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Rotationally inelastic scattering of NO(A^2Σ^+) + Ar: Differential cross sections and rotational angular momentum polarization

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We present the implementation of a new crossed-molecular beam, velocity-map ion-imaging apparatus, optimized for collisions of electronically excited molecules. We have applied this apparatus to rotational energy transfer in NO(A^2Σ^+, v = 0, N = 0, j = 0.5) + Ar collisions, at an average energy of 525 cm⁻¹. We report differential cross sections for scattering into NO(A^2Σ^+, v = 0, N’ = 3, 5, 6, 7, 8, and 9), together with quantum scattering calculations of the differential cross sections and angle dependent rotational alignment. The differential cross sections show dramatic forward scattered peaks, together with oscillatory behavior at larger scattering angles, while the rotational alignment moments are also found to oscillate as a function of scattering angle. In general, the quantum scattering calculations are found to agree well with experiment, reproducing the forward scattering and oscillatory behavior at larger scattering angles. Analysis of the quantum scattering calculations as a function of total rotational angular momentum indicates that the forward scattering peak originates from the attractive minimum in the potential energy surface at the N-end of the NO. Deviations in the quantum scattering predictions from the experimental results, for scattering at angles greater than 10°, are observed to be more significant for scattering to odd final N’. We suggest that this represents inaccuracies in the potential energy surface, and in particular in its representation of the difference between the N- and O-ends of the molecule, as given by the odd-order Legendre moments of the surface. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4935962]

I. INTRODUCTION

Electronically excited radical species, such as OH, CN, CH, and the subject of this study, NO, are important in the chemistry of a range of gas-phase environments, including combustion,1 technological plasmas,2 and planetary atmospheres.3 They are also frequently generated when optical probe methods are used to interrogate their ground electronic states.4 Within these environments, they will undergo collisions with the surrounding atoms or molecules, and there is thus a requirement to understand and be able to model these excited-state collisions. Experimentally, significant effort has been expended on determining the electronic quenching rate constants of these radicals with different atomic and molecular collision partners.5–7 There have also been a substantial number of studies that have measured state-to-state vibrational, or rotational energy transfer (RET), cross sections or rate constants within the electronically excited states.8–11 However, there have been very few studies of the stereodynamics of inelastic energy transfer within electronically excited states, generally as a result of the additional challenges imposed by their short lifetime. This is unfortunate, as measurements of the stereodynamics of collisions have been shown to be an excellent method to test the results of scattering theory,12 and hence of electronic structure calculations of the forces acting in the collisions, as described by the potential energy surface (PES).8,13,14

In contrast, the ground electronic states of small free radicals such as NO and OH have seen extensive experimental and theoretical study. Most relevant to this work has been the recent application of crossed molecular beams (CMBs) with resonance enhanced multi-photon ionization (REMPI) velocity-map imaging (VMI) detection to study the stereodynamics of inelastic collisions resulting in RET. As an example of the power of this technique, Brouard and co-workers have used hexapole state-selection to perform fully state-to-state RET in collisions of NO(X^2Π) with rare gas colliders, determining the differential cross section (DCS) and scattering angle-resolved rotational angular momentum polarization moments.15–22 Quantum scattering (QS) calculations on ab initio PESs show excellent, near quantitative agreement, with the experimental measurements. The DCSs show a strong dependence on the symmetry of the final rotational state, a result of interference effects arising from collisions sampling the different ends of the molecule. Another example of interference effects has been observed in the work of van der Meerakker and co-workers, who have used a Stark decelerator to provide extremely high collision energy resolution (0.3 cm⁻¹) in NO(X) + He, Ne, and Ar collisions.23–26 In the forward scattered regions of the DCS, they observe very rapid oscillations as a function of angle, the result of interference arising from diffraction.

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As noted, stereodynamical measurements of excited electronic states of molecules are comparatively rare. One approach that has been successfully applied by several groups, including our own, is to use an optical-optical double resonance technique to prepare and probe rotational angular momentum polarization in the excited state in the presence of a thermal collider bath. Examples of this include our own work using non-linear polarization spectroscopy on OH(A₂Σ⁺)+Ar/He,⁷⁷-⁷⁸ the work of Brouard and co-workers on NO(A₂Σ⁺)+Ar/He and OH(A₂Σ⁺)+Kr/Ar/He using Zeeman quantum beat spectroscopy;¹⁴-²⁹ ³³ our work on collisions of CN(A²Π)+ Ar using frequency modulated transient stimulated emission spectroscopy;³⁴-³⁶ and accompanying theoretical developments.³⁷-³⁹ In these experiments either the collisional removal of the initial polarization is observed or alternatively the degree of preservation of the prepared polarization in a state-to-state transfer process is measured. However in stereodynamical terms, these experiments are all intrinsically limited by the isotropic distribution of relative velocities of the bulk environment in which the polarized molecules are prepared.

