interaction potential. We define the label \( K_{\text{NO}} = \Lambda - \Lambda' \) and \( \Pi \) and from here on denote the expansion coefficients in Eq. (2) by \( v_{L_{\text{NO}}, K_{\text{NO}}, L_{\text{D₂}}, L} (R) \). It is observed that for \( K_{\text{NO}} = 2, L_{\text{D₂}} = 2, L = 4 \), both the diagonal expansion coefficients with \( K_{\text{NO}} = 0 \) and the off-diagonal expansion coefficients with \( K_{\text{NO}} = \pm 2 \) are dominant. This is because these terms correspond in the long range to the interactions between the quadrupole moments of NO and D₂. The quadrupole moments of closed-shell linear molecules only have components with \( K = 0 \), but for NO with its \( \Pi \) ground state, the quadrupole also has components with \( K = \pm 2 \), which are off-diagonal between the substates with \( \Lambda = \pm 1 \). The terms with \( L_{\text{NO}} = 1, L_{\text{D₂}} = 2, L = 3 \) that contain the dipole–quadrupole interactions are smaller because NO has only a small dipole moment and the dipole has no off-diagonal component with \( K_{\text{NO}} = \pm 2 \).

From the matrix elements of the potential over the channel basis in Eq. (A1), we can derive which expansion terms of the interaction potential contribute to a specific inelastic collision process. The SO-states of NO are labeled with the quantum number \( \Omega = \Lambda + \Sigma \), with \( \Sigma = \pm 1/2 \) being the axial component of the spin \( S = 1/2 \). SO-changing transitions from SO-states with \( \Omega = \pm 1/2 \) to states with \( \Omega = \pm 3/2 \) that are very different in energy (see Fig. 2) are caused almost exclusively by the off-diagonal interaction potentials that couple the...
states with $\Lambda = \pm 1$. This puts limitations on the dominant coupling terms in the potential, as there exists no off-diagonal dipole-quadrupole coupling term. Therefore, the SO-changing transitions are described by higher coupling terms such as the off-diagonal quadrupole coupling term. Consequently, the SO-changing transitions in the potential, as there exists no off-diagonal dipole–quadrupole couplings with $L_{\text{NO}} = 2, L_D = 2, L = 4$, and $K_{\text{NO}} = \pm 2$.

III. SIMULATIONS

Comparison of our experimental results with theory proceeds through the comparison of the experimentally obtained scattering images with simulated images based on the theoretical state-to-state integral and differential cross sections. The simulation and analysis procedures have been explained in detail elsewhere.

For the present work, however, there is an additional complication related to parity mixing of rotational levels due to the electric field in the interaction region that is induced by the VMI optics. This field is small but causes a mixing of the field-free wave functions representing the upper and lower $\Lambda$-doublet levels of the NO radical of $f$ and $e$ parity, respectively. Consequently, the field-free selection rules for optical transitions do not apply anymore when the NO radicals are probed with the detection laser, i.e., post-collision populations in the upper and lower $\Lambda$-doublet levels are not detected independently anymore. Since the DCS for collisional excitation into the $e$ or $f$ component of a given rotational level can be different, this mixing due to the electric field must be taken into account when analyzing the scattering images. As we will show below, this effect is particularly relevant for collision-induced excitation into the $F_2$ manifold of NO.

To quantify the parity mixing between two $\Lambda$-doublet states, we illustrate the Stark effect. The energy spacings between the rotational energy levels of the NO radical are much larger than the Stark energy, so we can neglect the interaction between rotational levels with different values of $j$. The Stark shift induced by the interaction between two $\Lambda$-doublet components for a given rotational level follows from the Stark energy matrix

$$
\begin{pmatrix}
0 & Q \\
Q & E_{\text{Stark}}
\end{pmatrix}
$$

In this matrix, the field-free energy of the lower $e$ state is set to zero, $E_{\text{Stark}}$ is the field-free energy of the upper $f$ state, and the Stark coupling $Q$ is given by

