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Direct Measurement of the Preferred Sense of NO Rotation After Collision with Argon

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The preferred sense of product molecule rotation (clockwise or counterclockwise) in a bimolecular collision system has been measured. Rotationally inelastic collisions of nitric oxide (NO) molecules with Ar atoms were studied by combining crossed molecular beams, circularly polarized resonant multiphoton ionization probing, and velocity-mapped ion imaging detection. The observed sense of NO product rotation varies with deflection angle and is a strong function of the NO final rotational state. The largest preferences for sense of rotation are observed at the highest kinematically allowed product rotational states; for lower rotational states, the variation with deflection angle becomes oscillatory. Quantum calculations on the most recently reported NO-Ar potential give good agreement with the observed oscillation patterns in the sense of rotation.

Crossed molecular beam studies of inelastic and reactive bimolecular collisions have provided the most detailed information on the elementary processes fundamental to an understanding of chemical reactions (1, 2). The power of the crossed beam experiment arises from the control of initial conditions such as collision energy and the direction of reactant approach. Scalar quantities measured in such experiments include chemical reaction probabilities and energy partitioning among product states. Measurements of vector quantities, such as product velocity or rotational angular momentum, reveal the correlations among the directional properties of the reactant and product trajectories. The vector quantity measured in traditional crossed beam experiments is the differential cross section (DCS), which gives the probability of product formation as a function of the angle between the directions of product approach and reactant recoil. Recent advances have made possible the measurement of product recoil direction in coincidence with the direction of product angular momentum. Such measurements provide a detailed picture of the final reaction trajectory, which is highly sensitive to the topology of the potential energy surface (PES) along the reaction pathway.

Case and Herschbach have shown that measurements of four vectors provide a complete account of the scattering dynamics of an atom-diatom system (3). The important vectors are \mathbf{v} , \mathbf{v}' , \mathbf{j} , and \mathbf{j}' , which describe the reactant and product relative velocity and the reactant and product angular momentum, respectively (3-5). If the reactant diatom is nonrotating, then the angular correlation among the directions of reactant approach v, product ejection v', and product angular momentum \mathbf{j}' is of interest. The full \mathbf{v} - \mathbf{v}' - \mathbf{j}' correlation includes both rotational alignment (the preferred plane of product rotation) and the rotational orientation (the preferred sense of product rotation) with respect to the scattering plane defined by v and v'. Recent advances in Doppler spectroscopy (6, 7), laser ionization/time-of-flight techniques (8-10), and ion imaging (11, 12) have made possible experimental measurements of rotational alignment for a number of reactive and inelastic scattering systems. However, theoretical studies have indicated that rotational orientation may be a more sensitive probe of the scattering dynamics (13-15). In this paper, we report the first experimental observations of molecular rotational orientation in a full two-body collision.

Our experiments study rotationally inelastic collisions of nonrotating, nonvibrating, ground-electronic-state NO molecules with Ar atoms [NO ${}^{2}\Pi_{1/2}(v = 0, j = 1/2) + Ar \rightarrow$ NO ${}^{2}\Pi_{1/2}(v' = 0, j') + Ar]$ at a center-ofmass (CM) frame collision energy of 66 meV. The highest NO rotational state that can be populated at this collision energy is j' =16.5. Figure 1 shows a schematic representation of one type of trajectory for classical scattering superimposed over image data described below. The NO molecule, tilted by an angle α , approaches from the right with initial velocity v. The Ar atom approaches from the left, offset by impact parameter b. After collision, the initial NO velocity, v, is deflected through the angle θ . For simplicity in this illustration, we have chosen the reactant NO internuclear axis to lie in the scattering plane, so that the product NO angular momentum

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vector, \mathbf{j}' , is perpendicular to the figure. The collision dynamics illustrated in Fig. 1 result in a preferred sense of NO rotation in the $(\mathbf{v}, \mathbf{v}')$ scattering plane with j' = 15.5 and the sense of rotation depends on the ejection direction, \mathbf{v}' . Because the dynamics has reflection symmetry about the vector \mathbf{v} in the scattering plane, opposite senses of product rotation must be observed for deflection to the right [counterclockwise (CCW) in the top half of Fig. 1] and left [clockwise (CW) in the bottom half of Fig. 1]. Our scattering experiment samples a statistical distribution of initial NO impact parameters b and angular orientations.