In experiments performed at Sandia National Laboratory, we have previously shown that it is possible to perform state-to-state resolved RET in NO(A)+ rare gases with a CMB-VMI apparatus.⁴⁰-⁴² An initial molecular-beam pulse of NO(X) seeded in a rare gas was crossed with another molecular-beam pulse of the chosen collider gas. NO(A, v = 0, N = 0, j = 0.5) was then prepared in the crossing region of the molecular beams via excitation on the Q₁(0.5) transition of the A₂Σ⁺-X²Π(0,0) band. This laser pulse provides a zero time for the experiment, whilst the fluorescence lifetime of NO(A) (∼200 ns) limits the time available for collisions.⁴³-⁴⁵ This well-defined short time for collisions is in marked contrast to a conventional ground-state scattering experiment, where collisions occur throughout the molecular beam pulses. In ground-state scattering experiments, slower moving products in the laboratory frame preferentially build up in the probe volume, and a density-to-flux transform is required to remove what can be a very substantial bias from the experimental data.⁴⁶ In the excited-state experiments, the well-defined start and short build-up time mean that all scattered products are probed with equal sensitivity, removing the need for a density-to-flux transform. Scattered NO(A, v = 0, N') products were probed state-selectively using resonant excitation on the E²Σ⁺-A²Σ⁺(0,0) band at wavelengths near 600 nm, followed by ionization with a photon at 532 nm and VMI. In scattering of NO(A) from Ne at a collision energy of 500 cm⁻¹, we observed strong angle-dependent oscillations in the rotational angular momentum alignment, which were reproduced by quantum scattering calculations.⁴² This oscillatory behavior is in stark contrast to the equivalent collisions in the NO(X)+ Ne system, where the rotational angular momentum alignment follows a smooth trend with scattering angle, matching the predictions of conservation of the angular momentum projection onto the kinematic apse (KA) for the collision. This KA behavior is consistent with the rigidity of the repulsive wall in the NO(X)+Ne PES.¹⁷ In contrast, the NO(A)+Ne repulsive wall is much less steep than NO(X)+Ne, which led us to speculate that the observed different polarization dynamics was a consequence of this “soft” repulsive potential.⁴⁸,⁴⁹

In this paper, we present a new CMB-VMI apparatus, constructed at Heriot-Watt University, and designed specifically for collisional energy transfer studies of electronically excited molecules. We describe the design of the molecular beam sources and scattering chambers, VMI ion optics and detection system. We present the first polarization-sensitive velocity-map ion-images for NO(A, v = 0, N' = 3, 5, 6, 7, 8, and 9) formed by RET of NO(A, v = 0, N = 0, j = 0.5) in collisions with Ar at an average collision energy of 525 cm⁻¹, together with the results of collision-energy averaged close-coupled QS calculations performed using a literature ab initio PES.⁵⁰ We describe a new Monte-Carlo routine to simulate the experimental ion-images from assumed DCS and scattering angle-dependent rotational alignment moments, and its implementation in a back-fitting procedure to extract these directly from the experimental images. We discuss the observed scattering dynamics in the context of the results of the QS calculations, highlighting the dynamical similarities and differences between NO(A)+Ar and the previously studied NO(A)+Ne, and expand on the origins of the contrast between collisions of NO(A) and NO(X) with rare gases.

II. METHODS

A. CMB-VMI apparatus

This section provides a detailed description of a new CMB-VMI apparatus optimized for measurements of the collision dynamics of electronically excited species. The focus here is on the description of the instrument, with a discussion of the conditions under which the experiments reported in this paper were conducted reserved for part B of this section.

The apparatus described here is broadly similar in form to the compact CMB-VMI apparatus of Jansen et al.⁵¹ but optimized for collisions of electronically excited molecules. Two molecular beam source chambers are attached to a central scattering chamber, where the molecular beams intersect at 90° in the focal region of a set of VMI ion optics. Ions are accelerated along a grounded flight tube and focused onto a microchannel plate detector coupled to a phosphor screen, where the light generated by ion strikes is recorded using a CCD camera. Figure 1 shows a schematic of the crossed molecular beam sources and main scattering chamber.

The main scattering chamber is a “spherical square” (Kimball Physics, MCF600-SphSqd-F2E4A4), with DN100CF ports at the top and bottom, and an octagonal arrangement of ports arranged around the central axis, alternating between DN63CF and DN16CF. The molecular beam sources are formed from DN63CF cubes (Lewvac), connected to the main chamber at right angles via close couplers (Kimball Physics, MCF450-ClsCplr-E2). Each consists of a differentially pumped chamber and contains a pulsed valve (Parker Series 9 General Valve) with a 500 µm diameter orifice. The molecular beams generated by these valves pass into the main chamber through 500 µm diameter electroformed skimmers (Beam Dynamics, Inc.), positioned 20 mm from the valves. In order to minimize the distance between the beam sources...
The scattering chamber and source chambers, viewed as a cut-through a vertical plane containing one of the molecular beam axes.

and scattering region, the skimmers are mounted on custom flanges that project into the main scattering chamber. The valves are mounted on rods attached to the rear flange of each source chamber, allowing optimization of the beam-skimmer distance and easy removal for routine replacement of valve components. Guide rods attached to the skimmer mounting flange pass through holes in the valve faceplate to ensure a reproducible alignment of the valve and skimmer.

The main and detector chambers are linked by a DN63 flight tube, with a gate valve (V AT Series 10) allowing isolation of the detection chamber. The main chamber and source chambers are pumped by turbo molecular pumps (Edwards nEXT300D and EXT75DX, respectively), and the detector region is separately evacuated by a further EXT75DX pump. The turbomolecular pumps are backed by dry scroll pumps to ensure an oil-free vacuum (Edwards nXDS10 and two nXDS6). Base pressures in the scattering chamber and detector regions are \(<1 \times 10^{-8} \text{ mbar}\), with a typical pressure during scattering experiments of \(1 \times 10^{-7} \text{ mbar}\).

