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Pair-correlated stereodynamics for diatom-diatom rotational energy transfer: NO(A^2Σ^+) + N_2

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ABSTRACT

We have performed a crossed molecular beam velocity-map ion imaging study of state-to-state rotational energy transfer of NO(A^2Σ^+, v = 0, N = 0, j = 0.5) in collisions with N_2, and have measured rotational angular momentum polarization dependent images of product NO(A) rotational levels N′ = 3 and 5-11 for collisions at an average energy of 797 cm⁻¹. We present an extension of our previously published [Luxford et al. J. Chem. Phys. 145, 174304 (2016)] image analysis which includes the effect of rotational excitation of the unobserved collision partner, and critically evaluate this methodology. We report differential cross sections and angle-resolved angular momentum alignment moments for NO(A) levels N′ = 3 and 5-11 as a function of the rotational excitation of the coincident N_2 partner. The scattering dynamics of NO(A) + N_2 share similarities with those previously reported for NO(A) + Ne and Ar, although with detailed differences. We use comparison of the measurements reported here to the scattering of NO(A) with Ne, and the known NO(A)-Ne potential energy surface, to draw conclusions about the previously unknown NO(A)-N_2 potential.

I. INTRODUCTION

The experimental study of the stereodynamics of inelastic rotational energy transfer has been a field of rapid progress in recent years, driven largely by the development and application of velocity-map ion imaging (VMI) techniques, coupled to crossed molecular beam (CMB) scattering. The collisions of small stable molecules, and small radicals, with rare gas (Rg) atoms have seen the most extensive study. These have provided direct insight into the fundamental dynamics of molecule-atom collisions, helping the development of empirical models, and have tested ab initio potential energy surfaces (PESs) via quantum or quasi-classical scattering calculations. The most extensive recent work has been performed on NO(X^2Π) + Rg systems by the groups of Stolte, Brouard, and van de Meerakker.¹-¹⁴ These experiments included a Stark-effect-based state-preparation step, ensuring the selection of a single rotational quantum state of the NO(X) before collision. Probing by resonance-enhanced multi-photon ionization with linear or circular-polarized resonant photons has enabled the measurement of fully rotationally and fine-structure resolved state-to-state differential cross sections (DCSs) and angle-resolved rotational angular momentum orientation
and alignment.\textsuperscript{5,8,9} Brouard and co-workers have also used a static electric field in the crossing region of the molecular beams to orient the NO bond axis preferentially parallel or anti-parallel to the relative collision velocity. They have thereby separately measured the stereodynamics of scattering from both the N or O-ends of the NO, the so-called steric asymmetry.\textsuperscript{10,11} Van de Meerakker and co-workers have used a Stark decelerator to finely-control the velocity of a state-selected NO molecular beam, providing very-high collision-energy resolution down to collision-energy regimes that are not accessible with conventional supersonic molecular beams. They have used this to demonstrate the insight into the PESs that may be gained by directly observing diffractive scattering and the DCSs for scattering resonances.\textsuperscript{12-15} While NO(X) remains the ‘star’ of molecule-atom stereodynamics, other systems have been studied using the CMB-VMI combination, including OH(X\textsuperscript{2}Π) + He,\textsuperscript{16} CO + He/Ne,\textsuperscript{17} O\textsubscript{2}(X\textsuperscript{3}Σ\textsubscript{g}\textsuperscript{-}) + He,\textsuperscript{18} HCl + Ne/Ar/Kr,\textsuperscript{19} and beyond diatomic molecules to H\textsubscript{2}O + He,\textsuperscript{22} ND\textsubscript{3} + He/Ne,\textsuperscript{23,24} and CH\textsubscript{3} + He/Ar.\textsuperscript{25,26}

While atomic colliders are experimentally convenient and provide attractive targets for theory, there are a limited number of environments where collisions with Rg-atoms are of practical importance. However, extension of these studies to scattering with the much more important molecular partners is much rarer. The introduction of a molecular collider complicates both the experiment, in the production of a cold molecular beam of the collider, and the analysis of the resulting data. This complication arises from the internal energy (rotational) levels of the molecular collider. As described above, the initial and final rotational states of the subject molecule (e.g. NO(X)) are usually fully state-selected by the preparation and probe steps. In collisions with an atomic partner, the laboratory-frame speed of the probed molecule is therefore fully determined by the collision energy, its known rotational energy excitation, and conservation of momentum. In velocity space, the scattering falls on the surface of a sphere with a known radius, or more usually in practice a relatively narrow known distribution of radii arising from the spread of collision energies. In contrast, the rotational energy level structure of a molecular collider provides additional \textit{unobserved} channels for collision energy partitioning. Rotational energy transferred to or from the collider will result in a lower or greater energy available for translation, respectively, and accordingly the scattering will now fall on the surface of a nested shell of spheres, which may well overlap when the collision energy spread is comparable to the rotational energy level spacings in the collider.

These problems could be overcome to some extent by state selection of the unobserved collider and restriction of the range of initial collision energies. An example is the work of Kirste \textit{et al.} who measured the collision energy dependence of state-resolved integral cross sections for NO(X) + OH(X) scattering in experiments using Stark-decelerated OH and electric hexapole-focused NO.\textsuperscript{27} Such elegant control of the initial conditions is challenging, however, and there have not yet been published reports of stereodynamics measurements from similar experiments. Perhaps unsurprisingly, in the majority of cases
where the stereodynamics of scattering with molecular colliders has been studied it has been with H₂ or its isotopologue, D₂. In principle, the large rotational spacing of H₂ and D₂ (B ≈ 60 cm⁻¹ and ≈ 30 cm⁻¹, respectively), coupled with the conservation of ortho/para symmetry, will restrict the number of open collider-product channels, simplifying the analysis complications discussed in the previous paragraph. However, what has generally been found is that H₂ and D₂ act as pseudo-atomic colliders, presumably because H₂ \( \chi \Sigma^+ \) appears near-spherical to its partner in the systems that have been studied, which include NO(X) + D₂,\(^{28}\) H₂O + H₂,\(^{29}\) ND₃ + H₂,\(^{30}\) and CH₃ + H₂ and D₂.\(^{31}\) No strong evidence for rotational excitation of the H₂ or D₂ was observed in those experiments. There are only a handful of CMB-VMI studies of inelastic scattering with heavier colliders. An early report from Chandler and co-workers studied HCl + N₂ and CH₄.\(^{21}\) They observed evidence in the images for high-\(N'\) HCl products of coincident rotational excitation of the N₂ and CH₄. However, they did not attempt to analyze the images to extract DCSs for this coincident scattering. More recently, Tkáč \textit{et al.} compared the scattering of CH₃ + N₂ to that for CH₃ + Ar.\(^{26}\) Again, evidence was observed in the images for CH₃ scattered from N₂ for rotational excitation of the unobserved N₂, but no detailed analysis of the DCS correlated with N₂ internal energy was attempted.

