Ion imaging studies of product rotational alignment in collisions of NO (X^2Π_{1/2}, j = 0.5) with Ar

Elisabeth A. Wade a,*, K. Thomas Lorenz a,1, David W. Chandler a, James W. Barr b, George L. Barnes b, Joseph I. Cline b

a Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94550, USA
b Department of Chemistry and Chemical Physics Program, University of Nevada, Reno, NV 89557, USA

Received 13 October 2003; accepted 17 February 2004
Available online 19 March 2004

Abstract

The collision-induced rotational alignment of NO (X^2Π_{1/2}, v = 0, j = 4.5, 5, 5, 8.5, 11.5, 12.5, and 15.5) is measured for rotationally inelastic scattering of NO (X^2Π_{1/2}, v = 0, j = 0.5) with Ar at 520 ± 70 cm^{-1} of center-of-mass collision energy. The experiments are performed by velocity-mapped ion imaging with polarized 1 + 1′ REMPI of the scattered NO product. Differential cross-sections (DCSs), corrected for alignment effects, are also reported. While the alignment correction is important, it does not change the positions of the observed rotational rainbows. The alignment moments and DCSs are compared with calculations using Alexander’s CCSD(T) PESs. The theoretical and experimental DCSs show excellent agreement, as do the theoretical and experimental alignment moments for low Δj. For high Δj collisions and back-scattered trajectories, which sample the hard wall of the PES, the theoretical and experimental alignment moments show less agreement.

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1. Introduction

In the last 25 years, there have been many experimental and theoretical studies of rotational state-to-state inelastic collisions of the NO–Ar system. NO typifies the complex dynamics of chemically interesting open-shell molecules. Its ground state is 2Π_{1/2}, with each rotational state having two Λ-doublet levels. The excited 2Π_{3/2} state is accessible at thermal collision energies. NO is also experimentally appealing because it is chemically stable and spectroscopically convenient.

Early experimental work on the NO + Ar system, by Anderson et al. [1] measured integral state-to-state cross-sections, which were later refined by Joswig et al. [2]. Bieler et al. [3] used resonance-enhanced multiphoton ionization (REMPI) to measure integral state-to-state cross-sections for rotational state, Λ-doublet, and spin–orbit changing collisions, at center-of-mass collision energies between 750 and 2500 cm^{-1}. Lin et al. [4] made similar measurements at 1770 cm^{-1}, and showed that scattering preferentially populates the Π(A^0) Λ-doublet levels. Jons et al. [5] measured state-to-state differential cross-sections in a crossed beam experiment at collision energies between 117 and 1694 cm^{-1}, using LIF detection and a variable molecular beam intersection angle. van Leuken et al. [6] and de Lange et al. [7] measured the steric asymmetry of oriented, state-selected NO colliding with Ar at a collision energy of 442 cm^{-1}, demonstrating experimentally for the first time the role of orientation in inelastic collisions. Meyer used a counter-propagating pulsed molecular beam apparatus with REMPI/TOF detection to determine both state-to-state differential cross-sections and A_{0,0}^{COL}(θ), the projection of the angular momentum vector, j, on the relative velocity vector of the collision. Meyer [8] performed this experiment at a collision energy of 1590 cm^{-1}.
Suits et al. [9] and Bontuyan et al. [10] were the first to apply ion imaging techniques in a crossed molecular beam study of this system, measuring state-to-state differential cross-sections at a collision energy of 1690 cm$^{-1}$. Since then, ion imaging techniques have been widely applied to collisions of Ar and NO. Yonekura et al. [11] have used velocity-mapped ion-imaging to observe the rotational rainbows of the differential cross-section. Lorenz et al. [12] have used ion imaging techniques to measure the orientation, or sense of rotation, following biomolecular collisions of NO and Ar as a function of rotational state. Kohguchi et al. [13] and Elioff and Chandler [14] used ion imaging techniques to measure state-resolved differential cross-sections for spin–orbit changing transitions following bimolecular collisions of NO and Ar.

Because NO is a model system for collisions involving $^2\Pi_{1/2}$ electronic states, it is the subject of great theoretical interest. The interaction between a diatomic molecule in a $^2\Pi_{1/2}$ electronic state and a spherical collider is described by two potential energy surfaces (PESs) [15]. In particular, for NO + Ar, the unpaired $\pi^1$ electron of NO can reside in an orbital either in the plane ($A'$) or perpendicular to the plane ($A''$) of the three nuclei [16], resulting in two non-degenerate potential energy surfaces [17]. Nielson et al. [18] used density functional methods to determine the two PESs for the Ar + NO system. Alexander used the correlated electron pair (CEPA) method to determine more accurate PESs [19], which have then been used to determine integral [4,19–22] and differential [19,22] cross-sections, which compared quite well with the available experimental results of Pons et al. [5], Suits et al. [9], Bontuyan et al. [10], and Lin et al. [4]. Recently, Alexander [23] has developed new coupled-cluster (CCSD(T)) PESs, which have been used to calculate integral cross-sections for Ar + NO at collision energies of 442 and 1774 cm$^{-1}$ [23], for an investigation of steric asymmetries due to the initial orientation of the NO [24,25], and for calculations of differential cross-sections (DCSs) following collision [13,14].

In this work, we use velocity-mapped ion imaging [26], combined with linearly polarized REMPI probe light, to measure product state-resolved angular momentum alignment of NO ($X^2\Pi_{1/2}$, $v' = 0$) following collision of NO ($X^2\Pi_{1/2}$, $v = 0$, $j = 0.5$) with Ar. Angular momentum alignment has been of experimental and theoretical interest for over 30 years [27]. The earliest measurements of rotational alignment, by van Brunt and Zare [28], were for excited fragments produced by photodissociation, with the alignment detected by polarized fluorescence. Since that time, there have been many studies of rotational alignment following photodissociation [27], including several studies that made use of the sensitivity of velocity-mapped ion imaging [29,30].