Measurement of RET in electronically excited NO(A) imposes some unique constraints on the optimal ion optics design, which arise from the preparation and probe scheme. We first explain this scheme and its implementation in detail, outlining these constraints, and then discuss the ion-optics design.

The NO(A) state has a fluorescence lifetime of \(\approx 200 \text{ ns}\), during which time even the fastest moving molecules will travel \(<1 \text{ mm}\). As such, it is essential to prepare the NO(A) molecules in the crossing region of the two molecular beams. NO(X) is excited on the \(Q_1(0.5)\) transition of the \(\text{A} \leftarrow \text{X}(0-0)\) band, using the frequency-doubled output of a Nd:YAG pumped dye laser (Sirah CTSG/Continuum Surelite II-10), to form state-selected NO(\(\text{A}^2\Sigma^+; v = 0, N = 0, j = 0.5\)). A delay, typically 400 ns, is then introduced during which NO(A) can undergo inelastic collisions. The optimum length of this delay is determined by the competition between loss of NO(A) via fluorescence and the rate of RET. Subsequently, scattered NO(A, \(v = 0, N^\prime\)) molecules are probed in a \((1 + 1')\) REMPI scheme. A second Nd:YAG pumped dye laser (Sirah CSTR-DA24/Continuum Surelite I-10) generates tunable 600 nm light and excites the NO(A) on the \(E^2\Sigma^++A^2\Sigma^+(0,0)\) band. The NO \(E^2\Sigma^+\) produced is then ionized by a small fraction of the 532 nm light from the probe Nd:YAG pump laser. This ionization pulse is optimally delayed from the resonant probe pulse by 4 ns, determined to maximize the \(1 + 1'\) ion signal. The A and E states have very similar rotational and fine-structure constants, and the \(f_1-f_1\) and \(f_2-f_2\) transitions (e.g., \(R_1(5)\) and \(R_2(5)\)) are separated by much less than the Doppler width or laser bandwidth. The spectrum thus displays only single R and P branches, and this ionization scheme probes \(N^\prime\)-states, the average of the \(j^\prime = N^\prime - 0.5\) and \(j^\prime = N^\prime + 0.5\) spin-rotation states. The pump scheme and probe scheme are illustrated schematically in Fig. 2.

The pump and probe laser beams counter-propagate along the axis bisecting the angle between the two molecular beams. Measurement of the NO(A) rotational angular momentum alignment is best performed with images recorded with the polarization of the probe laser either lying in the plane of the two molecular beams (horizontal, H), or perpendicular (vertical, V). The polarization of the probe laser is controlled using a photo-elastic modulator (PEM-90, Hinds Instruments), to which the timing sequence of the rest of the experiment is synchronized. The 532 nm fluence is maintained in the saturating regime and to further minimize any sensitivity to its polarization is introduced to the chamber along two orthogonal axes. One beam has its polarization along the propagation direction of the probe beam, while the second...
ionization beam co-propagates with the probe beam, but with orthogonal polarization. In this way, a consistent probe-ionization geometry is maintained as the probe polarization is switched, with the ionization light polarized along two axes orthogonal to the polarization of the probe beam.

The fluences of all 3 laser beams were carefully controlled to optimize the experimental signal-to-noise. Under pump fluence conditions in which a sufficient population is prepared in the A-state, a significant fraction of the NO(A) will undergo ionization via absorption of a second 226 nm photon. This produces an intense signal at the velocity of the NO-containing molecular beam, which must be discriminated against by the ion-optics and detector. The pump fluence (0.65 mJ cm⁻² in a 2 mm diameter beam) was therefore set to provide the maximum measured A-state population whilst minimizing this 226 + 226 nm ionisation. The E-A (0,0) band is very strong, and to preserve polarization sensitivity, the probe fluence was reduced below 0.65 µJ cm⁻². To ensure that all prepared and scattered molecules were detected with equal probability, the probe beam was unfocussed, with a diameter of 3 mm. Finally, the ionization beams also had a diameter of 3 mm, with a fluence in the range 4–40 mJ cm⁻², depending on the quantum state probed.

The two principal constraints for the ion optics design are thus the relatively large volume over which scattered molecules are produced and probed, and the discrimination against pump-beam generated ions. The ion optics design was aided by ion trajectory simulations (SIMION 8.1, Scientific Instrument Services, Inc.), and the final design is described in more detail in the supplementary material.⁵²

The detector consisted of a pair of microchannel plates (MCPs) and a phosphor screen (Photolon, 40 mm active diameter, P47 phosphor), with the output from the phosphor imaged using a CCD camera (Basler scA780-54fm, 782 × 582 pixel array), and an avalanche photodiode (SensL, MicroFM-10035-X18). The front MCP was grounded while the voltage applied to the rear MCP plate was pulsed using a fast high-voltage switch (DEI PVX4140, ≤25 ns rise time). Typically, this voltage was maintained at 950 V and then switched to 1550 V for 100 ns, coinciding with the arrival of the packet of ions generated by the resonant E-A probe laser. This efficiently discriminated against any signals from other mass/charge ratios, and more significantly those arising from the pump laser ionization. A conical stainless steel shield surrounding the approach to the detector surface was employed to shield the ions from stray fields associated with the high-voltage wires supplying the detector, and all insulating mounting components were made from electrostatically dissipative plastic (Semitron 225, Quadrant Plastics), to avoid distortion of the images resulting from static electrical build-up.