We have previously shown that collisions of rotationally state-selected electronically excited NO(A) may be studied in a CMB-VMI apparatus, by introducing a pulsed laser excitation step before collision.\(^{32}\) We have used this technique in an extensive study of the stereodynamics of the NO(A) with Rg colliders, specifically He, Ne and Ar, determining the DCSs and the rotational alignment moments as a function of scattering angle.\(^{33-37}\) Comparison of these experimental measurements with the results of Quantum Scattering (QS) calculations has been used to test literature \textit{ab initio} PESs. This has shown that such measurements are capable of identifying which of two literature PESs is the more accurate and that they can suggest specific areas for improvement in the PESs. We have also compared the stereodynamics of the NO(A) + D₂ and He systems.\(^{37}\) We observed no evidence for rotational excitation of the D₂ in those experiments, in agreement with the general conclusions of the NO(X) + D₂ study discussed above, and consistent with the mismatch in NO(A) (\(B = 2\) cm⁻¹) and D₂ (\(B = 30\) cm⁻¹) rotational energy level spacings.\(^{28}\) The DCSs and rotational alignment moments for NO(A) + D₂ were very similar, although displaying small systematic differences, to those for the kinematically identical NO(A) + He system, which we used to predict the general form of the NO(A) + D₂ PES.

Here, we present an application of our CMB-VMI approach to a study of the stereodynamics of state-to-state RET of NO\( (A^2\Sigma^+) + N_2\). As before, we prepared NO\( (A^2\Sigma^+, \nu = 0, N = 0, j = 0.5)\) by pulsed excitation in the crossing region of the molecular beams, after which NO(A, \(\nu = 0, N'\)) that had undergone RET in collisions with a pure beam of N₂ was probed state-selectively via \((1+1')\) REMPI on the NO\((E^2\Sigma^- - A^2\Sigma^+)\) transition. The resulting product images display clear indications of rotational excitation in the \textit{unobserved} N₂ collider. We have extended our previously published image analysis and fitting
approach to determine the DCS and polarization moments as a function of the collider internal energy, which we report for a wide range of NO\( (A, N') \) product states. We consider the success of this fitting methodology in successfully returning accurate values of the DCSs and alignment moments. We then discuss these measurements in comparison to the previously measured dynamics and known PESs for NO\( (A) + \text{Ne and Ar} \), and also draw more general conclusions about the dynamics of RET involving colliders with similar rotational constants.

II. METHODS

A. Experiment

We have described the experimental methodology in detail in recent publications, and we therefore only provide a brief overview here.\(^{35-37} \) Two molecular beams crossed at 90° in the center of a high-vacuum chamber, within the extraction region of a set of velocity-map ion optics. The first molecular beam contained 10% NO (99.5%, BOC) seeded in Ne (99.999%, BOC) with a backing pressure of 3 bar, resulting in a Gaussian speed distribution for the NO with a mean of 822 m s\(^{-1} \) and a full width at half maximum (FWHM) of 60 m s\(^{-1} \). The second molecular beam contained neat N\(_2\) (100%, BOC) from a backing pressure of 5 bar, to give a Gaussian speed distribution with a mean of 800 m s\(^{-1} \) and a FWHM of 74 m s\(^{-1} \). These conditions led to a Gaussian distribution of center-of-mass collision energies, with a mean, \( \langle E_{\text{col}} \rangle = 797 \text{ cm}^{-1} \), and a FWHM of 92 cm\(^{-1} \). The methods used to obtain the speed distributions of the molecular beams are the same as those described in a previous publication.\(^{36} \) No independent measurements of the N\(_2\) rotational distribution were made, but based on the rotational distribution of a small quantity of NO seeded in the N\(_2\) molecular beam in separate experiments, the majority of the N\(_2\) population will be in rotational levels \( j = 0 \) and 1, with a smaller but still significant population in \( j = 2 \).\(^{14} \)N has nuclear spin, \( I = 1 \), and the nuclear spin statistics result in a 2:1 ortho:para ratio for the rotational states, where \( j \)-even are ortho and \( j \)-odd are para. As the nuclear spin is a spectator to the collision process to a very high level of approximation, the ortho or para character of the N\(_2\) will be conserved in the collision, resulting in only \( \Delta j = \text{even} \) transitions being allowed. In the remainder of this paper we use \( j \) to refer to N\(_2\) rotational states, distinguishing them from \( N \) for NO\( (A) \) states (see below).

The molecular beams were intersected in the crossing-region by the output of a Nd:YAG pumped dye laser (Continuum Surelite II-10 and Sirah Cobra-Stretch), pumping NO to its first excited electronic state, NO\( (A^2\Sigma^+, v = 0, N = 0, j = 0.5) \). After a 400 ns delay, the NO\( (A, v = 0, N') \) products resulting from RET with N\(_2\) were probed by 1+1′ resonance-enhanced multiphoton ionization via the R-branch of the NO \( E^2\Sigma^+\text{-}A^2\Sigma^+ \) transition, using the 600 nm + 532 nm outputs of a second Nd:YAG pumped dye laser (Continuum Surelite I-10 and Sirah Cobra-Stretch). NO\( (A) \) is well-described as a Hund’s case-(b) system, where the nuclear rotation, \( N \), is coupled to the electron spin, \( S = \frac{1}{2} \), resulting in spin-rotation split states \( f_1/f_2 = N \pm \frac{1}{2} \). However,
the very similar spin-rotation constants in the NO(A) and NO(E) electronic states prevent this probe scheme from independently probing the product \( f_1/f_2 \) states. Instead we resolve only the rotational level, \( N' \), probing the \( f_1/f_2 = N' \pm \frac{1}{2} \) states equally. In the remainder of the paper we use \( N \) to refer to NO(A) rotational levels. The resonant probe-laser beam was linearly polarized, with the polarization switched between horizontal (H, in the plane of the molecular beams) and vertical (V). The resulting ions were velocity mapped onto a micro-channel plate detector, and their positions recorded by a camera. Velocity-map images were acquired with each probe laser polarisation in an interleaved cycle. Ions which did not arise from the inelastic scattering were recorded in background images in which the \( N_2 \) molecular beam was absent (in practice, delayed by 1 ms). Over the course of a single acquisition, \( 6.4 \times 10^4 \) individual camera shots were recorded, split equally between V and H probe polarizations for both signal and background cycles. Velocity-map images were recorded in this way for the final NO(A) rotational levels, \( N' = 3 \) and 5-11. For each final rotational level, six independent acquisitions were made across multiple days, except for \( N' = 11 \), for which twelve independent acquisitions were made to compensate for the low observed signal levels.