There have been substantially fewer studies of rotational alignment induced by bimolecular collisions. Matteus et al. [31] measured the $m_j$-dependent differential cross-section for Na$_2$ + Ne. Chapman et al. [32] have determined upper limits for the net rotational alignment for HF ($J = 1 - 0$) after collision with He and Ar. Meyer has used a counter-propagating pulsed molecular beam apparatus to measure the rotational alignment moment, $A_{0^+}(2^{\text{col}}\Theta)$, which quantifies the projection of the angular momentum vector, $j$, on the relative velocity vector of the collision as a function of recoil angle, for $\text{NH}_3 + \text{He}$ [33], $\text{NH}_3 + \text{Ar}$ [34], NO + He [35] and NO + Ar [8]. Velocity-mapped ion imaging is a powerful technique for the study of bimolecular collisions [9–14,36–39], and is sensitive to collision-induced product angular momentum alignment [36]. Imaging detection captures the entire product scattering sphere, without averaging over the azimuthal angle of the recoil vector. Imaging potentially allows the determination of all three collision frame alignment moments, $A_{0^+}(2^{\text{col}}\Theta)$, $A_{1^+}(2^{\text{col}}\Theta)$, and $A_{2^+}(2^{\text{col}}\Theta)$, that are detectable using one-photon spectroscopic probe techniques [36]. In this experiment, however, the symmetry of our experimental geometry limits us to measuring two of the alignment moments, $A_{0^+}(2^{\text{col}}\Theta)$ and $A_{2^+}(2^{\text{col}}\Theta)$, as is discussed in Section 4.1, and contrary to a previous communication [36].

2. Experimental

The crossed molecular beam apparatus with velocity-mapped ion imaging detection used in this study has been described elsewhere [37]. Two skimmed and collimated pulsed molecular beams intersect perpendicularly in the interaction region of the velocity-mapped ion imaging apparatus. The target beam contains 4% NO in Ar (Matheson) and the collider beam is neat Ar (Praxair, Analytical Grade). 1 + 1$'$ REMPI spectra of NO using the $A^2\Sigma$ ← $X^2\Pi$ transition show that the NO in the target beam is >99% in the $j = 0.5$ state.

In order to avoid saturation effects in the NO $A^2\Sigma$ ← $X^2\Pi$ probing transition, a two-color 1 + 1$'$ REMPI probe scheme is used [40]. Images are collected for each of five product rotational states, $j' = 4.5$, 8.5, 11.5, 12.5, and 15.5, detected with the $R_{21}$ branch, which probes the $F_1(j)$, $A'\Pi$ A-doublet state. The intensity of the Q-branch is twice as sensitive to alignment as the intensity of the R- and P-branches, and depends on alignment in an opposite manner, so that if alignment causes the intensity of the R- and P-branches to increase, it will cause the intensity of the Q-branch to decrease. However, the Q-branch transitions for NO ($A^2\Sigma$ ← $X^2\Pi$) are nearly overlapped by an R- or P-branch transition of the same rotational state. If these two overlapping branches had the same center wave-
length, then the observed alignment effect would be the average of the effect on the Q-branch and on the R- or P-branch. However, since they are slightly offset in frequency from each other, the laser probes a different part of the Doppler profile for each of the two branches, leading to “unbalanced” images that are difficult to analyze. Because of this effect, only the images taken using the spectroscopically clean R\textsubscript{21}-branch transitions are reported here.

Before each image is collected, the relative amounts of one- and two-color signal are measured. All images presented here are due to at least 97\% two-color signal. The probe and ionization laser pulses are focused by a 1.5 m lens and propagate collinearly bisecting the interaction region in the plane of the molecular beam at a 45° angle to both molecular beams. The probe laser pulse, at 225–226 nm, tuned to selected rotational lines of the A\textsuperscript{2}Σ(v′ = 0) – X\textsuperscript{2}Π(v = 0) band, is \(\approx 3\) ns (FWHM) in pulse width and <4 \(\mu\)J in energy. It is produced by doubling the output of a Nd:YAG pumped dye laser operating at 30 Hz. Its polarization is controlled by a \(\lambda/2\) plate, which is rotated to provide probe light whose electric vector, \(\varepsilon_p\), is either parallel (V) or perpendicular (H) to the time-of-flight axis. The time-of-flight axis is orthogonal to both molecular beams. The intensity of the probe laser pulse is varied by passing it first through a half-wave plate which rotates the polarization, and then through a glan prism.

Under these focusing conditions, the laser intensity at the focal point is less than 1 mJ/cm\(^2\), so saturation of the transition should be minimal [41]. The laser intensity varied with the final rotational state, with higher laser intensities used to measure higher \(j\) states, which are less populated. Power dependence studies confirmed that, while some degree of saturation cannot be ruled out, saturation should not significantly affect our results, especially for low \(\Delta j\) transitions.

The 317 nm ionization laser pulse is \(\approx 3\) ns (FWHM) in pulse width and 2–3 mJ in energy. It is produced by doubling the output of a Nd:YAG pumped dye laser operating at 30 Hz. Its polarization state is not controlled, but is instead significantly depolarized by passing it through the same \(\lambda/2\) plate used to control the polarization of the probe laser.

Measurements of the size of the scattering spheres for each rotational state [37] and calibration of the ion-imaging apparatus using the well-defined photodissociation of O\textsubscript{2} by 225 nm light [42] are used to determine the velocity magnification factor of 1.33 \(\pm\) 0.09 and the center-of-mass collision energy of 520 \(\pm\) 70 cm\(^{-1}\).

The images are background-subtracted, with the collider beam turned on and off for successive images, as described previously [37]. H and V images are interleaved, so that an initial H image was taken, with an exposure time of 5–10 min, followed by two V images with the same exposure time, followed by two H images, and so forth, to give equal numbers of V and H images. The V and H images are then summed separately, using cross-correlation techniques to center the images on each other. This procedure minimizes systematic errors due to laser fluence drift and any drift associated with ion detection.