Experimental timings were set using a digital pulse generator (Quantum Composers, 9520 series, 250 ps resolution) under computer control. Timing sequences, data acquisition, handling, and storage were automated using software custom-written on the LabVIEW™ (National Instruments) platform. Synchronization of the 10 Hz data acquisition sequence to the 50 kHz cycle of the PEM was achieved by frequency down-counting using a counter/timer and digital I/O module (National Instruments, NI 9402). Electronic noise in the camera was rejected by setting all pixels below a preset threshold to zero intensity for each image, prior to summation. Signals from the photodiode were averaged on an oscilloscope (Lecroy, Waverunner 44Xi, 400 MHz bandwidth, 10 GS/s) over batches of 100-200 laser shots before being transferred to the PC and integrated to monitor ion signal during experiments, and when necessary to record REMPI spectra.

B. Experimental details

A 10% NO in Ar (BOC, 99.998%) molecular beam, generated with a backing pressure of 3 bar, was crossed with a pure Ar beam (99.998%) at 5 bar backing pressure. Under these conditions, the velocities of the beams were measured to be 593 ms⁻¹ and 617 ms⁻¹, respectively, with FWHM of 52 ms⁻¹, giving a Gaussian distribution of collision energies with a mean of 525 cm⁻¹, and a FWHM of 64 cm⁻¹. Further details of how these measurements were performed may be found in the supplementary material.⁵²

Images were collected for final states N’ = 3, 5, 6, 7, 8, and 9 by probing R(N’)/ transitions of the E ← A (0-0) band. Camera frames for individual laser shots were collected in batches of 100-200 over a sequence of experimental cycles. First, a batch of frames with vertical probe laser polarization and synchronized molecular beam pulses were acquired (V signal). The Ar collider molecular beam pulse was then delayed by 1 ms (sufficiently late to eliminate all collisions with the NO(A)), and a second batch of frames were acquired (V background). This background image contains non-scattered ion signals that were not discriminated against by the detector gating. The most significant of these is a signal at the velocity of the NO-containing molecular beam, which arises from 2-photon non-resonant ionization of NO(A) by the 532 nm ionization beam (as included in Fig. 2). The probe laser polarization was then rotated to horizontal, and equivalent H signal, and background frames were acquired. This cycle of vertical and horizontal probe scattering and background signals was repeated as the probe laser was step-scanned (typically over 16 points in 5 × 10⁻⁴ nm steps) over the Doppler width of the chosen E ← A transition. Finally, this Doppler scan was typically repeated 5-10 times to give a single measurement of the scattering. Multiple measurements were taken on different days and were subsequently summed for each final state, with each final image containing from 512 000 frames for stronger signals up to 960 000 frames for the weakest signals for N = 9.

C. Theoretical methods

The aim of the experiments is to measure the DCS, and scattering-angle-dependent rotational angular momentum polarization, for RET of NO(A). We express the angular momentum polarization in terms of Hertel-Stoll renormalized real polarization parameters, A_{ij}^{R}(\theta), defined in the scattering frame of reference (x,y,z) whose z axis lies along the initial relative collision velocity, k, with the xz plane defined to contain the post-collision relative collision velocity k.⁵³
One-photon probing with linearly polarized light restricts the measurable moments to \( K = 2 \), while the reflection symmetry of the system through the \( xz \) plane means that for even \( K \), only the \( A^{(K)}_0(\theta) \) parameters are non-zero. As discussed in Section II D, the experimental geometry employed in these experiments yields images with almost no dependence on the \( A^{(2)}_1 \) moment, and calculated values of this moment are not reported in this paper.

The DCS and second rank alignment moments have been calculated in a close-coupled scattering calculation using the HIBRIDON suite of codes.\(^{54-56}\) The calculations employ the PES of Kłos et al., which was generated using the spin-restricted coupled cluster method with single, double, and perturbative triple excitations (RCCSD(T)), and then rescaled to match the experimental zero point energy for this system.\(^{50}\) Calculations were performed at 11 individual energies in the restricted coupled cluster method with single, double, and triple excitations (RCCSD(T)), which was generated using the spin-restricted coupled cluster method with single, double, and perturbative triple excitations (RCCSD(T)), and then rescaled to match the experimental zero point energy for this system.\(^{50}\)

DCSs and alignment moments for each final \( N' \) are obtained from fully open-shell calculations of these quantities for each final \( j' \), the DCSs for each \( N' \) being the sum of the DCSs for the two \( j \) states of the same \( N \), and the alignment moments being a DCS-weighted sum of the results for the two \( j \) states. The NO(A) was treated as a rigid rotor with \( B = 1.9869 \text{ cm}^{-1} \) and spin-rotation coupling constant of \( \gamma = -0.0027 \text{ cm}^{-1}. \)\(^{57}\) For each energy, scattering calculations were performed for total angular momentum, \( J_{\text{tot}} \), up to 450.5, with a basis of rotational states up to \( N = 20 \). The hybrid propagator of Alexander and Manolopoulos employed in the numerical solution of the close-coupled equations extended from 4.2 to 200 bohr.\(^{55}\)

It has previously been found that the scattering-angle dependent alignment in the NO(X) + Rg systems is well-predicted by the KA model.\(^{21,22,58}\) In the limit of a hard shell potential, the component of the rotational angular momentum along the “kinematic apex” vector, \( \mathbf{a}_k = \mathbf{k}' - \mathbf{k} \), is conserved during the collision. For an ensemble of molecules that are initially not rotating, the result is that all final rotational angular momenta lie in the plane perpendicular to \( \mathbf{a}_k \) for any \( \mathbf{k}' \), i.e., any scattering angle. The moments thus do not depend on the PES and may be simply determined in the scattering frame knowing \( \mathbf{k} \) and \( \mathbf{k}' \).\(^{52}\) In contrast to the NO(X) + Rg systems, the previous experiments on the NO(A) + Ne system showed strong deviations from the KA-model.\(^{52}\) We have therefore also calculated the KA-model rotational alignment parameters for comparison to the QS and experimental results.