The collision of achiral reactant species such as NO and Ar cannot create an overall preferred sense of molecular rotation for the full product state distribution. However, as shown in Fig. 1, within the distribution preferred senses of rotation can be observed at particular deflection angles θ for a given product state, j'. We are able to observe this effect because our state-selective detection scheme allows the sense of product rotation to be measured as a function of deflection angle. Our experimental technique combines a standard crossed molecular beam apparatus with laser photoionization of the scattered products and subsequent imaging of the ions onto a position-sensitive detector. Figure 2 shows a schematic representation of the crossed molecular beam apparatus (16). Scattered NO molecules are rotational-state selectively ionized (17) using 1 + 1' resonant enhanced multiphoton ionization (REMPI) through the R_{21} branch of the $A^2 \Sigma_{1/2}^+ \leftarrow$ $X^2 \Pi_{1/2}$ transition (18). Velocity-mapping ion



Fig. 1. A sample classical trajectory for rotationally inelastic scattering of NO(j = 0.5) with Ar in the CM frame at 66 meV collision energy. The underlying NO⁺ velocity-mapped image is the smoothed experimental (R - L)/(R + L) scaled difference measured when probing NO(j' = 15.5) with RCP and LCP light. For this image, the NO recoil velocity scale is 250 m/s per division. The color map represents the (R - L)/(R + L) amplitude with positive (red) indicating counterclockwise rotation.

optics (19) accelerate the NO^{+.} onto a twodimensional (2D) position-sensitive microchannel plate detector coupled to a phosphor screen viewed by a cooled charge-coupled device camera. The captured ion image represents a 2D projection of the product recoil velocity distribution onto the detector plane. The intensity at the periphery of this ion image arises from product trajectories in the scattering plane parallel to the plane of the detector.

In order to detect the NO product sense of rotation in the detector plane, we compare the images of scattered NO molecules obtained with right circularly polarized (RCP) and left circularly polarized (LCP) probe light. When the NO is probed via R_{21} branch transitions, RCP probe light preferentially ionizes molecules with a CCW sense of rotation, as viewed by an observer looking toward the source of the probe light. Molecules with a CW sense of rotation are preferentially ionized by LCP light (20).

Velocity-mapped NO⁺ images were measured for both RCP (Fig. 3A) and LCP (Fig. 3B) probing of the NO product j' = 6.5 and

15.5 rotational states. Conservation of the 65 meV of collision energy requires that the product recoil translational energy decrease with increasing NO rotational state. The recoil velocity v' for the NO(j' = 15.5) product, proportional to the diameter of images in Fig. 3, is noticeably smaller than the NO(j'= 6.5) product. Recovery of a 3D product recoil distribution from the full image has been discussed elsewhere (21). Here we focus only on the probe polarization dependence of the signal intensity at the rim of the image arising from trajectories in a scattering plane parallel to the detector. A typical annular region of interest is shown for these product states in Fig. 3B. The RCP-LCP difference images in Fig. 3C highlight the probe polarization dependence. To eliminate the complicating effects of the DCS and apparatus detectivity, we divide the difference images in Fig. 3C by RCP + LCP sum images, producing the images in Figs. 1 and 3D, which are a direct map of the preference for sense of rotation in the product state that was selectively ionized.



Fig. 2. Schematic representation of the crossed molecular beam apparatus with rotationally state-selective, polarized 1 + 1' REMPI probing and ion imaging detection. The NO and Ar molecular beams intersect at a right angle, and probe and ionization laser beams overlap the intersection region. Velocity-mapped ion optics direct the REMPI-ionized NO(j') product toward an imaging detector located perpendicular to the plane of the molecular beams. The CP probe beam propagates along the detection axis and is sensitive to the sense of product rotation in the scattering plane defined by the molecular beams. The probe polarization helicity is set by a Glan polarizer and quarter-wave plate. The ionization beam bisects the molecular beams in the scattering plane. The measured NO⁺ image represents a 2D projection of the NO(j') product recoil velocity onto the detector plane.