**B. Data Analysis**

As discussed in the Introduction, RET with molecular colliders opens up the possibility of rotational excitation in the unobserved collision partner, which we expect to complicate the analysis of the resulting images. In photofragment imaging experiments, where unobserved internal fragment energy is a common theme, a variety of methods have been developed to deal with this problem. We are unable to apply the usual experimental approach, slice-imaging\(^{38} \) because ‘crush’ imaging is required to separate the scattered signal ions from background ions generated by the excitation pulse in our experiments. Commonly applied photofragment data analysis procedures, e.g. polar onion peeling,\(^{39,40} \) are not well suited to the analysis of images with the non-uniform instrument function typical of CMB experiments, and would not be compatible with the dependence of the image on rotational alignment moments \( \psi \) via the azimuthal scattering angle. As a first step, we therefore fitted our experimental images using the approach and fitting codes that we have previously developed for RET of NO(A) with atomic colliders.\(^{35-37} \) As we show in the Results (Section III) below, this results in large residuals between experiment and fitted images that are consistent with rotational excitation in the unobserved \( N_2 \). We have consequently gone on to extend the fitting codes that we developed for atomic colliders to include the unobserved product rotation. Since we have described our atomic collider fitting approach in detail in previous publications,\(^{35-37} \) we only briefly summarize it in the following paragraph, before describing our extension of this to RET with molecular colliders.

In our previously published experiments with atomic colliders, we determined the DCS, and the angle-resolved rotational angular momentum alignment moments, \( A_{q+}^{(2)}(\theta) \). An iterative fitting procedure was used, which treated the DCS and
alignment moment distributions as separable, and proceeded in the following fashion. Monte-Carlo selection from appropriate experimentally determined distributions was used to integrate over the initial molecular beam conditions and experimental geometrical factors. The introduction of a definite start time to the collision process, through the excitation laser pulse, simplifies this Monte-Carlo analysis in comparison to a more conventional CMB-VMI experiment, as it removes the requirement for a density-flux transform. Basis images for both the V and H laser polarizations were then generated for a range of Legendre moments of the scattering angle, either \( P_\lambda(\cos \theta) \) or \( P_\lambda(1-\theta/90^\circ) \), using an assumed angular momentum distribution, which initially typically came from QS calculations. These basis images were fitted to the experimental images using a downhill simplex algorithm to adjust their relative weights. This resulted in an initial fitted DCS. This DCS was then used to simulate a new set of basis images, expanding the \( A^{(2)}_{\eta \nu}(\theta) \) distributions in either \( P_\lambda(\cos \theta) \) or \( P_\lambda(1-\theta/90^\circ) \) functions. These alignment-dependent basis images were then fitted to the experimental images, resulting in experimental \( A^{(2)}_{\eta \nu}(\theta) \) distributions. The \( A^{(2)}_{\eta \nu}(\theta) \) determined from this fit were then used to generate a new set of DCS-dependent basis images, and this DCS and \( A^{(2)}_{\eta \nu}(\theta) \) fitting cycle was iterated until the resulting distributions determined across successive cycles converged to a user-defined level of agreement.

We have extended this approach to molecular collision partners by simulating additional basis images dependent on different amounts of rotational energy transferred to the unobserved collision partner, \( \Delta E \). Consider an idealized experiment, in which the collider is initially in a single rotational state, and the minimum rotational excitation is substantially larger than the spread in collision energy. In that case, the velocity-mapped product ions would form discrete shells, which in our ‘pancake’ imaging would be projected as multiple rings in the final image. This projection from 3-d to 2-d will, of course, result in some overlap between products formed in coincidence with different collider excitations; for example, out-of-plane sideways-scattered fast products will appear at the same point in the image as slower-moving in-plane products. However, it seems reasonable to assume that in this ideal case a simultaneous fit to the data of basis functions describing each collider internal excitation independently would successfully return the scattering dynamics for these different collider excitations.