3. Results

The diagram in Fig. 1 shows how, in the center of mass frame, the initial velocity of Ar, \(v_{\text{Ar}}\), and the initial and final relative velocities of NO, \(v_{\text{NO}}\) and \(v'_{\text{NO}}\), are related, and how the recoil deflection angle \(\Theta\) is defined. In Fig. 1, \(v_{\text{NO}}\) and \(v'_{\text{NO}}\), which define the scattering plane, are in the same plane defined by the molecular beams, \(v_{\text{NO}}\) and \(v_{\text{Ar}}\). In the ion images, forward scattered or small recoil angle NO appears on the left of the image while back scattered or large recoil angle NO appears on the right. The dashed circle is a two-dimensional representation of the scattering sphere of NO (\(f = 8.5\)).

The ion images for V polarization for each rotational state are shown in the first column of Fig. 2. The second column shows normalized difference images, constructed by computing \((I_V - I_H)/(I_V + I_H)\) from the intensities \(I_V\) and \(I_H\) at each pixel location in the V and H images. The third column shows the least squares fit of the normalized difference images used to extract alignment.
moments, which will be discussed in detail in Section 4.1. The fourth column shows the theoretical predictions of the normalized difference images, which will be discussed in detail in Section 5.1.

The value of $(I_V - I_{H1})/(I_V + I_{H1})$ at each pixel in a $(V - H)/(V + H)$ image is constrained to the range $-1 \leq (I_V - I_{H1})/(I_V + I_{H1}) \leq 1$, with a value of zero indicating that probe polarization has no effect on the relative signal of the V and H images. The detected signal in a V or H image, $D(j', \Theta, \chi; \chi_p)$, is given by

$$D(j', \Theta, \chi; \chi_p) = \int_{\chi_{NO}} \int_{\chi_{Ar}} Z(j', \Theta, \chi; \chi_p) DCS(j', \Theta) \times f(\Theta, \chi, \nu_{NO}, \nu_{Ar}) \, d\chi_{Ar} \, d\nu_{NO}.$$  \hspace{1cm} (1)

In this equation, $j'$ is the final rotational quantum number, $\Theta$ is the deflection or recoil angle of the NO in the scattering plane, and $\chi$ is the azimuthal deflection angle for the NO. While $D(j', \Theta, \chi; \chi_p)$ depends on the initial rotational state of NO, in this experiment the initial rotational state of NO is assumed to be constant ($j' = 0.5$) and for simplicity will not be included in these equations. $\chi_p$ is the probe polarization angle which is $0^\circ$ for H polarization and $90^\circ$ for V polarization, $Z(j', \Theta, \chi; \chi_p)$ is a factor that contains the polarization dependence of the system, DCS $(j', \Theta)$ is the differential cross-section, and $f(\Theta, \chi, \nu_{NO}, \nu_{Ar})$ is the apparatus function. Integration over a range of initial velocities of NO and Ar is used to account for the velocity spread in both molecular beams. Since $Z(j', \Theta, \chi; \chi_p)$ is the only factor that will vary with laser polarization, the $(V - H)/(V + H)$ images approximately separate the effect of angular momentum alignment from the differential cross-section and apparatus-dependent detectivity. Using these definitions, the normalized difference images in the second column of Fig. 2 can be written as

$$\frac{V - H}{V + H} = \frac{D(j', \Theta, \chi; \chi) - D(j', \Theta, \chi; \chi_p = 0^\circ)}{D(j', \Theta, \chi; \chi_p = 90^\circ) + D(j', \Theta, \chi; \chi_p = 0^\circ)}$$

$$\approx \frac{Z(j', \Theta, \chi; \chi_p = 90^\circ) - Z(j', \Theta, \chi; \chi_p = 0^\circ)}{Z(j', \Theta, \chi; \chi_p = 90^\circ) + Z(j', \Theta, \chi; \chi_p = 0^\circ)}. \hspace{1cm} (2)$$

In fact, the $(V - H)/(V + H)$ images are affected by the velocity spreads of the molecular beams, which can be seen most clearly as a slight blurring at the bottom of the $(V - H)/(V + H)$ images relative to the top.

The experimental $(V - H)/(V + H)$ images in the second column of Fig. 2 reveal some qualitative trends with $j'$. In these images, black indicates no polarization dependence, red or green indicates that $I_V > I_H$, and blue or purple indicates that $I_V > I_H$. For $I_V > I_H$, white shows the largest difference and yellow shows the smallest difference. In all of the $(V - H)/(V + H)$ images, $I_H > I_V$ dominates overall but is concentrated in the back-scattered regions. For the lowest $j$ states, $j' = 4.5$ and 8.5, the most forward scattered products show some $I_V > I_H$ character (red or green color map). The extent of the forward-scattered $I_V > I_H$ pattern diminishes with increasing $j'$ and in the $j' = 11.5$ image, the most forward scattered products show $I_V \sim I_H$. For $j' = 15.5$, the $I_V \sim I_H$ pattern has further diminished so that nearly the entire image shows $I_H > I_V$ character (blue or purple color map).

These intensity patterns can be interpreted qualitatively by a simple model. The NO $(A^2\Sigma - X^2\Pi)$ probe transition is polarized perpendicular to the molecular axis. The selection rules for the $R_{21}$-branch transitions require the $j$-vector to be perpendicular to both the transition dipole and the molecular axis. Since the absorption cross-section is largest when the laser polarization is aligned with the transition dipole, $I_H > I_V$ character indicates that the NO internuclear axis lies preferentially in the scattering plane (“frisbee” or “cartwheel”-like rotation) and when $I_V > I_H$ behavior dominates, the NO internuclear axis is preferentially perpendicular to the scattering plane (“propeller”-like rotation).
4. Analysis

4.1. Alignment moments

The polarization-dependent term, $Z(j', \Theta, \chi, \chi_p)$, in Eq. (1), is a sum of two terms. For each pixel, the two azimuthal coordinates above and below the interaction region will project onto the same position of the detector

$$Z(j', \Theta, \chi, \chi_p) = \frac{I(j', \Theta, \chi, \chi_p)}{\sin \Theta \sin \chi} + \frac{I(j', \Theta, 2\pi - \chi, \chi_p)}{\sin \Theta \sin \chi}, \quad (3)$$

where $I(j', \Theta, \chi, \chi_p)$ is the absorption cross-section of the linearly polarized probe light. Following Fano and Mack [43], $I(j', \Theta, \chi, \chi_p)$ is given by

$$I(j', \Theta, \chi, \chi_p) = C_{det} \left\{ 1 - \frac{1}{2} h^2(j') \left[ A_{0+}^{PRB} (j', \Theta, \chi, \chi_p) + 3A_{2+}^{PRB} (j', \Theta, \chi, \chi_p) \right] \right\}. \quad (4)$$