$$
Q = \frac{\mu \cdot E \cdot \Omega_{\text{eff}}}{j(j+1)},
$$

where $\mu$ is the magnitude of the molecular electric dipole moment (0.159 D for NO), $E$ is the strength of the electric field, the quantum number $M$ denotes the projection of the rotational angular momentum $j$ onto the external axis defined by the electric field, and $\Omega_{\text{eff}}$ denotes the projection of $j$ onto the internuclear axis of the NO radical. The value of $\Omega_{\text{eff}}$ depends on the amount of SO-mixing between the $F_1$ and $F_2$ manifolds but takes the values 1/2 and 3/2 for the $(j = 1/2, F_1)$ and $(j = 3/2, F_2)$ ground states, respectively.

By calculating the eigenvalues of the Stark energy matrix (3), the Stark energies are found to be

$$
E_{\text{Stark}} = \frac{E_f}{2} \pm \sqrt{\left(\frac{E_f}{2}\right)^2 + Q^2}.
$$

Here, the plus and minus sign represent the Stark energies of the perturbed upper $f$ and lower $e$ states, respectively. Figure 5 shows the Stark shifts for both the $(j = 1/2, F_1)$ and $(j = 3/2, F_2)$ states of NO. The Stark shift in the $(j = 3/2, F_2)$ state is almost two times larger than the Stark shift in the $(j = 1/2, F_1)$ state for the same electric field.

In the presence of an external electric field, the wavefunction of NO will be a superposition of the field-free eigenfunctions $|j, \Omega, M, e\rangle$ and $|j, \Omega, M, f\rangle$. For the upper and lower $\Lambda$-doublet states, they are expressed as

$$
|j, \Omega, M, +\rangle = C_{11}|j, \Omega, f\rangle + C_{12}|j, \Omega, e\rangle,
$$

$$
|j, \Omega, M, -\rangle = C_{21}|j, \Omega, f\rangle + C_{22}|j, \Omega, e\rangle,
$$

respectively, with the mixing coefficients given by

$$
C_{11} = \left(\frac{E_{\text{Stark}}^2}{Q^2 + E_{\text{Stark}}^2}\right)^{1/2},
$$

$$
C_{12} = \left(\frac{Q^2}{Q^2 + E_{\text{Stark}}^2}\right)^{1/2},
$$

$$
C_{21} = \left(\frac{Q^2}{Q^2 + E_{\text{Stark}}^2}\right)^{1/2},
$$

$$
C_{22} = \left(\frac{E_{\text{Stark}}^2}{Q^2 + E_{\text{Stark}}^2}\right)^{1/2}.
$$

The parity mixing ratios can be directly obtained from the square of the coefficients, which are calculated for both setups with the known values for the electric field strength present in the interaction region of the colliding beams.

![Figure 5](image-url)
For rotational states in the $F_1$ manifold, the $\Lambda$-doublet splittings are relatively large such that the parity mixing in these levels is less than 0.01% under all our experimental conditions. Therefore, the parity mixing can safely be neglected in the simulations for SO-conserving collisions. By contrast, as also illustrated in Fig. 5, the $\Lambda$-doublet splitting of the rotational levels in the $F_2$ manifold is about three hundred times smaller than in the $F_1$ manifold.\textsuperscript{4,44} The smaller $\Lambda$-doublet splitting results in a relatively strong mixing of the $\Lambda$-doublet states at low electric field strengths and therefore in a higher degree of parity mixing in our VMI region. In the simulations for SO-changing collisions, the parity mixing should therefore be included.

In our experiment, the incoming parent NO beam is almost perfectly state-selected with the help of the Stark decelerator. After the NO radical is scattered into a rotational state of the $F_2$ manifold, the outgoing scattered NO radical is populated in a mixed parity manifold. The detection dye laser has a bandwidth of about 0.08 cm$^{-1}$ that is much broader than the sum of $\Lambda$-doublet splitting and Stark shift in the electric field of the VMI optics. The mixing of the $\left| j, \Omega, f \right>$ and $\left| j, \Omega, e \right>$ wavefunctions causes a breakdown of the field-free selection rules for optical dipole allowed transitions such that the scattering signal can originate from population in both the $\left| j, \Omega, M, + \right>$ and $\left| j, \Omega, M, - \right>$ states.