D. Data analysis

In principle, the scattering images are sensitive to the DCS as well as the second-rank tensor moments describing the rotational angular momentum distribution. However, extraction of this information from the images is non-trivial for a number of reasons, the most significant of which is the influence of kinematic blurring, i.e., the fact that signals from a range of scattering angles occur in the same pixel as a result of the distributions of initial velocities of the colliders. Rather than adopt a direct extraction approach to the analysis of images such as that described by Suits et al.,\(^{59}\) we have chosen to follow a basis image simulation and fitting methodology similar to that of Brouard and co-workers.\(^{15-22}\) We note that cancellation of the alignment dependence by construction of a composite image is not possible in a system in which only parallel, i.e., P or R branch transitions are present, such as the \( \Sigma^+ \Sigma^- \) probe scheme used here.\(^{60}\)

Fitting to extract only the DCS, using assumed values of the angular momentum polarization, significantly simplifies the problem, as previously demonstrated by Brouard and co-workers.\(^{15}\) In that work, a KA model was used to predict the angular momentum polarization. In our previous work on NO(A) + Ne scattering, the largest deviations between experiment and QS calculations were found to be in the DCSs, while the QS angular momentum polarization was in good agreement with experiment, but in poor agreement with a KA prediction.\(^{42}\) To test the sensitivity of the extracted DCS to the polarization moments, we have therefore run separate fitting procedures assuming either the angular momentum polarization moments from the QS calculations reported in this paper, or the moments predicted by a KA model, which we henceforth refer to as either the QS-fit or KA-fit. In addition, since the relative velocity vector, \( \mathbf{k} \), and the propagation direction of the probe laser are very close to perpendicular for this particular collision energy, the images are only sensitive to the \( A^{(2)}_0(\theta) \) and \( A^{(2)}_1(\theta) \) moments and are almost completely insensitive to the \( A^{(2)}_1(\theta) \) moment.\(^{22}\) In the Secs. III and IV that follow, only the \( A^{(2)}_0(\theta) \) and \( A^{(2)}_1(\theta) \) moments are considered.

Simulation of the basis images proceeded in the following fashion. The DCS was expressed as a suitably weighted sum over Legendre polynomials, \( P_\lambda(1 - (\theta/90^\circ)) \), and a pair of basis images corresponding to the V and H probe polarizations, respectively, were simulated for each value of \( \lambda \), up to an empirically determined maximum. This Legendre expansion provides a compact description of very forward-scattered DCSs, as the functions are sharply-peaked around \( \theta = 0^\circ \). To generate images from these DCS basis functions and the assumed alignment moments, the final positions on the detector of a set of \( 50 \times 10^6 \) trajectories representing individual scattering events were first calculated using a Monte Carlo simulation. The sampling involved selection of the initial velocities of the two colliders; which were assumed to lie along fixed, perpendicular directions, with the speeds drawn from Gaussian distributions representing the measured speeds of the two beams.\(^{52}\) The center of mass velocity, \( \mathbf{v}_{\text{cm}} \) and \( \mathbf{k} \) were determined from the initial collider velocities, and conservation of energy and momentum were used to determine the center of mass speed of the scattered products. A pair of center-of-mass scattering angles (\( \theta, \phi \)) were selected from an isotropic distribution and used with the quantities already determined to calculate the laboratory-frame velocity. Finally, a velocity, \( \mathbf{v}_{\text{exp}} \) selected to represent the effect of experimental blurring factors affecting the arrival position of ions was added to the calculated laboratory-frame velocity to
obtain the detected laboratory-frame velocity. Further details of the determination of the speed distributions of the two molecular beams and the calculation of \( v_{\text{exp}} \) are presented in the supplementary material. The final position on the detector for each sample is then calculated using the velocity calibration of the images, determined from images of the photolysis of \( \text{O}_2 \) in a manner which is now standard for VMI experiments.

In order to generate images from the set of Monte Carlo samples, the pixel corresponding to each ion’s final position was recorded, as well as the selected scattering angles and the direction of \( k \) relative to the propagation direction of the probe laser. For each basis function, the intensity for each pixel \( I(a, b) \) was then calculated as a sum over all \( n_{ab} \) sampled collision events assigned to the pixel \((a, b)\), weighted by a detection sensitivity,

\[
I(a, b) = \sum_{i} P_{\lambda} \left(1 - (\theta_i/90^\circ)\right) I_{\text{det}}(\phi_i, k_i, A^{(K)}_{q^\pm}(\theta_i), \chi). \tag{1}
\]

Expressions for \( I_{\text{det}} \) for both H and V geometrical experiments are given by Brouard et al., where \( \phi \) is the azimuthal scattering angle, \( k \) is the relative collision velocity, \( \chi \) is the angle between the scattering plane and the electric polarization vector of the probe laser, and \( A^{(K)}_{q^\pm}(\theta) \) is the QS calculation (QS-fit) or KA model (KA-fit) scattering angle dependent polarization moments.