In Eq. (4), $C_{det}$ is an apparatus sensitivity constant and $h^2(j')$ is a depolarization factor that depends on the branch of the probe transition. For pure R-branch transitions, $h^2(j') = -j'/(2j' + 3)$, for pure P-branch transitions, $h^2(j') = -(j' + 1)/(2j' - 1)$, and for pure Q-branch transitions, $h^2(j') = 1$. In the high-$j$ limit, $h^2(j') = -1/2$ for both pure R- and P-branches. In this work, the high-$j$ limit is not appropriate and the $j$-dependent $h^2(j')$ is used. $A_{0+}^{PRB} (j', \Theta, \chi, \chi_p)$ and $A_{2+}^{PRB} (j', \Theta, \chi, \chi_p)$ are the two leading alignment moments of a spherical tensor expansion of the angular distribution of $I_{NO}$ [43], which we will generally refer to as differential alignment moments.

Differential alignment moments can be parameterized in a number of coordinate frames, three of which will be discussed here. They are shown schematically in Fig. 1. In the laboratory $(X_1Y_1Z_1)$ frame, the $X_1Z_1$ plane contains the molecular beams, with the initial center-of-mass velocity of the NO molecule along the direction of the $+Z_1$-axis and the $+Y_1$-axis pointing at the detector.

In the collision $(XYZ)$ frame, the $+Z$-axis is along $v_{NO}$ and $v_{NO}'$ lies in the $+X$ half of the $XZ$ plane. The $Z$-axis of the collision frame is always parallel to the $Z_L$-axis of the laboratory frame. For simplicity, Fig. 1 shows the special case in which $\chi = 0^\circ$ and in which $v_{NO}'$ lies in the $+X$ half of the $X_1Z_1$ plane. Under these conditions, the laboratory $(X_1Y_1Z_1)$ and collision $(XYZ)$ frames are identical, but in general the collision $(XYZ)$ frame can have any azimuthal orientation with respect to the laboratory $(X_1Y_1Z_1)$ frame. Most published alignment moments are defined in the collision $(XYZ)$ frame [8,32-35].

The differential alignment moments in Eq. (4), however, are defined in the probe $(X''Y''Z'')$ frame. In the probe $(X''Y''Z'')$ frame, the $+Z''$-axis is parallel to the $k_p$ propagation axis of the probe light and the $X''$-axis is parallel to the electric vector $e_p$ of the probe light. The probe $(X''Y''Z'')$ frame is related to the laboratory $(X_1Y_1Z_1)$ frame through an Euler rotation of $(90^\circ, 180^\circ, \chi_p)$, for our experimental geometry. While the differential alignment moments defined in the probe $(X''Y''Z'')$ frame are directly connected to the measured signal intensity, they are not directly connected to the scattering dynamics. In particular, since the $X''$-axis of the probe $(X''Y''Z'')$ frame is parallel to the electric vector $e_p$ of the probe light, the probe and laboratory frames have different relative orientations for vertically and horizontally polarized laser light.

When the three alignment moments are rotated from the probe frame to the collision frame, using the rotation matrices given in Hertel and Stoll [44], the following relationships are obtained, for our experimental geometry:

$$A_{0+}^{PRB} (j', \Theta, \chi, \chi_p) = \frac{1}{2} \left[ A_{0+}^{COL} (j', \Theta) + 3A_{2+}^{COL} (j', \Theta) \right], \quad (5)$$

$$A_{2+}^{PRB} (j', \Theta, \chi, \chi_p) = \cos \chi_p A_{2+}^{COL} (j', \Theta), \quad (6)$$

$$A_{2+}^{PRB} (j', \Theta, \chi, \chi_p) = 3A_{2+}^{COL} (j', \Theta), \quad (7)$$

In Eq. (4), the absorption cross-section of the linearly polarized probe light depends only on $A_{0+}^{PRB} (j', \Theta, \chi, \chi_p)$ and $A_{2+}^{PRB} (j', \Theta, \chi, \chi_p)$, not on $A_{2+}^{PRB} (j', \Theta, \chi, \chi_p)$. Therefore, in our experimental geometry where $Z''$ and $Z$ are perpendicular, we can only determine two of the three collision frame moments, $A_{2+}^{COL} (j', \Theta)$ and $A_{2+}^{COL} (j', \Theta)$. If $Z''$ were not perpendicular to $Z$, then $A_{2+}^{COL} (j', \Theta, \chi, \chi_p)$ could also be measured, as the probe frame moments would depend on all three collision frame moments. In our preliminary work [36], we found the best least-squares fit for all three moments, but in fact we had an over-defined system, so that we could not uniquely define all three moments. Our previous analysis implied a sensitivity to $A_{2+}^{COL} (j', \Theta, \chi, \chi_p)$ which the experiment does not have.