The parity mixings for different rotational states in the electric field of 244.7 V/cm pertaining to the low energy setup are given in Table I. A tilde over the coefficient is used to represent the average over the different possible $M$ values. It is seen that for low values of $j$, the wavefunctions of the upper and lower $\Lambda$-doublet components are almost completely mixed in the presence of the VMI field. For higher $j$, the mixing becomes smaller. The parity mixings in the electric field of 35.1 V/cm present in the high energy setup are much smaller. They amount to 24% for the $j = 3/2$, $\Omega = 3/2$ state and quickly become negligible for higher rotational states.

We further assume that the DCS for collision induced excitation into the $\left| j, \Omega, M, + \right>$ or $\left| j, \Omega, M, - \right>$ states is identical to the zero-field DCSs, i.e., we assume that the effect of the small electric field in our experiment exclusively affects the state-selective detection of the scattered products but not the inherent collision dynamics. Furthermore, when probing a given rotational level in our experiments, we assume that molecules in different $M$ components are detected with equal probability. Under these assumptions, the DCS that is needed as input to the simulations to compare to our experimental results is given by

\begin{equation}
\text{DCS}(\left| j, \Omega, M, + \right>) = \tilde{C}_{11} \text{DCS}(\left| j, \Omega, f \right>) + \tilde{C}_{21} \text{DCS}(\left| j, \Omega, e \right>),
\end{equation}

\begin{equation}
\text{DCS}(\left| j, \Omega, M, - \right>) = \tilde{C}_{12} \text{DCS}(\left| j, \Omega, f \right>) + \tilde{C}_{22} \text{DCS}(\left| j, \Omega, e \right>).
\end{equation}

**IV. RESULTS**

In this section, we present the experimental scattering images together with the simulated images based on theoretically predicted DCSs. The results pertaining to high and low collision energies are presented in Secs. IV A and IV B, respectively.

**A. Scattering at a collision energy of 750 cm$^{-1}$**

In Fig. 6, the experimental and simulated state-to-state scattering images are shown for both SO-conserving (left panel) and SO-changing collisions (right panel) for a collision energy of 750 cm$^{-1}$. All images are presented such that the relative velocity vector is aligned horizontally and the forward scattered direction is found on the right. Some images are masked around the forward direction with a small black block to cut out the intense beam spot measured from the parent NO packet.

For the SO-conserving transitions, in some images, three distinct rings are clearly observed, such as the $3/2e$, $5/2f$, and $7/2f$ states. For the other states, additional rings are unclear visually because of the low signal-to-noise. On the basis of energy conservation and the relation between the magnitude of velocity and radius, the different rings can be assigned to different transitions in the $D_2$ molecule. The middle most intense ring corresponds to the elastic $D_2$ scattering channel in which the quantum state of the $D_2$ molecule remains unchanged during the collision. The inner much weaker ring corresponds to the inelastic $D_2$ ($j_{D_2} = 0 \rightarrow 2$) excitation channel. In the molecular excitation process, the radius of this ring becomes smaller because of the increased internal energy of the collision system, which is obtained from the kinetic energy. Inversely, as the internal energy of the collision partner is released to kinetic energy in a molecular de-excitation process, the radius of the ring will be larger. Therefore, the outer weak ring in the images pertains to the inelastic $D_2$ ($j_{D_2} = 2 \rightarrow 0$) de-excitation channel. It is noted that the $j_{D_1} = 1 \rightarrow 3$ excitation and the $j_{D_1} = 3 \rightarrow 1$ de-excitation channels are not observed.