The collisions align \( N' \), which subsequently couples to both the electron spin, \( S = \frac{3}{2} \), and the nuclear spin of \( ^{14}\text{N} (I = 1) \), both of which are initially unpolarized. We do not spectroscopically resolve either the nuclear hyperfine, \( F' = j' + I \), or the spin-rotation, \( j' = N' + S \), levels, and consequently in principle these couplings would result in quantum beat patterns in the measured alignment. However, as the scattering events happen stochastically during the 400 ns pump-probe delay, and the quantum beat time scales for both fine and hyperfine interactions are much shorter than this, we observe a time-averaged reduction in the magnitude of the measured alignment. The spin-rotation and hyperfine splittings are consistent with Hund’s case-b\(_{ij}\)J coupling, and we observe reduced alignment moments given by

\[
A^{(K)}_{q^\pm}(\theta, N'_\text{obs}) = A^{(K)}_{q^\pm}(\theta, N') \tilde{g}^{(K)}(N'), \tag{2}
\]

\[
\tilde{g}^{(K)}(N') = \sum_{j'F'} \frac{(2F' + 1)^2(2j' + 1)^2}{(2S + 1)(2I + 1)} \left\{ j' j' K \left( \begin{array}{ccc} F' & F' & K \\ N' & N' & S \end{array} \right) \right\} \left( \begin{array}{ccc} j' & j' & I \end{array} \right) \right\}^2. \tag{3}
\]

The most significant reduction for the states probed is for \( N' = 3 \), where \( \tilde{g}^{(K)}(N' = 3) = 0.615 \), which increases to 0.940 for \( N' = 9 \). The appropriate calculated \( \tilde{g}^{(K)}(N') \) factors were included in the forward simulations for all \( N' \).

Basis images were simulated for Legendre polynomials up to order \( \lambda = 15 \), which was a sufficiently large basis that the simulated images described all of the major features of the experimental images. A linear combination of basis images was fit to the experimental images using a downhill simplex \( \chi^2 \)-minimization algorithm, with the constraint that the DCS remain positive applied. Coefficients of the expansion of the QS DCS were taken as an initial trial solution. It was verified for \( N' = 8 \) that replacing the QS results with a random initial set of coefficients returned the same solution, giving confidence in the ability of the algorithm to return the global best fit, and the QS results were employed as starting points purely to reduce the number of iterations of the fitting code required to achieve convergence.

### III. RESULTS

Figure 3 shows the sum of images acquired in the H and V geometries for \( N' = 9 \) as a false-color intensity map, superimposed with a Newton diagram indicating the mean laboratory-frame velocities of the incident molecular beams, the relative collision velocity, \( \mathbf{k} \), the velocity of the center of mass, \( \mathbf{v}_{\text{cm}} \), and a ring representing the in-plane final scattering velocities. A beam spot region is visible outside the scattering ring in the forward direction, resulting from imperfect subtraction of the background signal produced from non-resonant 2-photon ionization of \( \text{NO}(A) \ N' = 0 \). The artifact is largest for this product \( N' \), as the small total scattering cross section into this final level required an increased 532 nm ionization fluence to achieve an acceptable number of scattered ions per laser shot. Figure 4 shows the images acquired in the H and V geometries for all of the observed product states, \( N' = 3, 5, 6, 7, 8, \) and 9. The images clearly show that all of these product states are strongly forward scattered, and that only for the highest observed state, \( N' = 9 \), is there appreciable intensity in the sideways scattering. The strong forward scattering for \( N' = 3, 5, 6 \)

![Newton diagram showing the initial velocities of the colliders, \( v_{\text{NO}} \) and \( v_{\text{Ar}} \), the relative velocity \( \mathbf{k} \), and centre of mass velocity \( v_{\text{cm}} \)-superimposed on the sum of the V+H images for the \( N' = 9 \) state. The scattering ring, indicating possible values of the final lab frame velocity in the scattering plane, is indicated by the white circle.](http://example.com/figures/newton_diagram.png)
FIG. 4. Experimental ion-images for the scattering process NO(A, v = 0, N = 0) + Ar → NO(A, v = 0, N′) + Ar at an average collision energy of 525 cm⁻¹, for the two probe laser polarizations. Top row vertical polarization (V), bottom row horizontal polarization (H).

makes differences in the H and V images resulting from rotational angular momentum polarization difficult to discern, but differences are clearly visible for the sideways scattering in N′ = 7, 8, and 9.

FIG. 5. Three-dimensional plots of the V + H sum of the ion-images, for the product states N′ = 3, 5, 6, 7, 8, and 9. Left column, experimental results. Center column, results of the QS-fit described in the text. Right column, simulation using the full results of the QS calculation.

Figure 5 shows the sum (V + H) images for N′ = 3, 5, 6, 7, 8, and 9, with the experimental data in the left hand column, the results of the QS-fit in the center column, and simulations assuming the full results (DCS and alignment moments) of the QS calculations in the right hand column. Here, they are presented as 3-dimensional plots, to better illustrate the full dynamic range of the data. The sum images have a reduced dependence on the angular momentum polarization and are very strongly dominated by the DCS. Although the experimentally observed DCSs are very strongly forward scattered, these plots clearly show that there are also oscillatory features at wider scattering angles in the forward hemisphere (e.g., for N′ = 7), as well as very weak scattering to the backward hemisphere (e.g., N′ = 6). The sum images from the KA-fit are very similar to those from the QS-fit, as a result of the dominance of the DCS in the sum images, and we have not therefore presented them in Fig. 5.