We therefore proceeded by replacing the previous one-dimensional array of \( \lambda = 0 \) to \( \lambda_{\text{max}} \) DCS basis images with a two-dimensional array of DCS basis images, with \( \eta = 0 \) to \( \eta_{\text{max}} \) discrete values of the rotational energy transferred to the unobserved collider, \( \Delta E_\eta \), and \( \lambda_\nu^0 = 0 \) to \( \lambda_\nu^\eta_{\text{max}} \) Legendre moments of the DCSs, where we have allowed for different ranges of Legendre moments of the scattering angle distribution for different \( \Delta E_\eta \). The \( A^{(2)}_{\eta \nu}(\theta) \) basis image arrays were also expanded to include different values of \( \Delta E_\eta \) in a similar fashion. We confirmed that fitting to simulated data with two or three selected values of
$\Delta E_0$ separated by approximately the FWHM of the collision energy distribution (i.e. 100 cm$^{-1}$) successfully returned the input DCSs, $A^{[2]}_{q>}(\theta)$, and relative cross sections for different $\Delta E_0$. However, in the experiments presented here, the N$_2$ rotational constant, $B_0 = 2.00$ cm$^{-1}$, results in closely spaced product spheres for small $\Delta j$, even including the $\Delta j = \text{even ortho/para}$ constraint. We would not expect to be able to resolve scattering into separate N$_2$ rotational states for which the energy gaps are significantly less than the FWHM of the collision energy distribution. We therefore performed further tests with simulated data to determine the minimum energy spacing of product states for which the correct DCSs were returned. These test images including all the sources of blurring appropriate to the experimental conditions for NO(A) + N$_2$, but no additional random noise. We simulated experimental data for rotational excitation of N$_2$, $j = 0$ to $j' = 0$ to 10 and $j = 1$ to $j' = 1$ to 9 in even-$\Delta j$ steps, with the appropriate N$_2$ rotational transition energies listed in Table I, using for this purpose DCSs available from previously published NO(A) + He QS calculations, and assuming an isotropic angular momentum distribution. We then fitted these simulations, using singular value decomposition (SVD), to basis energies corresponding to discrete N$_2$ rotational transitions, sequentially increasing the energy-basis density until the returned DCSs showed significant deviations from the simulation input. The results of this procedure are shown in the Supplementary Material, and demonstrate that with these noiseless simulations the minimum spacing was around 40 cm$^{-1}$, approximately half the collision-energy FWHM. With significant initial N$_2$ rotational population in $j = 0$, 1 and 2 we would expect 4 rotational transitions in the $\Delta E = 0$ – 40 cm$^{-1}$ range ($j \rightarrow j' = 0 \rightarrow 2$, 0 $\rightarrow$ 4, 1 $\rightarrow$ 3 and 2 $\rightarrow$ 4), and 3 in the $\Delta E = 40$ – 84 cm$^{-1}$ range. Transitions arising from $j = 0$ and 2 to the same final $j'$ will certainly be indistinguishable, as they are separated by only 12 cm$^{-1}$. Only for large $\Delta j$ will transitions arising from $j = 1$ be distinguishable from those arising from $j = 0$ and 2, e.g. $j = 1 \rightarrow 11$ ($\Delta E = 260$ cm$^{-1}$) bracketed by $j = 0 \rightarrow 10$ ($\Delta E = 220$ cm$^{-1}$) and $j = 2 \rightarrow 12$ ($\Delta E = 300$ cm$^{-1}$). This implied that we could not expect to determine the DCS for specific N$_2$ rotational transitions, except at high-$j'$. Having established the limiting resolution that was likely to be achievable, we turned to the experimental data, and ran further fitting trials, using SVD, to determine the minimum possible energetic spacing of the basis images before significant over-determination of the data became evident. We found that when the basis-energy spacing was less than 60 cm$^{-1}$, the SVD fits indicated that the data were overdetermined, with correlated positive and (clearly non-physical) negative regions of the DCS for adjacent basis energies. We therefore chose basis energies separated by approximately this spacing, but centered on the energies of specific $j = 0 \rightarrow j'$ transitions, namely $j' = 0, 6, 8, 10$ and 12 at 0, 84, 144, 220 and 312 cm$^{-1}$, respectively. As we show in the Supplementary Material, further SVD analysis of the sensitivity of fit to the number of basis energies indicated that there was no strong evidence to support the use of the $j' = 10$ and 12 basis energies.
We have therefore obtained the final fits to the experimental data in the following fashion. Basis images were simulated for the transfer of 0, 84 and 144 cm\(^{-1}\) into N\(_2\) rotation, which we henceforth refer to as \(j' = 0, 6\) and 8 respectively. Although we refer to them as individual levels as a shorthand, we emphasize again that we do not intend to imply that the results are specific to those levels. Instead, these basis images represent scattering for a range of rotational transitions, which are respectively close to elastic, resulting in moderate (\(\Delta j = 4-6\)), and larger (\(\Delta j = 7-9\)) N\(_2\) excitation. The basis images for H and V polarizations were fitted simultaneously to the experimental images from individual data acquisitions, optimizing both the DCSs, \(A_0^{(2)}(\theta)\), and \(A_{2m}^{(2)}(\theta)\) moments for each of \(j' = 0, 6\) and 8 independently, using the iterative procedure described above. A downhill simplex algorithm was used, which optimized the fit while applying physically appropriate constraints to the DCSs (positive only), \(A_0^{(2)}(\theta)\) (-1 to +2 limits), and \(A_{2m}^{(2)}(\theta)\) \((\pm \sqrt{3}\) limits). With the exception of the highest NO(A) \(N'\) levels, a very intense and localized feature is seen in the images in the extreme forward scattering direction. In order to fit a very sharp DCS feature the \(P_A(1 - \theta/90^\circ)\) basis is needed and a large number (>20) of Legendre moments of the DCS are required. These functions are not well suited to simultaneously fitting the low-amplitude, but dynamically more interesting, sideways and backwards scattering. Attempts to fit the entire scattering-angle range in this fashion proved to be unstable. We have therefore excluded the intense feature resulting from the extreme forward-scattered region from the fit for \(N' = 3\) and 5-10. The size of the excluded region was determined and minimized by trial fitting. We used the Monte-Carlo simulation to determine the forward scattering angles that were determined by the excluded image pixels, and do not report these angles in our fit results. For each product \(N'\) we report the mean of fits to six individual pairs (V and H) of images acquired on different days (with the exception of \(N' = 11\), where 11 pairs of images were fitted), and quote errors as twice the standard error in the mean of these individual fits.

III. RESULTS

Figure 1 shows a Newton diagram for \(N' = 11\), superimposed on the sum of images recorded in the V and H probe polarization geometries. In Fig. 1(a) the rings indicate the in-plane velocities for scattering with different even-\(\Delta j\) rotational transitions in the unobserved N\(_2\) collider, specifically for initial \(j = 0 \rightarrow j' = 0, 2, 4, 6, 8, 10, 12\) and 14, and initial \(j = 1 \rightarrow j' = 3, 5, 7, 9, 11, 13\) and 15. This illustrates the relatively dense packing at low levels of N\(_2\) internal excitation which we do not expect to be able to resolve, as discussed Section II.B. In Fig. 1(b) rings for scattering with in-plane velocities for initial \(j = 0 \rightarrow j' = 0, 6\) and 8 only are shown, representing the N\(_2\) rotational transition energies used to construct the image basis functions used in fitting the experimental data. The Newton diagrams also show the probe laser propagation direction, \(k_p\). The average angle between the
relative collision vector, \( \mathbf{k} \), and \( \mathbf{k}_p \) is 89°, and as a consequence the experiment is sensitive to the \( A_0^{[2]}(\theta) \) and \( A_2^{[2]}(\theta) \) moments, but not the \( A_{4r}^{[2]}(\theta) \) moment.\(^5\)\(^{,}\)\(^{34-37}\)