Compared to the SO-conserving transitions, the images for the SO-changing transitions show different trends. The most intense ring remains to be the elastic $D_2$ scattering channel, but two rather intense outer rings are visible for the $3/2e$, $5/2e$, and $7/2e$ states. These outer rings can be assigned to the de-excitation channels $j_{D_2} = 2 \rightarrow 0$ and $j_{D_2} = 3 \rightarrow 1$, respectively. These outer rings become progressively weaker for higher rotational levels of NO. In comparison to SO-conserving collisions, the de-excitation signals in the SO-changing collisions are much stronger visually. This can also be quantitatively compared in the radial distributions of the images for both SO-manifolds *vide infra*. The $j_{D_2} = 0 \rightarrow 2$ excitation channel of $D_2$ is so weak that it can hardly been seen, even though the

| $j, \Omega = 3/2$ | $|j, \Omega, M, +\rangle$ | $|j, \Omega, M, -\rangle$ |
|-----------------|----------------|----------------|
| $\tilde{C}_{11}$ (%) | $\tilde{C}_{12}$ (%) | $\tilde{C}_{21}$ (%) | $\tilde{C}_{22}$ (%) |
| 3/2 | 55.0 | 45.0 | 45.0 | 55.0 |
| 5/2 | 71.3 | 28.7 | 28.7 | 71.3 |
| 7/2 | 89.1 | 10.9 | 10.9 | 89.1 |
| 9/2 | 97.0 | 3.0 | 3.0 | 97.0 |
| 11/2 | 99.2 | 0.8 | 0.8 | 99.2 |
| 13/2 | 99.8 | 0.2 | 0.2 | 99.8 |
| 15/2 | 99.9 | 0.1 | 0.1 | 99.9 |
collision energy is sufficient for this excitation process. Again, the \( j_D = 1 \rightarrow 3 \) excitation transition is not observed.

The experimental and simulated images are analyzed quantitatively by extracting the radial and angular scattering intensity distributions from the images, following a procedure as explained in detail elsewhere.\(^{27,28}\) Note here that the images of the \( 13/2e \) and \( 15/2f \) states for SO-changing transitions show a slight mismatch between experiment and simulation regarding intensity between the upper and lower halves of the images. Consequently, these images were normalized according to the scattering intensity found in the lower half part of the images. We speculate that this small mismatch originates from collision induced alignment effects, which are expected to become more important for excitation of NO into higher rotational levels.\(^{12,47}\) Collision induced alignment effects are beyond the scope of this article and will be neglected in the following discussion.

Figure 7 shows the radial scattering intensity distribution extracted from both the experimental and simulated scattering images, within an angular segment of the images near forward scattering. In these profiles, the vertical dashed lines indicate the position of the different rings corresponding to inelastic excitation (\( j_D = 0 \rightarrow 2 \)), elastic scattering (\( j_D = j_D \)), and inelastic de-excitation (\( j_D = 2 \rightarrow 0 \)) of \( \text{D}_2 \). In addition to these three transitions, for SO-changing transitions, a fourth one corresponding to the rotational de-excitation channel (\( j_D = 3 \rightarrow 1 \)) is visible at the outermost radius position with weak intensity.

From these radial distributions, it is clear that collisions in which \( \text{D}_2 \) scatters elastically is the dominant scattering process in all cases. However, compared to the elastic channels, rotational de-excitation of \( \text{D}_2 \) appears much stronger for SO-changing transitions than for SO-conserving transitions. The experimental radial profiles show excellent agreement with the corresponding simulated ones, both with respect to the position and the intensity of each peak. It is noted that for the \((11/2e, F_1)\) state, one can observe an additional peak adjacent to the \( \text{D}_2 \) elastic peak, which is absent in the simulation. This peak originates from an additional weak velocity ring that is also visible in the corresponding VMI image in Fig. 6, which is caused by a partially overlapped REMPI transition that probes the \((5/2f, F_1)\) final state of NO.\(^{27}\)

The experimental and simulated images are shown in Figs. 8 and 9 for the SO-conserving and SO-changing transitions, respectively. For the SO-conserving transitions, only the angular distributions of the ring pertaining to the \( \text{D}_2 \) elastic channels (\( j_D = j_D \)) are shown, as the excitation and de-excitation channels are too weak to extract the angular distributions. For the SO-changing transitions, the angular distributions are shown for both the \( \text{D}_2 \) (\( j_D = j_D \)) elastic channel and the \( j_D = 2 \rightarrow 0 \) rotational de-excitation channel.