Figure 6 shows color intensity maps of the difference (V-H) images for N′ = 3, 5, 6, 7, 8, and 9, with the experimental data in the top row, results of the QS-fit in the second row, simulations assuming the full QS results in the third row, and KA-fit results in the bottom row. The V-H image is dominated by the angular momentum polarization, although it is important to note that the intensity is still weighted by the DCS, hence the low intensity in the backward hemisphere for all of the images is the result of the low overall backward scattering probability. For N′ = 5, 6, 7, 8, and 9, the V-H images from experiment, QS-fit, and QS-simulation change sign multiple times as a function of scattering angle, clearly visible as changes between blue and red around the edges of the images. Although it is important to recognize that the projection of the rotational angular momentum onto the laser polarization changes as a function of scattering angle, that cannot be the cause of the multiple changes in sign observed in the forward scattering hemisphere. This is a clear indication of oscillatory behavior in A_0^{(2)}(θ) and A_2^{(2)}(θ), as previously observed in NO(A) + Ne. Figure 7 shows A_0^{(2)}(θ) and A_2^{(2)}(θ) from the QS calculations, together with the predictions of the KA model. Strong oscillations...
are seen in both QS-predicted moments as a function of scattering angle for all product states, in contrast to the smooth variation in the alignment moments predicted by the KA model. Returning to Fig. 6, the KA-fit results displayed in the bottom row are clearly not in agreement with the experimental data, indicating that the alignment moments are not well described by the KA model. The generally good agreement between the QS-fit and experiment in the number, location, and intensity of the oscillations indicates that the QS angular momentum polarization is in general agreement with experiment. This provides support for our decision to use the QS $A_{0}^{(2)}(\theta)$ and $A_{2}^{(2)}(\theta)$ as assumptions in our fitting procedure. The QS simulations in the bottom row are necessarily very similar to the fit results, as they use the same values for $A_{0}^{(2)}(\theta)$ and $A_{2}^{(2)}(\theta)$. Their agreement with the experiment is not as good as that of the fit results however, and because the DCSs are also contributing to the observed intensity in the V-H images, this is an additional indication that there are differences between the QS-fitted and QS-calculated DCSs. Returning to Fig. 5, the QS-fit results for the V + H images also show excellent agreement with the experimental results, accurately reproducing the sharp forward scattered peaks, as well as the lower intensity oscillations at larger scattering angles. The combined agreement shown between experiment and QS-fit in Figs. 5 and 6 therefore gives us confidence in the DCSs extracted using this fitting procedure.

Figure 8 shows the DCSs resulting from both the QS and KA-fits to the experimental data for $N' = 3, 5, 6, 7, 8,$ and $9$, together with the results of the QS calculations. The fit results have been scaled to the QS results by normalizing their areas. The QS-fit and KA-fit DCSs are very similar for all $N'$, the result of the strong dependence of the combined V and H images on the DCS, and suggesting that the DCSs extracted from the data are robust with respect to any inaccuracies in the assumed angular momentum polarization. The experimental and QS results agree very well for the extreme forward scattering peak in all cases for both fits. The high-frequency oscillations in the $0^\circ$ - $20^\circ$ range for $N' = 3$ in the QS calculations are diffraction oscillations, which are not resolved in the experiment owing to its finite angular resolution. We estimate from trial simulations that the angular resolution varies from $\sim 7^\circ$ for forwards and backwards to $\sim 5^\circ$ for sideways scattering. There is broad agreement at larger scattering angles for most $N'$, but not in the specific details of the location and amplitude of the oscillations in the DCS. That these are real differences, and not an artefact of limited experimental resolution is apparent from comparison of the experimental and fit result V + H images in Fig. 5. For example, for $N' = 6$, the amplitude of the feature at $45^\circ$ reported by the QS calculations results in a secondary maximum in the simulated V + H image that is clearly not present in the experiment or fit images. For $N' = 9$, the maxima at $20^\circ$, $45^\circ$, and $90^\circ$ in the QS DCS result in multiple oscillations in the simulated V + H image,
FIG. 7. (a)-(f) Rotational angular momentum polarization moments, $A_{2}^{(2)}(\theta)$ and $A_{2}^{(2)}(\theta)$, from QS calculations (red solid line) and from a KA model (blue dashed line) for $N' = 3, 5, 6, 7, 8$, and $9$, respectively.

which are also not present in the experimental or fit result images.

IV. DISCUSSION

We first discuss the angular momentum polarization. The results of the QS- and KA-fits to the data presented in Fig. 7 clearly show that the rotational alignment moments observed in these experiments are generally consistent with those predicted by the QS calculations, with large angle-dependent deviations from the KA-predictions. As previously noted, this is similar to the behavior of the alignment moments observed in our previous study of NO(A) + Ne.\textsuperscript{42} This is in stark contrast to the alignment moments observed in NO(X) scattering with either He, Ne, or Ar, for which the KA model has been found to describe the alignment near quantitatively.\textsuperscript{21,22,68} On closer inspection of Figs. 7 and 8, the angular locations of the maximum deviations from KA behavior are observed to be strongly correlated with the oscillations in the DCSs. Oscillations in the DCSs in similar diatom + rare gas scattering systems, including NO(X) + He/Ne/Ar\textsuperscript{15–17,21,68} and CO(X $^1\Sigma^+$) + Ne/Ar,\textsuperscript{59,69} are known to arise from interferences between multiple pathways to the same scattering angle, resulting from collisions sampling the different ends of the molecules. It therefore seems likely that the origin of the oscillations observed here and in the NO(A) + Ne system in both the DCS and the rotational alignment are also the result of related interference effects. Very recently, oscillations in the alignment have been observed in NO(X) + Kr scattering, reproduced by close-coupled QS calculations on a full ab initio PES, but not by rigid-shell QS calculations, suggesting a QM origin through interactions on the non-rigid regions of the PES.\textsuperscript{20} However, although oscillations in the alignment are observable in the experimental results presented here, the very strong forward scattering observed makes a detailed analysis and extraction of the alignment moments very challenging. As such, we suggest the NO(A) + Ne system would make a more suitable subject for an extensive study of the origin of this rotational alignment behavior, and we subsequently focus the rest of this discussion on the DCSs.