In order to compare the measured rotational orientation preference with theory, we further quantify the results shown in Fig. 3. When probing product state j' with probe polarization ε , the variation of the rim intensity with deflection angle is given by

$$I_{j'}(\theta,\varepsilon) = \sigma_{j'}P_{j'}(\theta)F_{j'}(\theta)Z_{j'}(\theta,\varepsilon)$$
(1)

where $\sigma_{j'}$ is the total probability for scattering into state j' and $P_{j'}(\theta)$ is the DCS. The apparatus detectivity factor $F_{j'}(\theta)$ accounts for the spatial overlap of the laser and molecular



Fig. 3. Experimentally measured NO⁺ velocitymapped images for rotationally inelastic scat-tering into the NO j' = 6.5 and 15.5 product channels. The NO recoil velocity scale is 500 m/s per division, and the initial reactant velocities are identical to those shown in Fig. 1. Images were measured with (A) RCP and (B) LCP probe light. Images (C) and (D) are R - Ldifferences and (R - L)/(R + L) scaled differences that are a direct indication of the NO product rotational orientation. Images in (B) schematically show how the rim intensities in Eq. 1 are extracted from experimental data by summing the image intensity over an angular range $\Delta \theta$ for a narrow annulus around the perimeter of the image. The color map represents the ion intensity, as shown at the bottom of the figure. Black indicates zero intensity in (A) and (B) or zero polarization sensitivity in (C) and (D). In (C) and (D), a positive amplitude (red) indicates CW NO product rotation, and negative amplitude (violet) indicates CCW rotation.

beams and the nonuniform detection probability for different laboratory-frame recoil velocities. It is the probe polarization-dependent photoionization probability, $Z_{j'}(\theta, \varepsilon)$, for NO(*j'*) deflected by angle θ that reveals the CW or CCW orientational preference for product rotation in the scattering plane.

The (RCP – LCP)/(RCP + LCP) ratio images, shown in Fig. 3D and also reproduced in Fig. 1, are sensitive only to the $Z_{j'}(\theta,\varepsilon)$ factor in Eq. 1. For positive deflection angles θ in Fig. 1, the value of the (RCP – LCP)/(RCP + LCP) ratio of rim intensities

$$Q_{j'}(\theta) = [I_{j'}(\theta, \varepsilon_{\rm RCP}) - I_{j'}(\theta, \varepsilon_{\rm LCP})]/[I_{j'}(\theta, \varepsilon_{\rm RCP}) + I_{j'}(\theta, \varepsilon_{\rm LCP})]$$
$$= [Z_{j'}(\theta, \varepsilon_{\rm RCP}) - Z_{j'}(\theta, \varepsilon_{\rm LCP})]/[Z_{j'}(\theta, \varepsilon_{\rm RCP}) + Z_{j'}(\theta, \varepsilon_{\rm LCP})] \quad (2)$$

is positive for preferred CW product NO

rotation in the scattering plane, negative for preferred CCW rotation, and zero if there is no rotational orientation. The measured $Q_{j'}(\theta)$ amplitude, the annular ring intensity of Fig. 3D, is plotted in Fig. 4 for selected product NO rotational states.

A semiclassical description of the alignment and orientation of the angular momentum vector is typically given by an expansion in real spherical harmonics with coefficients $A_{q+}^{k}(\theta; j')$. Using the Hertel-Stoll description of angular momentum polarization (22), the $Q_{j'}(\theta)$ ratio can be shown to be

$$Q_{j'}(\theta) = 3h_{j'}^{(1)}A_{1-}^{1}(\theta;j')/\{2+h_{j'}^{(2)} \\ [A_{0+}^{2}(\theta;j')+3A_{2+}^{2}(\theta;j')]/2\}$$
(3)

where the $A_{q+}^{k}(\theta; j')$ are deflection angledependent real moments of the angular distribution of \mathbf{j}' , and $h_{j'}^{(1)}$ and $h_{j'}^{(2)}$ are specific to the branch and rotational level of the probe



Fig. 4. Velocity-mapped polarization NO⁺ difference images and $Q_{j'}(\theta)$ ratios for selected NO product rotational states, j'. Exp, experimental; calc, calculated. The NO recoil velocity scale is 500 m/s per division, and the initial reactant velocities are identical to those shown in Fig. 1. The color map represents the (R - L) difference amplitude with positive (red) indicating CW rotation and negative (violet) indicating CCW rotation. The center column shows experimentally measured $Q_{j'}(\theta)$ ratios extracted from the top ($\theta > 0$) and bottom ($\theta < 0$, red trace) perimeter of the images as shown in Fig. 3B. The right column shows $Q_{j'}$ ($\theta > 0$, blue trace) ratios calculated by a classical rigid-ellipsoid Monte Carlo model (green trace) and a close-coupling quantum calculation (red trace) for the 1999 Alexander ab initio potential (29). For comparison, the analogous quantum calculation for the 1993 Alexander ab initio potential (30) is shown as a dotted trace.