The experimental distributions are in excellent agreement with the simulated ones, except for the \((5/2e, F_1), (7/2f, F_1)\), and \((9/2e, F_2)\) final states. For these states, a significant forward scattering component is observed in the experiment, which is not present in the simulation. A similar discrepancy between experiment and simulation has been observed for the \((5/2e, F_1)\) and \((7/2f, F_1)\) states in other collision systems involving the NO radical before,\(^{32}\) consistent with the findings reported here. The origin of this puzzling discrepancy is at present unknown, and we here will not further discuss it. For the
(13/2,e,F\textsubscript{2}) and (15/2,f,F\textsubscript{2}) transitions, the experimental angular distributions around the forward direction within the areas indicated by gray bars show a larger intensity than the simulated distribution. It is believed that this higher intensity is caused by the relatively large background near forward scattering due to the relatively large laser powers needed to record these weak transitions.

**B. Scattering at a collision energy of 100 cm\textsuperscript{-1}**

In NO–D\textsubscript{2} collisions at a collision energy of 750 cm\textsuperscript{-1}, the kinetic energy of the collision is sufficient to induce rotational and SO-excitations of NO. In collisions in which the D\textsubscript{2} molecule is deexcited from \( j_{D\textsubscript{2}} = 2 \) to \( j_{D\textsubscript{2}} = 0 \), an additional amount of 180 cm\textsuperscript{-1} is available. Transitions in NO can thus occur through transfer of kinetic to rotational energy and through the exchange of rotational energy alone. It is not clear what the partitioning is between these two processes. We therefore conducted additional scattering experiments at a collision energy of 100 cm\textsuperscript{-1}, well below the energetic threshold of 125 cm\textsuperscript{-1} for SO-excitation, i.e., SO-changing transitions are energetically forbidden for pure kinetic-to-rotation energy transfer processes.

Figure 10 shows the VMI images of NO scattered into various levels of the \( F\textsubscript{2} \) SO-manifold measured at a collision energy of 100 cm\textsuperscript{-1}, together with the simulated ones based on theory. For all images, the most intense ring with largest diameter corresponds to the rotational de-excitation of D\textsubscript{2} (\( j_{D\textsubscript{2}} = 2 \rightarrow 0 \)). In addition, for the (3/2,e,F\textsubscript{2}), (5/2,e,F\textsubscript{2}), and (7/2,e,F\textsubscript{2}) transitions, a small portion of the collision signal is present at the center of the scattering images, which is caused by direct kinetic-to-rotation excitation from the high energy wing of the collision energy distribution that exceeds the threshold energy of 125 cm\textsuperscript{-1}. For the higher rotational states, the effect of the kinetic-to-rotation excitation is completely eliminated.
FIG. 9. Angular distributions of the scattered NO radicals for SO-changing transitions from Fig. 6 for both the $D_2$ elastic channel ($j_D' = j_D$) and the $D_2$ rotational de-excitation channel ($j_D' = 0$). The experimental (red) and simulated (blue) profiles are normalized with respect to each other.

FIG. 10. Experimental (Expt.) and simulated (Sim.) state-to-state VMI images of NO–$D_2$ collisions at a collision energy of 100 cm$^{-1}$ for SO-changing $F_1 \rightarrow F_2$ transitions. The right-hand side of each image corresponds to the forward scattered direction. The zero velocity point in the laboratory frame is located in the lower part of each image.
From the energy levels in Fig. 2, it can be seen that the excitation energy of NO (11/2e, F2) is almost identical to the \( j_D = 2 \rightarrow 0 \) de-excitation energy of \( D_2 \). For excitation to the (13/2f, F2) state, the de-excitation energy of \( D_2 \) alone is not sufficient to induce the transition. Consequently, excitation into this state originates from the combination of rotation-to-rotation and kinetic-to-rotation energy transfer. Note here that one additional outermost ring is observed in the image of the (13/2f, F2) state, which is the result of the partially overlapped REMPI detection of population in the \( (3/2, F_2) \) state.