The above frames are defined to be consistent with the notation developed by Aoziz et al. [45] and de Miranda et al. [46], in their semiclassical descriptions and calculations of angular momentum polarization in elementary gas-phase bimolecular reactions. The alignment moments of interest, and their physically realizable limits are defined as follows:

$$A_{0+}^{2} = (3f_2 - 1) \quad 1 \leq A_{0+}^{2} \leq 2, \quad (8)$$

$$A_{2+}^{1} = (2f_2 f_2) \quad 1 \leq A_{2+}^{1} \leq 1, \quad (9)$$

$$A_{2+}^{2} = (f_2 f_2) \quad 1 \leq A_{2+}^{2} \leq 1. \quad (10)$$
When all three alignment moments equal zero, then the \( \mathbf{J} \)-vector has no preference to point in any direction, so its distribution is isotropic. The value of \( A_{0+}^{2\text{COL}}(\mathbf{J}, \Theta) \) gives the propensity of the \( \mathbf{J} \)-vector to lie along \( \mathbf{V}_{\text{NO}} \). When \( A_{0+}^{2\text{COL}}(\mathbf{J}, \Theta) = 2 \), the \( \mathbf{J} \)-vector is parallel to \( \mathbf{V}_{\text{NO}} \) (which is \( Z \) in the collision frame). When \( A_{0+}^{2\text{COL}}(\mathbf{J}, \Theta) = -1 \), the \( \mathbf{J} \)-vector is perpendicular to \( \mathbf{V}_{\text{NO}} \). The value of \( A_{0+}^{2\text{COL}}(\mathbf{J}, \Theta) \) gives propensity of the \( \mathbf{J} \)-vector to be parallel to the \( X \)-axis or to the \( Y \)-axis. If \( A_{2+}^{2\text{COL}}(\mathbf{J}, \Theta) = 1 \), then the \( \mathbf{J} \)-vector is parallel to the \( X \)-axis, while if \( A_{2+}^{2\text{COL}}(\mathbf{J}, \Theta) = -1 \), then the \( \mathbf{J} \)-vector is parallel to the \( Y \)-axis. \( A_{1+}^{2\text{COL}}(\mathbf{J}, \Theta) \) is the propensity of the \( \mathbf{J} \)-vector to be tilted in the \( XZ \) plane, with \( A_{1+}^{2\text{COL}}(\mathbf{J}, \Theta) = \pm 1 \) indicating a \( 45^\circ \) tilt in either direction.

\( A_{0+}^{2\text{COL}}(\mathbf{J}, \Theta) \) is obtained from the \((V-H)/(V+H)\) images by summing the intensities over vertical, 5-pixel-wide stripes through the image. This is equivalent to integrating over \( \chi \), the azimuthal angle. The experimentally determined values of \( A_{0+}^{2\text{COL}}(\mathbf{J}, \Theta) \) are shown in Fig. 3. Once \( A_{0+}^{2\text{COL}}(\mathbf{J}, \Theta) \) has been measured, the best value of \( A_{2+}^{2\text{COL}}(\mathbf{J}, \Theta) \) is determined for the stripe using a least-squares optimization and Eqs. (2)–(5) and (7), with \( A_{2+}^{2\text{COL}}(\mathbf{J}, \Theta) \) as the only adjustable parameter. The normalized difference images resulting from these fitted parameters are shown in the third column of Fig. 2. The experimental values of \( A_{2+}^{2\text{COL}}(\mathbf{J}, \Theta) \) are shown in Fig. 4.

There is significant scatter in \( A_{2+}^{2\text{COL}}(\mathbf{J}, \Theta) \), especially for low \( j \) transitions and for recoil angles near \( 90^\circ \). At these angles, which include the center of the image, there is relatively little signal, as most of the signal is found on a ring around the outside of the image. This effect is especially pronounced for low \( j \) transitions where most of the signal is found in the first few degrees. As the total signal is small, the normalized difference images are relatively noisy, which leads to scatter in the least-squares optimization.

In Figs. 3 and 4, the differential alignment moments are plotted in terms of the recoil angle, \( \Theta \). However, vertical stripes of equal width sample these quantities uniformly in \( \cos \Theta \), so that even though the extracted stripes are of a fixed pixel width, the angular interval between each measured differential alignment moment is not constant. In particular, the angular interval between differential alignment moments increases as \( \Theta \) approaches \( 0^\circ \) or \( 180^\circ \). The interpretation of these differential alignment moments will be discussed in Section 5.1.

4.2. Differential cross-sections

Once the differential alignment moments are determined, they can be used to extract alignment-corrected DCSs. The general extraction procedure has been described in detail elsewhere [37]. Eqs. (1)–(4) were used to include alignment effects in the intensity calculations. As the alignment moments were originally measured for a discrete set of recoil angles, the values were smoothed and then splined to provide interpolated and extrapolated values for each angle between \( 0^\circ \) and \( 180^\circ \).

Differential cross-sections measured using electron impact ionization are not sensitive to alignment of the products. When products are detected using light, the measurement is generally sensitive to alignment, unless the transition is saturated. Since we measure the quan-
tum-state specific DCS with 1 + 1 ’ REMPI, our measured DCSs are sensitive to the alignment of the products and it is important to know what impact alignment has on our measured DCSs. In Fig. 5, three different experimental DCSs are shown for \( j_0 = 11.5 \): the DCS extracted from the V image without alignment correction (dashed line), the DCS extracted from the H image without alignment correction (solid line), and corrected DCS, which is the average of the two alignment-corrected DCSs extracted independently from the V and H images (dotted line). As expected based on the \((V + H)/\) (V + H) images, the V uncorrected DCS is larger at small recoil angles and larger at large recoil angles than the H uncorrected DCS. Also, the corrected DCS is not simply the average of the two uncorrected DCSs. The relative heights of the two rotational rainbows do change depending on the conditions under which the DCS was extracted. For V without alignment correction, the ratio of the 45\(^\circ\) rainbow to the 130\(^\circ\) rainbow is \(~1.5\), while for H without alignment correction, the ratio between the two rainbows is only \(~1.1\). However, the positions of the rainbows are not strongly dependent on the alignment moments.

The averaged, alignment-corrected DCSs for each rotational state are shown in Fig. 6. The error bars show the differences between alignment-corrected DCSs extracted from V and H images. The error bars are largest at high and low angle, because it was necessary to extrapolate the values of the alignment moments to \( \Theta = 0^\circ \) and \( 180^\circ \). This is inherent in the data since when the three-dimensional scattering sphere is compressed to two dimensions, the deflection angles near \( 0^\circ \) and \( 180^\circ \) occupy relatively few pixels in the same “stripe” of the image and the alignment moments must be extracted as a function of \( \cos \Theta \).