transition (23). For probing on an *R*-branch transition, in the high-j' limit,

$$Q_{j'}(\theta) = -3A_{1-}^{1}(\theta;j')/\{2- [A_{0+}^{2}(\theta;j')+3A_{2+}^{2}(\theta;j')]/4\}$$
(4)

The A_{q+}^2 moments specify the preferred plane of NO product rotation (rotational alignment), and their physical limits make the denominator of Eqs. 3 and 4 always positive. The mathematical sign of $Q_{j'}(\theta)$ and the preferred sense of NO product rotation are determined only by A_{1-}^1 . We have calculated the $A_{q+}^k(\theta; j')$ moments directly from the scattering matrix obtained in full close-coupled quantum calculations using two recent ab initio NO-Ar potentials of Alexander (24, 25) and the Hybridon scattering package (26). These moments and Eq. 3 are used to obtain the theoretical $Q_{j'}(\theta)$ amplitudes in Fig. 4.

The NO(j' = 15.5) product shows the largest rotational orientation in Fig. 4. The large rotational inelasticity of this product channel likely originates from strongly repulsive collisions with small impact parameters. Such collisions have traditionally been modeled as impulsive collisions between a hard sphere and a rigid ellipsoid. We model our data using a 3D Monte Carlo sampling of initial conditions for classical 66-meV hard sphere-rigid ellipsoid collisions. Figure 4 shows the resulting $Q_{i'}(\theta)$ amplitude obtained from the classical calculation (27). Bosanac (28) has shown that such a model gives rotational orientation only if there are multiple encounters, or "chattering collisions." Our classical simulation confirms that the NO(j'= 15.5) rotational orientation originates because trajectories in which NO(j' = 15.5) is produced in an initial encounter are subsequently removed by scattering into a lower rotational state in a second encounter with the recoiling Ar atom. The large NO(j' = 15.5) angular velocity and its small recoil velocity make the probability of a second encounter high. The quantum and impulsive classical models are in good qualitative agreement with experiment for NO(j' = 15.5), suggesting that the large rotational orientation indeed arises from multiple encounter collisions. Within the classical impulsive model, the trajectories removed from the i' = 15.5 final distribution by chattering collisions ultimately contribute to rotational orientation in the lower j' states of the NO product.

For lower rotational states of the NO product, the sense of rotational orientation alternates with deflection angle in a complicated way, which is well reproduced by quantum close-coupling calculations. The classical rigid ellipsoid model does predict a rotational orientation but not the complex oscillatory patterns observed experimentally. There are two major deficiencies of the classical model that may account for its failure at low j'. First, the classical calculation does not include the attractive parts of the interaction potential that are important in producing lower rotational states. Second, the classical model does not account for quantum interference among the product trajectories. These interferences include those between multipleencounter and single-encounter paths leading to the same NO product rotational state and deflection angle, and between the nearside and farside paths that characterize potentials with attractive components (29). Within a semiclassical description of the collision dynamics, we speculate that multiple-encounter trajectories generate the possibility of rotational orientation, and that interference creates the complex oscillation patterns observed experimentally.

The calculated oscillation patterns in the NO rotational orientation are compared in Fig. 4 for two similar ab initio Ar-NO potential energy surfaces that differ in size of basis set and well depth. The two PESs predict similar NO product rotational distributions and rotational alignments. For high-j' products, the two PESs also predict virtually identical rotational orientations. which are also in rough qualitative agreement with the classical prediction. The similarity of all three predictions of rotational orientation at high j' suggests that the dynamics for highly inelastic collisions is dominated by relatively simple repulsive kinematics. However, the oscillation patterns predicted from the two PESs significantly differ at low j', with the more recent potential better predicting the measured oscillatory pattern of rotational orientation. This result demonstrates the unusual sensitivity of the θ -dependent pattern of product rotational orientation to the PES. We note that both PESs predict a larger overall magnitude of orientation than is observed experimentally. The origin of this difference in magnitude remains unclear.

The observation of a high degree of preference for molecular rotation in simple inelastic scattering and the sensitivity of the orientation to details of the intermolecular potential demonstrate that rotational orientation provides a demanding test of potential energy surfaces. This technique should have special utility in the study of reactive scattering, because reactive trajectories may be highly stereospecific, with stringent requirements for reactant orientation.

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