In comparison to those previously reported for NO(A) + Ne at the same collision energy, the most striking feature of the calculated and measured DCSs reported here is the

FIG. 8. (a)-(f) Differential cross sections from QS-fits to experiment (black), KA-fits to experiment (red), and from QS calculations (blue) for $N' = 3, 5, 6, 7, 8$, and $9$, respectively. Insets, expanded view of the 0°–70° scattering range.
extreme forward scattered peak visible for \( N' = 3, 5, 6, \) and 7.\(^{42}\) The NO(A)-Ne and NO(A)-Ar PESs are shown in Fig. 9.\(^{49}\) Both PESs show the shallow-gradient repulsive core previously identified as a possible cause of the oscillatory rotational angular momentum polarization in NO(A) + Ne, supporting our discussion in the previous paragraph.\(^{42}\) The most notable difference between the PESs is the presence of an attractive well on the NO(A)-Ar PES, reaching a minimum energy (i.e., maximum depth) of \(-70 \text{ cm}^{-1}\) at the N-end, whilst for the NO(A)-Ne PES the minimum is \(<-10 \text{ cm}^{-1}\) and is essentially isotropic, lying at long range beyond the 0 cm\(^{-1}\) contour in Fig. 9. Since the only differences in the systems lie in the PESs and the reduced masses (NO + Ar, \( \mu = 17.1 \text{ u; NO} + \text{Ne, } \mu = 13.3 \text{ u} \)), to test which is responsible for the observed dynamical differences, we have performed single collision energy QS calculations on both PESs (500 cm\(^{-1}\) for the NO(A)-Ar PES, and 504 cm\(^{-1}\) for the NO(A)-Ne PES) with the appropriate reduced masses for both Ar and Ne colliders. The calculated DCSs for \( N' = 5 \) and 7 are shown in Fig. 10. The sharp forward-scattered features at \( \theta < 10^\circ \) are present in both calculations performed on the NO(A) + Ar PES and absent from both performed on the NO(A) + Ne PESs. In contrast, the sideways scattered features are broadly similar in all cases for both \( N' = 5 \) and 7. This clearly shows that the changes in the PES, rather than in the reduced masses, are responsible for the differences in the DCSs observed for NO(A) + Ar and NO(A) + Ne.

As the attractive well in the NO(A)-Ar PES is present at a larger interaction radius \( R \) than the repulsive core of either the NO(A)-Ar or NO(A)-Ne PESs, we have tested the proposition that the forward scattering is the result of this attractive well by exploring the QS-calculated DCS as a function of the total angular momentum, \( J_{\text{tot}} \). Figure 11 shows the DCS for \( N' = 5 \) for NO(A) + Ne including all partial waves up to \( J_{\text{tot}} = 85.5 \), together with the DCSs for \( N' = 5 \) for NO(A) + Ar including all partial waves up to \( J_{\text{tot}} = 85.5, 100.5, \) and 250.5, respectively. These correspond to classical impact parameters up to 4.5 Å for NO(A) + Ne, and 4.4 Å, 5.5 Å, and 11 Å for NO(A) + Ar, respectively. The NO(A) + Ne DCS is essentially converged at \( J_{\text{tot}} = 85.5 \), consistent with the range of the anisotropy of the PES shown in Fig. 9. The NO(A) + Ar DCS for \( J_{\text{tot}} = 85.5 \) does not display the extreme forward scattering peak observed experimentally but does display sideways scattering amplitude, consistent with repulsive wall interactions. In contrast, the NO(A) + Ar
Quantum scattering calculated differenti... the rescaled PES of Klos et al. has been shown to predict NO(A) + Ar RET and elastic depolarization rate constants with good accuracy. This study provides clear evidence that the repulsive interactions of the PES are not completely accurate, and furthermore, that the discrepancy is largest in the odd-order Legendre moments of the PES, reflecting the differences between the N- and O-ends of the molecule.

V. CONCLUSION

We have presented a new, miniature, CMB-VMI apparatus optimized for the measurement of the stereodynamics of collisions of electronically excited molecules. This apparatus has been used to determine the DCS and angle-resolved rotational angular momentum polarization for RET in NO(A) + Ar at an average collision energy of 525 cm$^{-1}$. The DCS display strong forward scattered peaks, together with rainbow oscillations to larger scattering angles, whilst the angular momentum polarizations also show oscillatory behavior that is inconsistent with the KA model. QS calculations on an ab initio PES reproduce most, but not all of these features, showing that whilst the attractive forces are accurately represented, the repulsive regions of the PES require refinement, with the greatest error lying in the odd-order Legendre moments of the PES. This example provides an excellent illustration of our extension of the CMB-VMI technique to RET of excited states, and its application in testing our understanding of RET dynamics and the underlying PESs.

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