For \( j = 4.5 \), the DCS is peaked strongly in the forward direction. For \( j = 8.5 \), the NO is still forward scattered, but a rotational rainbow appears at \( \sim 30^\circ \) and back-scattering becomes significant. For \( j = 11.5 \), the NO is primarily side scattered, and two rotational rainbows, the first at \( \sim 45^\circ \) and the second at \( \sim 125^\circ \), are observed. For \( j = 12.5 \), the NO becomes largely back-scattered, the first rotational rainbow shifts to \( \sim 60^\circ \), and the second rotational rainbow, which merges into the back-scattered part of the DCS, shifts to \( \sim 150^\circ \). Finally, for \( j = 15.5 \), the NO is entirely back-scattered. For many systems, the rotational rainbow(s) shift monotonically to increasing deflection angle as \( \Delta j \) increases [9,32,47–50]. While we did not measure DCSs for every energetically accessible rotational state for NO + Ar, it does appear that NO + Ar follows this trend.
and Alexander dotted lines are theoretical DCSs calculated using HIBRIDON [51,52]. The error bars indicate the difference between the DCS extracted theoretical values for A and can be compared with theory. Experimental and expanded axis. The experimental DCSs are normalized so that the integral cross-sections are the same as those predicted theoretically.

5. Discussion

5.1. Collision frame alignment moments

As described in Section 4.1, A \(^{(2)\text{COL}}\) (j, Θ) and A \(^{(2)\text{COL}}\) (j, Θ) have been extracted from our ion images, and can be compared with theory. Experimental and theoretical values for A \(^{(2)\text{COL}}\) (j, Θ) are shown in Fig. 3, and experimental and theoretical values for A \(^{(2)\text{COL}}\) (j, Θ) are shown in Fig. 4. Theoretical calculations of A \(^{(2)\text{COL}}\) (j, Θ) were performed using HIBRIDON [51,52] and Alexander’s CCSD(T) PESs [23].

Alignment moments were calculated for both of the A-doublet ground states, j = 0.5F\(_1\)e and j = 0.5F\(_1\)f. For the final alignment moments presented here, the values of A \(^{(2)\text{COL}}\) (j, Θ) and A \(^{(2)\text{COL}}\) (j, Θ) for the two initial states and three collision energies were averaged together, assuming equal populations in each A-doublet and a 0.5:1:0.5 ratio of three energies which are used to approximate the energy spread in the molecular beams. The theoretical value of A \(^{(2)\text{COL}}\) (j, Θ) is -1 at 0° and 180°, and the theoretical value of A \(^{(2)\text{COL}}\) (j, Θ) is 0 at 0° and 180°. These limits are defined by the geometry of the system; in a purely forward- or back-scattered collision, the j-vector must be perpendicular to the v\(_{NO}\)-vector.

Experimental values do not appear to show this behavior because we are not able to determine the alignment moments exactly at 0° and 180°, but instead measure an average alignment moment over a range of recoil angles.

The sign behavior of the theoretical A \(^{(2)\text{COL}}\) (j, Θ) is consistent with the experimental A \(^{(2)\text{COL}}\) (j, Θ). We can use this behavior to predict the outgoing trajectories of NO following collision, especially for angles near 0° and 180°. Since A \(^{(2)\text{COL}}\) (j, Θ) gives the propensity of the j-vector to lie perpendicular to the v\(_{NO}\)-vector, for highly forward- or back-scattered trajectories where v\(_{NO}\) and v\(_{NO}\) are nearly parallel, A \(^{(2)\text{COL}}\) (j, Θ) also approximately gives the propensity of the j-vector to lie perpendicular to the v\(_{NO}\)-vector. For small j collisions and forward-scattered trajectories, A \(^{(2)\text{COL}}\) (j, Θ) becomes positive, once the 0° limit no longer applies. Therefore, the j-vector tends to be parallel to the v\(_{NO}\)-vector, indicating “propeller”-like motion of the NO for the most forward scattered trajectories. However, as the recoil angle increases, A \(^{(2)\text{COL}}\) (j, Θ) decreases and becomes negative, which indicates a tendency for the j-vector to be parallel to the v\(_{NO}\)-vector and a propensity for “frisbee” or “cartwheel”-like trajectories. As j increases, A \(^{(2)\text{COL}}\) (j, Θ) becomes negative throughout, indicating trajectories that are “frisbee” or “cartwheel”-like for all recoil angles.

The magnitude of the theoretical A \(^{(2)\text{COL}}\) (j, Θ) is consistently greater than the magnitude of the experimental A \(^{(2)\text{COL}}\) (j, Θ) values, especially at larger recoil angles where the theoretical A \(^{(2)\text{COL}}\) (j, Θ) values are much more negative than the experimental A \(^{(2)\text{COL}}\) (j, Θ) values. The agreement between experiment and theory is best for j = 8.5, and worst for j = 15.5, where the experimental and theoretical A \(^{(2)\text{COL}}\) (j, Θ) are negative throughout.

The comparison of experimental and theoretical A \(^{(2)\text{COL}}\) (j, Θ) gives similar results. The theoretical and experimental A \(^{(2)\text{COL}}\) (j, Θ) show excellent agreement for j = 11.5 and 12.5. For the other j-states, however, the theory predicts greater alignment than is observed experimentally, where the experimental A \(^{(2)\text{COL}}\) (j, Θ) is closer to zero for all recoil angles than the theoretical A \(^{(2)\text{COL}}\) (j, Θ). The theoretical values for A \(^{(2)\text{COL}}\) (j, Θ) and A \(^{(2)\text{COL}}\) (j, Θ) were also used to simulate normalized...
difference images that are shown as the fourth column of Fig. 2. Here, the trends described above can be seen more clearly. Consistently, for all rotational states, the theory predicts greater alignment than is observed experimentally. The effect is most pronounced for back-scattered trajectories, where the theoretical normalized difference image is substantially more negative than the experimental observations. These back-scattered trajectories sample the hard wall of the PES, and there is typically less information available about that part of the PES. Therefore, it is possible that some of the disagreement between theory and experiment could be reduced by improving the hard wall of the PES.

We have also performed classical Monte Carlo trajectory simulations of this scattering process, using a hard-ellipse potential with major and minor axes of 3.63 and 2.82 Å [53]. The moments predicted by these calculations, for single collision processes, are shown in Figs. 3 and 4 as dotted lines. Khare et al. [54,55] showed that impulsive, classical collisions between a hard sphere and a hard ellipse conserve the angular momentum of the rotor along the direction of the kinematic apse vector, \( a_k = \Delta \nu_{\text{NO}}/|\Delta \nu_{\text{NO}}| \), where \( \Delta \nu_{\text{NO}} = \nu_{\text{NO}} - \nu_{\text{NO}} \). The effect of this conservation is that the j-vector should have no projection onto the kinematic apse vector. This kinematic apse conservation model has been used successfully to predict experimental alignment moments [8,35,56,57]. However, we consistently observe much less alignment than is predicted by the kinematic apse conservation model. It is also worth noting that the classical trajectory simulations compare very closely with the full quantum scattering results, in the collision frame. This implies that the quantum scattering results are largely sampling the hard wall part of the potential and that the differences observed here between experiment and theory could be corrected by improvements in that part of the PES.

As the theoretical alignment moments are consistently of greater magnitude than is observed experimentally, saturation of the probe transition could be suspected of diminishing the magnitude of the measured alignment. To test this, V and H images were collected at low probe laser power (\(-0.5 \text{ mJ/cm}^2\)) for \( j' = 15.5 \), and differential alignment moments were extracted. These low power differential alignment moments are much noisier, but within the limits of signal-to-noise are the same as the high power alignment moments and no closer to the theoretical alignment predictions. Since \( \tilde{A}^{(2)\text{COL}}_{0+}(15.5, \Theta) \) does not change significantly with probe laser power, the difference between the experimental \( \tilde{A}^{(2)\text{COL}}_{0+}(15.5, \Theta) \) and theoretical \( \tilde{A}^{(2)\text{COL}}_{0+}(15.5, \Theta) \) is unlikely to be explained simply by saturation effects. Furthermore, for the lower \( j' \) states, the integral cross-section is much greater so that we were able to obtain images in a reasonable amount of time using much lower laser powers. If the differences between the experimental and theoretical \( \tilde{A}^{(2)\text{COL}}_{0+}(j', \Theta) \) were purely saturation effects, then we would expect the best agreement for the lowest rotational state, which is not what we observe. Furthermore, saturation does not depend on scattering angle, so cannot account for the consistent disagreement between theory and experiment for back-scattered trajectories.

Meyer has observed the same sort of flattening or rising behavior for backscattered trajectories for large \( \Delta j \) in his measurements of \( \tilde{A}^{(2)\text{COL}}_{0+}(j', \Theta) \) for NO + He [35], and did not observe \( \tilde{A}^{(2)\text{COL}}_{0+}(j', \Theta) \) reaching \(-1 \) at \( 180^\circ \) for any observed \( j' \) state of NO + He [35], NH\(_3\) + He [33], or NO + Ar [8]. For NO + Ar, Meyer measured \( j' = 8.5 \) and 12.5, where the flattening of \( \tilde{A}^{(2)\text{COL}}_{0+}(j', \Theta) \) in back-scattered trajectories would not be observed.

It is possible that the loss of alignment is due in part to interactions of the molecules' dipole moment with the Earth’s magnetic field. As NO rotates, its dipole will begin to precess about the Earth’s magnetic field. The precession time can be calculated as [58]

\[
T = \left[ \frac{h(j'(j' + 1))^{1/2}}{|B|F(j') \mu_B} \right],
\]

where \( T \) is the precession time in seconds per radian, \( B \) is the magnetic field strength of the Earth which we estimate as 0.5 G, and \( F(j') \) is the factor needed to calculate the magnetic moment of NO in Bohr magnetons \( (\mu_B) \). For NO (X\(^2\Pi_{1/2}\)), \( F(j') \) ranges from 0 for \( j' = 0.5 \) to a maximum value of 1 [25]. The longer the precession time, the less depolarization will be observed. Meyer [35] was concerned about this effect, and observed that it decreased with increasing \( j' \). However, his collision energy was much higher than ours, so that he was in the regime where \( F(j') \) approaches one and is nearly constant, so that \( T \) increases roughly as \( (j'(j' + 1))^{1/2} \). We have estimated \( T \) as ranging from 9.1 \( \mu \text{s/rad} \) for \( j' = 4.5 \) to 7.6 \( \mu \text{s/rad} \) for \( j' = 15.5 \). For the range of \( j' \) we observe, we would expect this depolarization to be slightly more significant for higher \( j' \) but we would not expect strong \( j' \) dependence.

While our probe laser pulse is \(~3 \text{ ns}\), our gas pulses are hundreds of microseconds long. We typically probe in the first third to half of the gas pulse. Following a collision, molecules move out of the volume of the focused laser beam, so for fast trajectories, which have a short residence time in the probe volume, corresponding to the left, right, and bottom of the image, we observe only those collisions that occur within 1 \( \mu \text{s} \) or less of the laser pulse and depolarization should be slight [37]. However, we also observe slow trajectories which lead to the intense ridge at the top of the image [59]. These slow trajectories can remain in the laser path for tens of microseconds and could experience significant depolarization. We would expect, therefore, that if depolarization...
were significant, that it should be most strongly observed for side scattered (θ = 90°) trajectories. Therefore, while this depolarization due to the interaction of NO dipoles with the Earth’s magnetic field may in part account for the depolarization of $A_{2v}^{(2)\text{COL}}(j', \Theta)$ for side-scattered trajectories, it cannot completely explain the deviation between experimental and theoretical $A_{0v}^{(2)\text{COL}}(j', \Theta)$, which show good agreement for forward- and side-scattered trajectories but poor agreement for back-scattered trajectories.

It is also possible that the flattening behavior is due to the mixing of trajectories arising from $j = 0.5$ and NO in rotational excited states before the collision, which may disproportionately contribute to the largest $j$ collisions. However, while these effects could explain disagreements between theory and experiment for large $j$ collisions, they cannot explain the disagreement we observe for back-scattered trajectories, regardless of $j$.