Figure 11 shows the angular distributions of the experimental and simulated scattering images displayed in Fig. 10. Excellent agreement between the experimental and simulated curves is obtained for all the measured states. For the transitions into states with low rotational quantum numbers, such as the \( (3/2, F_2), (5/2, F_2), (7/2, F_2), \) and \( (9/2, F_2) \) states, the angular distributions are characterized by forward scattering. When NO is excited into higher rotational states, larger scattering angles gain intensity. The angular distribution becomes almost isotropic for scattering into the \( (11/2e, F_2) \) and \( (13/2f, F_2) \) states. For these states, the scattering behavior appears quite different compared to the lower rotational states.

V. DISCUSSION

To rationalize these findings, we first computed the integral cross sections for different final states of NO and \( D_2 \) based on the \emph{ab initio} NO-\( D_2 \) PEs. They are shown in Figs. 12 and 13 for the collision energies of 750 cm\(^{-1}\) and 100 cm\(^{-1}\), respectively, for the superimposed \( j_{D_2} = 2 \rightarrow 2, j_{D_2} = 1 \rightarrow 1, j_{D_2} = 0 \rightarrow 0 \) elastic \( D_2 \) channels (top row), and the \( j_{D_2} = 2 \rightarrow 0 \) inelastic \( D_2 \) de-excitation channel (bottom row). It is seen that generally ICSs decrease as the final NO state increases, following the well-known energy-gap law for inelastic energy transfer. Note also the oscillatory behavior of the ICS as a function of the final state, as is well known and understood for the scattering of NO with various targets. However, it is also seen that for the quenching of \( D_2 \) \((j_D = 2 \rightarrow 0)\), the SO-changing transitions have higher ICSs compared to the SO-conserving transitions. This unusual behavior is also a direct consequence of the energy gap law, as the change in kinetic energy before and after the collision is smaller for SO-changing collisions than for SO-conserving collisions in this case.

The large probability for SO-changing collisions compared to SO-conserving collisions is even more apparent at a collision energy of 100 cm\(^{-1}\) (see Fig. 13). As mentioned earlier, at this collision energy, the required energy to transfer NO into the \( F_2 \) manifold has to come from the rotational quenching of \( D_2 \) \((j_D = 2 \rightarrow 0)\), i.e., there is very little exchange of kinetic and rotational energy. The ICS for this process is observed to be about 20 times larger compared to excitation of NO within the \( F_1 \) manifold.

The relative strength of the SO-changing inelastic channels is further understood from the radial expansion coefficients of the interaction potential (see Fig. 4). SO-changing channels of NO are directly coupled by the off-diagonal potential terms with \( K_{NO} = \pm 2 \). Transitions elastic in \( D_2 \) are probably determined mainly by the terms with \( \Delta L_{D_2} = 0 \), while transitions with \( \Delta j_{D_2} = \pm 2 \) are determined by the \( v_{2,0,2,4} \) off-diagonal quadrupole–quadrupole term. The latter term dominates the long-range scattering behavior resulting in relatively large cross sections. This is illustrated by additional calculations with only the diagonal part of the interaction potential and with the combination of the diagonal potential and the quadrupole–quadrupole coupling term of the off-diagonal potential \((L_{NO}, K_{NO}, L_{D_2}, L = 2, \pm 2, 2, 4)\). The resulting ICSs are shown in Figs. 12 and 13. It is seen that, particularly for SO-changing collisions with \( \Delta j_{D_2} = \pm 2 \), the ICSs are almost perfectly reproduced by only taking into account the diagonal potential and the \((2, \pm 2, 2, 4)\) term of the off-diagonal potential. Similar conclusions are obtained when looking at the DCSSs (data not shown).

Finally, we note that the \( f'_{NO}(11/2e, F_2) + f'_{D_2}(0) \) and \( f'_{NO}(13/2f, F_2) + f'_{D_2}(0) \) final states at a collision energy of 100 cm\(^{-1}\) have a near-isotropic angular distribution and do not follow the trend of mainly forward scattering observed for final states with...
FIG. 12. Calculated integral cross sections for inelastic NO–D$_2$ collisions at a collision energy of 750 cm$^{-1}$ for SO-conserving (left column) and SO-changing (right column) transitions in NO and for elastic (top row) and inelastic (bottom row) transitions in D$_2$. The blue solid lines correspond to ICSs calculated with the full interaction potential, and the red dashed lines correspond to ICSs calculated with exclusively using the diagonal potential. The yellow dashed-dotted lines correspond to ICSs calculated including the diagonal potential and the quadrupole–quadrupole off–diagonal term $v_{2,2,2,4}$.