The experimental images for both V and H probe laser polarizations for product levels \( N' = 3 \) and 5-11, averaged across all individual acquisitions, are shown in Fig. 2. As noted in Section II.B, the images display a dramatic forward (ca. 0-10°) scattered peak, with reducing relative intensity as \( N' \) increases, which is very similar to that observed in NO(A) + Ar scattering.\(^{35}\) We emphasize that this forward-scattered peak is not an experimental artefact, for example the result of incomplete background subtraction. The images for \( N' = 7 – 10 \) clearly show both this forward peak and a background subtraction artefact which lies outside the maximum in-plane scattering radius. At larger \( N' \) an increasing fraction of sideways and backwards scattering is seen, as is commonly observed in inelastic scattering. The radius of the scattering ring decreases as \( N' \) increases, as required by conservation of energy. As expected from the combination of the experimental collision energy distribution and the possible \( N_2 \) rotational transition energies listed in Table I, no discrete scattering rings arising from separate \( N_2 \) rotational transitions are observed. However, energy transfer to \( N_2 \) rotation is *clearly visible* in the experimental images, most notably in the high-\( N' \) product levels (i.e. \( N' = 9, 10 \) and 11). For these levels the scattering ring is clearly ovate (egg-shaped) rather than circular, with the major axis lying along \( \mathbf{k} \). This is consistent with preferential transfer of the available energy into \( N_2 \) rotation for sideways scattering, and forwards and backwards scattering preferentially for low-\( N_2 \) rotational excitation, and consequently different DCSs for these NO(A) \( N'-\)levels as a function of coincident \( N_2 j'-\)state. Differences in intensity between the V and H images are clear evidence of collision-induced alignment of the NO(A) since, as noted in Section II, these images are collected in an interleaved fashion in order to ensure that image intensities are unbiased by slow variations in the experimental conditions. In Fig. 3 we show the difference (V-H) of the images in Fig. 2. This difference will be zero if there is no rotational angular momentum polarization, hence the blue-red colors present in all of the images in Fig. 3, that change as a function of scattering angle, are an indication of the presence of substantial scattering-angle-dependent alignment moments.

Figure 4 shows example single experimental acquisition V and H polarization images for three NO(A) product levels (\( N' = 5, 8 \) and 11) together with the simulated images resulting from fitting the DCS and \( A_{4r}^{[2]}(\theta) \) to the experimental data, assuming that *no* energy is transferred to rotation of \( N_2 \), henceforth referred to as the ‘atomic fit’. For \( N' = 5 \) and 8 the most intense part of the forward scattering has been excluded from the fit, as discussed in Section III. The agreement between the data and fit gets poorer as \( N' \) increases; for \( N' = 8 \) and 11 it is clear that the assumption of zero internal energy transfer to the \( N_2 \), which necessarily imposes a circular outer edge on the bright region of the image, is not supported by the data. The systematic
deviations of the simulation from the data that arise indicate that the derived DCS and $A_{q+}^{[2]}(\theta)$ are not an accurate reflection of the observed scattering.

Figure 5 shows example single experimental acquisition V and H polarization images for all of the NO(A) product levels studied, together with simulated images resulting from fitting the DCSs and $A_{q+}^{[2]}(\theta)$ moments to the three separate $j' = 0, 6$ and 8 basis energies, henceforth referred to as the ‘molecular fit’. In each case the DCS and $A_{q+}^{[2]}(\theta)$ for the different N$_2$ rotational energies were fitted simultaneously and independently to the data, with the most intense part of the forward scattering again excluded from the fit. Much better agreement between the experimental and fitted images is observed for the molecular fit than is achievable for the atomic fit in Fig. 4. The fitted images are now able to reproduce the ovate shapes of the high-$N'$ product levels, and show no significant systematic deviations from the data. Figure 6 provides a direct comparison of the quality of the atomic and molecular fits. Figure 6(a) and 6(b) show the residuals (data – fit) for the sum (V + H) images from the atomic and molecular fits, respectively. A strong residual ring is observed for the atomic fit, corresponding to a systematic overstatement of the intensity for scattering with no N$_2$ internal excitation. The residual for the molecular fit is greatly reduced in amplitude and no longer displays a single energetic signature. In Fig. 6(c) a projection through the image region containing sideways scattered products provides an alternative representation of the data, fits and residuals. This emphasizes how the atomic fit both systematically overstates the product average lab-frame speed, and understates the width of the lab-frame speed distribution, resulting in a fit projection that is both wider than the experimental data projection and more sharply peaked. In contrast, the molecular-fit projection provides a good fit to the width of the experimental projection, and a much closer match to its shape, although some systematic residual is still observed, consistent with the use of relatively coarsely grained discrete N$_2$ internal energies.

In Fig. 7 we present the DCSs, $A_{b}^{[2]}(\theta)$ and $A_{2+}^{[2]}(\theta)$ as a function of $j'$ for $N' = 3$ and 5-11. In each case the DCSs are truncated for the forward-scattered region excluded from the fit, and the alignment moments are only shown for regions where the relevant DCS is $> 10\%$ of its maximum. The DCSs for all $j'$ components are strongly forward scattered for low $N'$, and move increasingly to sideways and backwards scattered as $N'$ increases. The relative intensity of the $j' = 8$ component increases as $N'$ increases, from a relatively small contribution for $N' = 3$ to a substantial fraction of the overall scattering cross-section for $N' = 10$. The DCSs for the $j' = 0$ and 6 components are consistently quite similar, whereas the $j' = 8$ DCSs is systematically more sideways scattered. However, despite this trend for increased sideways scattering for higher N$_2$ rotational energy, for $N' = 9, 10$ and 11 a clear backward scattered $j' = 0$ peak is visible. That this is present in the data, and not an artefact of the fitting
procedure, is confirmed in Fig. 1(b), where a non-zero image intensity is clearly seen to extend to the scattering ring indicated for \( j' = 0 \) in the backward direction, but in contrast the image intensity is essentially zero for \( j' = 0 \) sideways scattering.

Turning to the alignment moments, we note that the uncertainties are considerably larger for \( A_0^{(2)}(\theta) \) and \( A_2^{(2)}(\theta) \) than the DCS. This is a natural consequence of the dependence of the alignment moments on differences in the intensities of the images as a function of the probe polarization and azimuthal scattering angle, which necessarily makes the alignment moments more challenging to extract than the DCSs. Considering \( A_0^{(2)}(\theta) \) first, very similar behavior is observed for \( j' = 0 \) and \( 6 \). For low-\( N' \) (e.g. \( N' = 3, 5 \) and \( 6 \)) we can only determine \( A_0^{(2)}(\theta) \) over a relatively small angular range in the forward hemisphere, where the scattering amplitude is large enough. Here \( A_0^{(2)}(\theta) \) is generally close to zero. As \( N' \) increases and we are able to determine \( A_0^{(2)}(\theta) \) over a larger angular range, we find that it becomes consistently negative, although it does not reach the negative limit of \( A_0^{(2)}(\theta) = -1 \). A negative value of \( A_0^{(2)}(\theta) \) implies a rotational angular momentum vector, \( N' \), that is orthogonal to \( k \). We do see a systematic difference between \( A_0^{(2)}(\theta) \) for \( j' = 0 \) and \( 6 \) and that for \( j' = 8 \). The higher energy in \( N_2 \) rotation is correlated with an \( A_0^{(2)}(\theta) \) alignment moment that is systematically positive in the forward hemisphere, switching to negative in the backward hemisphere, and is essentially always more positive than that observed for the lower \( N_2 \) rotational energy.

Finally, we see strongly negative \( A_2^{(2)}(\theta) \) for \( j' = 0 \) and \( 8 \), largely irrespective of scattering angle and \( N' \), and a consistently positive \( A_2^{(2)}(\theta) \) for \( j' = 6 \). \( A_2^{(2)}(\theta) \) is determined by the variation of intensity in the H and V polarization images as a function of azimuthal scattering angle, and therefore across the image perpendicular to \( k \). In images from scattering with an atomic collider this is well determined, but in the present molecular case there is a possibility of an interaction between the \( A_2^{(2)}(\theta) \) distributions determined for the relatively closely-spaced energies of the different \( j' \). We are confident that the negative value \( A_2^{(2)}(\theta) \) reported for \( j' = 0 \) and \( 8 \) across the sideways scattered region for \( N' \geq 7 \) is robust. The difference (V-H) images in Fig. 3 illustrate this. Any non-zero intensity in these images can only come from rotational alignment, and a shift from negative for scattering at low azimuthal angles (at the edges of the images), to positive for high azimuthal angles (in the center of the image) is the signature of the \( A_2^{(2)}(\theta) \) moment. However, we consider it unlikely, \textit{a priori}, that there would be a change in the sign of \( A_2^{(2)}(\theta) \) for the intermediate \( j' = 6 \) scattering. We therefore believe that this is an artefact of the fitting procedure and the poor determination of \( A_2^{(2)}(\theta) \) for the different \( j' \), and that it is more probable that all of the sideways scattering for \( N' \geq 7 \) has \( A_2^{(2)}(\theta) \leq 0 \). This corresponds to NO(A) rotating in the plane of scattering for these DCS angles. We also considered the possibility that
a cross-talk between the alignment moments, in particular $A_{2\pi}^{(2)}(\theta)$, and the DCSs, might result in systematic correlations between the reported DCSs and alignment moments for different $j'$. We tested this by repeating the analysis, fitting the DCS while holding $A_{2\pi}^{(2)}(\theta)=0$ and $A_{2\pi}^{(2)}(\theta)=0$ for all scattering angles. The resulting DCSs as a function of $j'$ are compared in Fig. S5 in the Supplementary Material for NO(A) product states $N'=3$, 8 and 11 with the DCSs determined by the complete fit with optimization of the angular momentum alignment. The DCSs for all $N'$ and $j'$ are almost identical, and lie well within the estimated uncertainties. We are therefore confident that the reported DCSs and alignment moments are independent of one another.

IV. DISCUSSION

What can be learned about the PES for NO(A) + N$_2$ from these experiments? The first notable element of the scattering dynamics is the one we chose to exclude from our quantitative fits to the DCSs. The experimental images for $N'=3$ and 5-10 all display an intense peak in the extreme forward direction ($\approx 0$ - 10°), which gradually broadens as $N'$ increases. This feature is strikingly similar to that observed in our previous experiments on the NO(A) + Ar and NO(A) + Ne systems. For the NO(A) + Ar system we were able to use analysis of QS calculations to identify the theoretically predicted tightly focused and relatively shallow well on the NO(A)-Ar PES, located at the N-end of the molecule, as the origin of this feature. Such a well is not present on the ab initio NO(A)-Ne PES, and as a result the QS calculations do not reproduce the observed forward scattered peak; this led us to propose that a modification of the NO(A)-Ne PES to include this feature would be appropriate. We propose that a similar well on the NO(A)-N$_2$ PES, located at one end of the NO molecule, is responsible for this sharp forward scattering at small to moderate $\Delta N'$. This is consistent with the only previous experimental and theoretical work on the NO(A)-N$_2$ PES. Wright and co-workers recorded 1 + 1 REMPI spectra of NO-N$_2$ van der Waals complexes which are consistent with a NO(A)-N$_2$ complex with a co-linear (or close to co-linear) minimum. Ab initio calculations on the co-linear NO-N$_2$ and ON-N$_2$ geometries found that the latter was the more stable, with a binding energy $\approx 230$ cm$^{-1}$.

Turning to the fitted DCSs in Fig. 6, we see a general increase in sideways and backwards scattering as $N'$ increases. This is very commonly observed in diatom-atom scattering; it is usually described as a straightforward consequence of linear to angular momentum transfer constraints, where the requirement for increasing product rotational angular momentum can only be met by lower impact parameter collisions, which result in more backward scattering. For each $N'$, we observe increased sideways and backwards scattering for the highest- $j'$, consistent with lower impact parameter collisions leading to increased rotational angular momentum in both products. Focusing on the $j'=8$ DCSs, we observe a clear trend from $N'=8$ to 11 in
increasing scattering angle for a secondary maximum, which is remarkably similar to the rotational rainbow structure observed in NO(A) + Ne scattering at $<E_{\text{col}}>$ = 523 cm$^{-1}$. One surprise is the preference for $N' = 10$ and 11 for the scattering at 180° to be preferentially correlated with $j'' = 0$, for which we do not at present have an explanation. Overall, the observed DCSs seem to be consistent with an NO(A)-N$_2$ PES which has a similar degree of anisotropy with respect to the NO(A) as those calculated for NO(A)-Ne and the other NO(A)-rare gas complexes.\textsuperscript{43}

What can be said about the anisotropy of the PES with respect to the N$_2$? The N$_2$ is clearly not a pseudo-sphere, since we have clear evidence of its rotational excitation. Although we have not fitted the forward scattered peak present in the data in Fig. 2, inspection of the DCSs in Fig. 7 for $N' = 6 - 8$ indicates that the forward scattered peak for these NO(A) product states is formed in coincidence with both elastic and rotationally excited N$_2$. This seems consistent with the predicted linear minimum for the NO(A)-N$_2$ PES; provided that the well is anisotropic with respect to both the NO and the N$_2$ then if it is capable of rotationally exciting NO(A) with forward scattering it should be able to do the same for the N$_2$, even in coincidence. A more general question is how the overall cross section for producing rotationally excited N$_2$ varies with $N'$. Figure 8 shows the relative excitation probabilities for $j'' = 0$, 6 and 8 resulting from an integration of the DCSs in Fig. 7. The sum of these excitation probabilities is normalized to unity for each $N'$ state, and so their absolute values cannot be compared between $N'$ states. We note again that the $j''$ label here refers only to a basis function corresponding to a single N$_2$ rotational excitation, and that these are accordingly not probabilities for the production of specific N$_2$ rotational states. In addition, only the fitted angular regions of the DCS were included in the integration, which we expect to have biased the results in favor of the more sideways scattered $j'' = 8$ relative to the results that would have been obtained by including the forward scattered region. For this reason, we have not included $N' = 11$, since with a complete 0-180° DCS range it would not be directly comparable to lower-$N'$. Despite this, some general trends may be drawn. Overall, the degree of rotational excitation of the N$_2$, as judged principally by the ratio of $j'' = 8$ to $j'' = 0$, does increase with increasing $N'$, but to a surprisingly small extent: there is not a particularly strong $N' - j''$ correlation beyond $N' = 6$. This suggests that the torques that each molecule experiences are determined independently. A moderate degree of N$_2$ rotational excitation is observed even for $N' = 3$. Compared to the overall available energy $<E_{\text{col}}>$ = 797 cm$^{-1}$, relatively little energy is partitioned into rotation. Even for $N' = 11$, with an NO rotational energy of 264 cm$^{-1}$, for which the full range of the DCS was fitted and hence it is meaningful to calculate an average rotational energy for the coincident N$_2$, we find that this is only $<E_{\text{rot}}>$ $\approx$ 80 cm$^{-1}$. This seems to be consistent with a PES is that is only moderately anisotropic with respect to the N$_2$, which is perhaps not surprising as N$_2$ has a quadrupole as the lowest electrostatic moment, in contrast to the relatively large dipole moment of NO(A) ($\mu \approx 1.1$ D).
To the best of our knowledge, there have been no previous reports of scattering angle-resolved alignment moments as a function of collider energy, or indeed with a molecular collider at all, other than our own report of NO(A) + D₂ scattering. The trend for a more negative $A^{(2)}_{0}(\theta)$ with increasing $N'$ is consistent with the behavior previously observed in NO(A) + Rg scattering. This is also generally in agreement with the predictions of conservation of angular momentum along the kinematic apse (KA), given by $a_k = (k' - k)/|k' - k|$. This arises from a hard-shell potential model of scattering, and has been found to be a very good prediction for the angular momentum correlations observed in ground-state NO(X) + Rg systems. However, for the NO(A) + Rg systems the KA-model is less successful, with systematic deviations being observed in the alignment moments, albeit within the aforementioned general trend for a more negative $A^{(2)}_{0}(\theta)$ with increasing $N'$ that is also predicted by the KA model. To test the degree of agreement of the KA model with the experimental data, we performed SVD fits of the DCSs to the averaged experimental images, assuming the $A^{(2)}_{0}(\theta)$ and $A^{(2)}_{2}(\theta)$ predicted by a KA model. Although the returned DCSs were essentially identical to those shown in Fig. 7, significant systematic residuals between the experimental and fitted images were observed which were consistent with the difference between the alignment moments reported in Fig. 7 and those predicted by the KA model. As a result, we are confident that KA conservation does not provide an accurate model of the observed angular momentum polarization, suggesting that, as for NO(A) + Rg, a purely hard-shell potential does not provide an accurate representation of the NO(A) + N₂ interaction. $A^{(2)}_{0}(\theta)$ is consistently larger for $j' = 8$ than for $j' = 0$, suggesting that rotational excitation of the N₂ results in NO(A) rotating with N' more parallel to k. We are unaware of any general models for angle-resolved angular momentum correlations in diatom-diatom scattering, and hence do not further elaborate on this observation at this stage, but hope that it will stimulate further theoretical effort in this direction.

As noted in Section III, we believe that the methodology presented here is particularly susceptible to systematic error in the determination of the $A^{(2)}_{2}(\theta)$ moment. As a result, we do not discuss the reported $A^{(2)}_{2}(\theta)$ moments further. We suggest that in future work, $A^{(2)}_{2}(\theta)$ could be more effectively determined using measurements in additional experimental geometries, in order to obtain images with different dependences of this moment on the azimuthal scattering angle.

V. CONCLUSION

There were two main aims of this paper. First, to demonstrate to what extent it is possible to extract the DCSs and alignment moments as a function of unobserved collider internal energy for a diatom-diatom collision system. Second, to apply this to the
NO(A) + N\(_2\) system, and thereby determine as much as possible about the (unknown) NO(A)-N\(_2\) PES, and more generally the stereodynamics of diatom-diatom RET with kinematically similar rotors.

We have shown that it is possible to extract DCSs and angle-resolved alignment moments as a function of internal energy of the N\(_2\) collider in the NO(A) + N\(_2\) system, but only for coarse-grained amounts of energy transferred to N\(_2\) rotation. We have been able to provide detailed information about the stereodynamics of RET of NO(A) with N\(_2\) for the first time. The presence of a sharp forward scattered peak for a range of NO(A) and coincident N\(_2\) rotational states provides evidence of a well in the NO(A)-N\(_2\) PES in a linear geometry, supporting previous spectroscopic and computational investigations.\(^{44}\) The DCSs as a function of \(N'\) and \(j'\) are consistent with repulsive interactions of moderate anisotropy, similar to those seen for NO(A) + Ne with respect to the NO(A) and of similar moderate anisotropy with respect to N\(_2\). The rotational excitation in the two products is not strongly correlated, as even the highest-\(N'\) NO(A) products are produced substantially in coincidence with low-rotational energy N\(_2\). The alignment moments describe angular momentum polarization consistent with repulsive interactions and broadly similar to the behavior observed for NO(A) + Rg, but inconsistent with a KA model, suggesting that a purely hard-shell potential is not a good model for the NO(A) + N\(_2\) PES.\(^{34\text{-}37}\)

Although we have succeeded in our overall aim, of measuring the stereodynamics as a function of correlated internal energy in the products, the initial distribution of rotational states of N\(_2\) in the molecular beam, and the small N\(_2\) rotational constant relative to the FWHM of the collision energy distribution, prevented the determination of the stereodynamics for discrete N\(_2\) rotational state-to-state transitions. In principle, this could potentially be overcome in future experiments, perhaps by application of Stark-effect selection of NO molecular beam velocity, as demonstrated for NO(X) + Rg scattering by van de Meerakker and co-workers.\(^{12\text{-}14}\) Additional improvements would come from a greater degree of state-selection in the collider, which in the case of a closed-shell molecule like N\(_2\) is essentially restricted to enhanced cooling in the supersonic expansion. The other primary restriction on the determination of the DCS and alignment moments comes from the difficulty of analyzing the ‘crushed’ image of overlapping product scattering spheres. In order to determine all of the alignment moments scattering out of the image plane must be measured, and even with high-collision energy resolution, in a ‘crush’ image ions for different collider product states scattering with different azimuthal angles will overlap on the detector. A dramatic improvement would therefore be made by measuring the full 3-d scattering sphere directly, for example using a time-resolved imaging detector such as the PImMS sensor.\(^{45}\)
SUPPLEMENTARY MATERIAL

See the Supplementary Material for details of fitting to simulated data to determine the limiting energy-resolution in the image basis functions, the results of fitting to experimental data to determine the range of collider energy basis functions required, and example fits to experimental data with and without angular momentum polarization.

ACKNOWLEDGEMENTS

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REFERENCES

FIG. 1. Newton diagrams for the collision of NO(A) with N$_2$ at $<E_{col}> = 797$ cm$^{-1}$ overlaid on $V + H$ experimental images for product state $N' = 11$. Arrows indicate the velocity vectors of the colliders: $v_{NO}$, $v_{N_2}$, the center of mass velocity: $v_{CoM}$, and the relative velocity vector, $k$. The rings represent the mean velocity of NO scattered into the plane of the detector, for N$_2$ rotational transitions: (a) $j = 0 \rightarrow j' = 0, 2, 4, 6, 8, 12, 14$, and $j = 1 \rightarrow j' = 1, 3, 5, 7, 9, 11, 13, 15$, (b) $j = 0 \rightarrow j' = 0, 6$ and 8. $k_p$ indicates the propagation direction of the probe laser beam.

(Single column)
FIG. 2. Experimental images averaged over all individual acquisitions, for the collision of NO(A) with N\textsubscript{2} at $\langle E_{\text{col}} \rangle = 797$ cm\textsuperscript{-1}, for final NO(A) rotational levels $N' = 3$ and 5-11, for both V and H probe laser polarizations.

(Double column)
FIG. 3. Difference (V-H) images constructed from the averaged experimental data images shown in Fig. 2, for product states $N' = 3$ and 5-11. Blue is negative intensity and red is positive intensity, each image is separately normalized.  
(Double column)
FIG. 4. Single acquisition experimental images for the collisions of NO(A) with N$_2$ at $\langle E_{cm} \rangle = 797$ cm$^{-1}$, for final NO(A) rotational levels $N' = 5, 8$ and 11, with both V and H probe laser polarisations (Row 1 and 3, labelled Exp V and H), and simulated images returned by the atomic fitting routine (Row 2 and 4, labelled Fit V and H). Note that the circular outer edges to the fits clearly fail to capture the asymmetries progressively apparent in the experimental data with increasing $N'$. (Single column)
FIG. 5. Single acquisition experimental images for the collisions of NO(A) with N₂ at \( \langle E_{\text{col}} \rangle = 797 \text{ cm}^{-1} \), for final NO(A) rotational levels \( N' = 3 \) and 5-11, with both V and H probe laser polarizations (Exp V and H), and simulated images returned by the molecular fitting routine (Fit V and H). (Double column)
FIG. 6. (a) Residual images from the atomic fitting code (blue = negative, red = positive) for final rotational levels $N' = 5, 8$ and 11. (b) Residual images from the molecular fitting code, with the same colour intensity scale as (a). (c) A projection of a strip of the experimental, fitted and residual images, running perpendicular to $\mathbf{k}$ between the dashed lines marked in (a) and (b). Black: experimental image, dashed blue: fitted image from the atomic code, dashed red: fitted image from the molecular code, blue: from residual image in (a), red: from residual image in (b).

(Single column)
FIG. 7. Differential cross sections and rotational angular momentum alignment moments for the collisions of NO(A) with N\textsubscript{2} at \(E_{\text{coll}}\) = 797 cm\textsuperscript{-1}, for final NO(A) rotational levels \(N' = 3\) and 5-11. Black line: N\textsubscript{2} internal energy \(j' = 0\), red line: N\textsubscript{2} internal energy \(j' = 6\), blue line: N\textsubscript{2} internal energy \(j' = 8\). Error bars represent 95% confidence limits. (Double column)
FIG. 8. Relative excitation probabilities for different levels of energy transfer to the N₂, plotted as a function of NO(A) rotational level, neglecting forward scattering angles covered by data excluded from the fitting procedure and scaled to sum to unity for each NO(A) state. Black filled squares: $j' = 0$, red filled circles: $j' = 6$ and blue filled triangles: $j' = 8$. Mean and standard error of the mean from individual fits to the independent single experimental acquisitions. $N' = 11$ is not reported as the inclusion of forward scattering angles in that case prevents a direct comparison with the other $N'$. (Single column)
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