5.2. Comparison of experimental differential cross-sections with theory

Theoretical DCSs were determined using close-coupled calculations with HIBRIDON [51,52] and Alexander’s CCSD(T) PESs [23]. These calculations were performed at 450, 520, and 590 cm⁻¹ of collision energy for $j' = 4.5$, 8.5, 11.5, 12.5, and 15.5, in the $F_{1/2}$ doublet state. DCSs were calculated for both possible initial $\Lambda$-doublet states, $j = 0.5F_{1/2}e$ and $j = 0.5F_{1/2}f$. For the final DCSs, the DCSs for the two initial states and the three collision energies were averaged together, assuming equal populations in each $\Lambda$-doublet and a 0.5:1:0.5 ratio of the three energies, used to approximate the energy spread in the molecular beams. These theoretical DCSs are shown in Fig. 6.

In general, the agreement between experiment and theory is excellent, although there are some minor differences. For $j' = 4.5$, the theoretical DCS predicts a slightly sharper forward peak, although some of this difference is due to limited experimental angular resolution near 0° and 180°. At $j' = 8.5$, 11.5 and 12.5, the theoretical DCS predicts that the rainbow is slightly more back-scattered, at ~35°, ~55°, and ~67° compared to ~30°, ~45°, and ~60°, respectively, for the experimental DCS. While these differences are small, the theoretical DCSs consistently predict rainbow peaks at slightly larger $\Theta$ than are observed. Additionally, for $j' = 12.5$ and 15.5, the theoretical DCSs predict less intensity in the back-scattered region than is observed experimentally. Since these large $j$ collisions sample the inner repulsive wall of the PES, this once again implies that the disagreement we observe between theory and experiment could be reduced by improving the repulsive wall of the PES.

6. Conclusions

We have used $1 + 1'$ REMPI with two orthogonal laser polarizations together with a crossed-molecular beam/ion imaging apparatus to measure velocity-mapped images of NO (X³Π) scattered inelastically from Ar. Two alignment moments, $A_{0v}^{(2)\text{COL}}(j', \Theta)$ and $A_{2v}^{(2)\text{COL}}(j', \Theta)$, were extracted from these images and used to extract alignment-independent DCSs. The alignment moments were found to affect the intensity of the extracted DCSs but not their peak positions. The alignment moments and DCSs were compared with theoretical calculations using HIBRIDON [51,52] and Alexander’s CCSD(T) PESs [23]. The agreement between experiment and theory was excellent for the DCSs and very good for some of the alignment moments. In general, the agreement was worst for back-scattered trajectories and for large $j$, which sample the back wall of the PES.

Acknowledgements

Funding for this work was provided by the US Department of Energy, Office of Basic Energy Science, Division of Chemical Sciences, Geosciences, and Biosciences. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under Contract DE-AC04-94AL85000. J.I.C. acknowledges support from the Department of Energy under Grant DE-FG02-98ER45708. J.W.B. acknowledges a Jerry and Betty Wilson Fellowship. We thank Millard Alexander for access to his CCSD(T) PESs, for help in using HIBRIDON™, and for many helpful discussions. We also thank Mark Jaska for technical assistance and Wenwu Chen for HIBRIDON assistance.

Appendix A. Rotation of alignment moments

The alignment moments in any reference frame, $A_{q+}^{(2)}$, can be converted to the alignment moments in any other, arbitrary reference frame, $A_{q'}^{(2)}$, by Euler rotation through the appropriate angles, ($\alpha, \beta, \gamma$). This rotation is described mathematically as

$$S_{q+}^{(2)} = \sum_{q'} D_{q'q}^{(2)}(\alpha, \beta, \gamma) S_{q'}^{(2)}.$$  \hspace{1cm} (A.1)

$S_{q+}^{(2)}$ is proportional to $A_{q+}^{(2)}$ (and $S_{q'}^{(2)}$ is proportional to $A_{q'}^{(2)}$) as follows:

$$A_{q+}^{(2)} = \frac{S_{q+}^{(2)}}{\sqrt{2}},$$  \hspace{1cm} (A.2)
\[ A_{1+}^{(2)} = \frac{S_{1+}^{(2)}}{\sqrt{2}}, \]  
\[ A_{2-}^{(2)} = \frac{S_{2-}^{(2)}}{\sqrt{2}}, \]  
\[ D_{q+1+}^{(2)}(x, \beta, \gamma) \text{ are the real rotation matrix elements:} \]

\[ D_{0+0+}^{(2)}(x, \beta, \gamma) = \frac{1}{2} (3 \cos^2 \beta - 1), \]  
\[ D_{0+1+}^{(2)}(x, \beta, \gamma) = -\frac{\sqrt{3}}{2} \sin 2\beta \cos \gamma, \]  
\[ D_{0+2+}^{(2)}(x, \beta, \gamma) = \frac{\sqrt{3}}{2} \sin^2 \beta \cos 2\gamma, \]  
\[ D_{1+0+}^{(2)}(x, \beta, \gamma) = \frac{\sqrt{3}}{2} \sin 2\beta \cos x, \]  
\[ D_{1+1+}^{(2)}(x, \beta, \gamma) = \cos x \cos 2\beta \cos \gamma \]  
\[ - \sin x \sin \gamma \cos \beta, \]  
\[ D_{1+2+}^{(2)}(x, \beta, \gamma) = -\cos x \cos \beta \cos 2\gamma \sin \beta \]  
\[ + \sin x \sin \beta \sin 2\gamma, \]  
\[ D_{2+0+}^{(2)}(x, \beta, \gamma) = \frac{\sqrt{3}}{2} \sin^2 \beta \cos 2\gamma, \]  
\[ D_{2+1+}^{(2)}(x, \beta, \gamma) = \cos 2x \cos \beta \cos \gamma \sin \beta \]  
\[ - \sin 2x \sin \beta \sin 2\gamma, \]  
\[ D_{2+2+}^{(2)}(x, \beta, \gamma) = \frac{1}{2} \cos 2x \cos 2\gamma(1 + \cos^2 \beta) \]  
\[ - \sin 2x \sin 2\gamma \cos \beta. \]  

For more detail, see Hertel and Stoll [44].

References