FIG. 13. Calculated integral cross sections for inelastic NO–D$_2$ collisions at a collision energy of 100 cm$^{-1}$, for SO-conserving (left column) and SO-changing (right column) transitions in NO, and for elastic (top row) and inelastic (bottom row) transitions in D$_2$. The blue solid lines correspond to ICSs calculated with the full interaction potential, and the red dashed lines correspond to ICSs calculated with exclusively using the diagonal potential. The yellow dashed-dotted lines correspond to ICSs calculated including the diagonal potential and the quadrupole–quadrupole off–diagonal term $v_{2,2,2,4}$. SO-changing transitions are energetically not allowed, which is why the ICSs for the channels in which D$_2$ scatters elastically are zero.
lower value for $j_{\text{NO}}$. One may speculate whether this behavior is related to the fact that the $j_{\text{NO}} = 11/2$ level is energetically near-resonant with the $j_{D_2} = 2$ level. To test this hypothesis, we performed additional scattering calculations with a modified rotational constant for the $D_2$ molecule that brings the $j_{D_2} = 2$ level in resonance with the $j_{\text{NO}} = 9/2$ or the $j_{\text{NO}} = 13/2$ level. No large differences in scattering behavior were observed, and we conclude that the transition from mainly forward scattering to isotropic distributions at $j_{\text{NO}} = 11/2$ is not related to the proximity of energy levels in the two molecules.

VI. CONCLUSIONS

We have presented high-resolution measurements of state-to-state rotational inelastic scattering between NO radicals and $D_2$ molecules at collision energies of 750 cm$^{-1}$ and 100 cm$^{-1}$ using the combination of Stark deceleration and velocity map imaging. Both SO-conserving and SO-changing transitions in NO were studied, and pair-correlated rotational excitation and de-excitation of $D_2$ was observed. In general, excellent agreement was obtained between experimental and theoretical predictions, both with respect to the angular distributions of the scattered NO radicals and with respect to the relative intensity of the pair-correlated channels. Rotational de-excitation of $D_2$ is preferentially accompanied by SO-excitation of NO. At a collision energy of 100 cm$^{-1}$, pure rotation–rotation energy transfer was observed. The observed trends in the scattering behavior are understood to originate from the strong quadrupole–quadrupole coupling term in the NO–$D_2$ off-diagonal interaction potential.

AUTHORS’ CONTRIBUTIONS

G.T. and M.B. contributed equally to this work.

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APPENDIX: MATRIX ELEMENTS OF DIABATIC POTENTIALS

Here, we give the expression for the matrix elements of the diabatic potentials in a primitive BF channel basis. Details about the basis and the full derivation of the expression for the matrix elements can be found in Refs. 39 and 47. After expanding the potential as in Eq. (2), the matrix elements become

\[
\langle \Omega', \Lambda', \Omega, \Lambda | J_{\text{NO}}, j_{\text{NO}}, j_{D_2}, j_{JAB} | V(R, \theta_{\text{NO}}, \theta_{D_2}, \phi) | \Omega, \Lambda, j_{\text{NO}}, j_{D_2}, j_{JAB}, K \rangle
\]

where $\Omega = \Sigma + \Lambda$ is the projection of the NO monomer angular momentum onto the NO-axis, $\Sigma$ is the spin projection, $j_{\text{NO}}$ and $j_{D_2}$ are the angular momentum quantum numbers of the NO radical and $D_2$ molecule, respectively, that couple to $J_{AB}$, and $K$ is the projection of the total angular momentum $J$ onto the intermolecular axis $R$. The last four factors are three $3j$ symbols and one $9j$ symbol.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES