Imaging the inelastic scattering of vibrationally excited NO \((v = 1)\) with Ar

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1. Introduction

Inelastic scattering of the open-shell radical NO with rare gases has been a benchmark for understanding collision dynamics for decades, and new aspects continue to be revealed. Measurements of angular distributions from the scattering experiments directly embody the differential cross sections (DCSs), providing a sensitive probe of the molecular interaction potential energy surfaces (PESs). The application of velocity map imaging combined with crossed-molecular beams has been found to be very powerful in studies of reactive and inelastic scattering to understand the underlying dynamics [1–3]. Houston and coworkers first employed imaging to probe the state-to-state DCSs for inelastic collisions of ground state NO \((X^2Π)\) with Ar [4,5]. They observed rotational rainbow peaks in the angular distributions and these peaks move to backward scattering angles with increasing final rotational level. This was followed by work from the Suzuki [6], and Chandler groups [7], in which fully state-resolved DCSs for the inelastic scattering of NO \((X^2Π, v = 0, j = 0.5)\) with Ar were measured resulting from spin-orbit conserving and changing transitions. These arise from scattering from sum and difference potentials built from PESs, of \(A^\prime\) and \(A^\prime\prime\) character. Their findings were consistent with quantum mechanical close-coupling (QM CC) calculations based on \textit{ab initio} coupled-cluster CCSD(T) and CEPA potential energy surfaces. Later, Stolte, Brouard and coworkers [8–11] were able to resolve the \(\Lambda\)-doublet effects on the DCSs for NO \((X^2Π)\) inelastic collisions with Ar by coupling a hexapole to the crossed beam velocity map imaging apparatus. They observed different quantum interference structures on DCSs for total parity-conserving and changing collisions. Rigorous quantum scattering calculations suggest that the heteronuclear nature of NO plays an important role in the DCSs for the parity-conserving collisions, but is less important for the parity-changing collisions [12,13]. Other work by Cline and coworkers [14] also revealed a high degree of directional preference for NO rotation during collisions with Ar. They reported that the NO product orientation varies with the deflection angle and for lower rotational states, the variation with deflection angle becomes oscillatory. More recently, van de Meerakker and coworkers in Nijmegen used a Stark decelerator to produce a well-defined and velocity-controlled NO radical beam that intersected with a conventional beam of rare gases. Using velocity map imaging [2], they observed diffraction oscillations in the DCSs from the inelastic scattering of NO radicals with the rare gases He, Ne, Ar, Kr, and Xe [15,16]. This phenomenon is in excellent agreement with high-level QM CC calculations based on the most accurate PESs.

Although NO inelastic scattering has long been of interest, most such studies have focused on the vibrational ground state and very little has been reported for vibrationally excited NO. The difficulty is very likely due to the challenge of preparing a vibrationally hot but rotationally cold NO molecular beam. Optical pumping has been used to generate the vibrationally excited NO by direct absorption of infrared radiation [17–19]. The rate constants were then measured for NO \((X^2Π, v = 1, 2, 3)\) with selected gas...
molecules including Ar. The thermally averaged cross-sections were reported for total removal of NO from the particular rovibronic levels $X^2Π_{1/2}$, $v = 3$, $j = 0, 3, 5, 6.5$ and 6.5 in collisions with Ar at various temperatures: 27, 44, 53 and 139 K [19]. Alternatively, the Houston group [20] prepared vibrationally excited NO at the exit of the valve nozzle through a photoinitiated reaction between O(1D) and N2O. Due to the nature of the reaction, they were only able to make vibrationally excited NO at $v = 5$. They measured the DCSs for rotationally inelastic scattering ($j = 6.5, 16.5$ and 20.5) of vibrationally excited NO ($v = 5$) from Ar for the first time by coupling crossed molecular beams with velocity map imaging. On comparing the results of $v = 5$ to $v = 0$, they observed a small shift in rotational rainbow maxima to smaller angles in $v = 5$ compared to the ground state $v = 0$. They concluded that the shift in the rainbow angle is a manifestation of the increased angular anisotropy during vibrational excitation.

In the present work, we prepared the vibrationally excited NO ($X^2Π, v = 1$) by resistively heating the nozzle of our valve. We present the results of our crossed-beam study on vibrationally excited NO ($X^2Π, v = 1$) with Ar by acquiring images for the inelastic scattered NO products using our DC slice imaging technique. After background subtraction and density-to-flux correction, the differential cross sections for various $j$-levels of NO ($v = 1$) are derived to unravel the underlying dynamics, and compared to those from the inelastic scattering of NO ($v = 0$) with Ar under same conditions.

2. Experimental section

The experiments are carried out in a crossed molecular beam apparatus combined with DC slice ion imaging, which has been previously described elsewhere [21]. The apparatus consists of one reaction chamber and two source chambers that are perpendicular to each other. The Ar beam is pulsed at 10 Hz with a backing pressure of 5.3 bar into one source chamber via a piezoelectric stack actuator (Physik Instrumente, P212.80) valve [22] with 120 μm poppet translation and 50 μs pulse duration. The vibrationally excited NO is generated with a home-built flash pyrolysis [23] source closely related to the pyrolysis design by Chen and coworkers [24]. The NO beam is introduced into the second source chamber by pulsing a piezoelectric pulsed valve operating at 10 Hz with a backing pressure of 5 bar. The NO beam is expanded into the SiC nozzle and resistively heated to 20 K before entering into the interaction chamber to be intersected by the Ar beam at 90°. The final scattered NO ($X^2Π, v = 0$ or 1) products are then state-selectively ionized using (1 + 1) resonance-enhanced multiphoton ionization (REMPI) near 226 nm via the $A^3Σ^+(v' = 0$ or 1) electronic state and detected with the DC slice ion imaging technique. The UV radiation near 226 nm is generated by the frequency tripling of the fundamental output of a pulsed dye laser (Sirah Cobra-Stretch, LDS 698 dye) pumped by the second harmonic of a seeded Nd:Yttrium aluminum garnet (Nd:YAG) laser (Quanta Ray, Spectra Physics). A four-electrode dc slice ion optics assembly accelerates the ions in the direction perpendicular to the scattering plane. After passing through a 75 cm field-free flight tube, the NO$^+$ ions are velocity focused onto a dual microchannel plate (MCP)/phosphor screen coupled detector. The detector is gated for the center slice of the scattered product ions and resultant images are recorded using a charge-coupled device (CCD) camera and analyzed with our data acquisition program. The background signal from the NO beam alone is subtracted and density-to-flux correction is performed before further analysis to obtain the angular distributions of the rotationally inelastic scattering.

3. Theory section

We performed QM CC calculations to compute state-to-state cross sections for NO ($v = 0$) + Ar. A scattering program for open-shell diatom–atom scattering was used that was originally developed for OH + rare gas collisions [25]. The ab initio potential energy surfaces constructed by Alexander were used as input [26]. Using the renormalized Numerov method, we propagated the wave function on an equidistant grid in R from 3.5 to 50 bohr with 1094 points, where R is the distance between the Ar atom and the center-of-mass of the NO molecule. We took all NO rotational levels up to $j = 25.5$ and all partial wave contributions up to a total angular momentum of $J = 200.5$ into account in the channel basis set. The scattering cross sections were computed for a collision energy of 3.0 kcal mol$^{−1}$ and for initial NO rotational levels up to $j = 6.5$.

4. Results and discussion

In this present work, the NO products at various rotational $j$ levels are detected after inelastic collisions of NO ($v = 0$, 1) with Ar at a collision energy of 3.0 kcal mol$^{−1}$. The experimental scattering results for the ground state NO ($v = 0$) with Ar were compared to the theoretical results. Further comparison was conducted on inelastic scattering of the vibrationally excited NO ($v = 1$) to the ground state NO ($v = 0$) under the same conditions. This study is directed to examining whether the different vibrational excitation of the diatomic molecule affects the angular distributions of the rotationally inelastic scattering under the same conditions. Superelastic scattering of NO ($v = 1$) giving ($v = 0$) product was not expected or observed, as it is a process of much smaller total cross section.

We first measured REMPI spectra for NO to characterize the NO molecular beam generated from the flash pyrolysis source. The 1 + 1 REMPI spectra of $A^3Σ^+ \rightarrow X^2Π_{0}(0,0)$ and (1,1) [27,28] bands were obtained at two different energy regions, corresponding to two different prepared vibrational levels for NO, $v = 0$ and $v = 1$, respectively (as shown in Fig. 1). The rotational band contour is simulated with known parameters [29–31] under the rotational temperature of 20 K using the PCOPHER program [32]. The good agreement of the REMPI spectra for both NO $v = 0$ and $v = 1$ between experimental and simulated results (as shown in Fig. 1) indicates that the generated NO beam is rotationally cold, ca. 20 K. At this rotational temperature, only the first few rotational levels ($j = 0.5$ to 5.5) are significantly populated for our NO molecular beam source at both $v = 0$ and $v = 1$, and these rotational levels thus dominate the inelastic collisions we observe with Ar.

The final rotational states populated by inelastic scattering are ionized by 1 + 1 REMPI employing the main R11 branch (overlapping with the Q21 satellite branch) of the $A^3Σ^+ \rightarrow X^2Π$ electronic transition. The vibrational ground state NO $v = 0$ is probed using the (0,0) band, while the vibrationally excited state NO $v = 1$ is probed using the (1,1) band. The inelastic scattering images of the final rotational states for NO $v = 0$ and $v = 1$ are shown in Fig. 2 with the nominal Newton diagrams superimposed on them. The images portray the forward scattered signal pointing down (the direction of the NO beam) and the backward scattered signal pointing up. The background signal arises from NO in the molecular beam that does not undergo inelastic collisions with Ar. This background is more intense for lower $j$ levels because of the low rotational temperature ($\sim 20$ K) for our molecular beam. Therefore,
The present study focuses on only high \( j \) levels, from 12.5 to 22.5, in order to reduce the interference in the inelastic scattering from the background.

The images in Fig. 2 show a single sharp scattering ring for each \( j \) level except for \( j = 20.5 \) after the inelastic collision between NO and Ar. The size of the image decreases with increasing \( j \), which is consistent with the conservation of energy. The inner ring of the image labeled \( j = 20.5 \) corresponds to signal at the \( j = 20.5 \) level whereas the outer ring corresponds to \( j = 15.5 \), since the \( R_{11}(20.5) \) transition is very close to the \( R_{21}(15.5) \) transition. Therefore, this image is analyzed to yield two separate DCS’s. The center-of-mass angular distribution is obtained by integrating the signal over a certain radial region of interest to characterize the rotationally inelastic scattering. We first compared the experimental angular distribution of NO(\( v = 0 \))/Ar system with the theoretically predicted differential cross sections (DCS) for this system at different \( j \) levels. At present only the \( v = 0 \) DCS is available for this system. In order to match our experimental condition of 20 K rotational temperature, each effective DCS distribution is generated by weighting the initial \( j \) states of NO \( v = 0 \) with a Boltzmann distribution at 20 K.

Both experimental and theoretical DCS distributions (as shown in Fig. 3) of NO(\( v = 0 \))/Ar system exhibit the expected rotational rainbow peak that shifts to a larger scattering angle with increasing rotational excitation. We observed forward scattering for \( j = 12.5 \) to 14.5 with the rotational rainbow maxima around 35° and 50° respectively. Sideways scattering was observed for \( j = 15.5 \), 16.5, 18.5, and 20.5 with the rotational rainbow maxima shifting to larger angles, and backward scattering was seen for our highest detectable \( j = 22.5 \) level with a collision energy of 3.0 kcal mol\(^{-1}\). We see evidence of the double rainbow phenomenon as predicted by theory, with two rainbow peaks around 60° and 120° for \( j = 15.5 \) and 16.5, despite averaging over the initial 20 K rotational distribution. This arises from scattering off either the O end or the N end of the molecule. These two peaks are more clearly resolved for \( j = 15.5 \), but the more forward peak is significantly reduced compared to theory. This may be due to interference from \( j = 20.5 \) which is also present in the image and enhances the more backscattered peak.

We then investigate whether vibrational excitation of the NO molecule significantly affects the angular distributions of the rotationally inelastic scattering with Ar. The experimental differential cross section for a particular final rotational state in the NO(\( v = 1 \))/Ar system is compared to that in the NO(\( v = 0 \))/Ar system in Fig. 4. The signal-to-noise level of the NO(\( v = 1 \))/Ar system is lower than that in the NO(\( v = 0 \))/Ar system. Nevertheless, the differential cross sections still show a rotational rainbow peak.

Fig. 1. 1 + 1 REMPI spectra of NO recorded for \( v = 0 \) (left panel) using \((0, 0)\) band and \( v = 1 \) (right panel) using \((1, 1)\) band of the \( A^2\Sigma^+ \rightarrow X^2\Pi \) transition. The lower spectra (blue) are the simulation at 20 K, whiles the upper spectra (black) are experimental results. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. DC slice images for inelastic scattering of NO with Ar with Newton diagram superimposed. Upper panel: \( v = 1, j = 12.5, 14.5, 16.5, 18.5, 20.5, \) and 22.5. Lower panel: \( v = 0, j = 12.5, 14.5, 16.5, 18.5, 20.5, \) and 22.5.
shifting to a larger scattering angle for NO \((v = 1)\). We also see that the position of the rainbow maxima for NO \((v = 1)\) at each final rotational state almost tracks that of NO \((v = 0)\). There is only one significant exception, that is \(j = 12.5\). At \(j = 12.5\), a modest enhancement of the backward scattering distribution is obtained in the NO \((v = 1)\)/Ar system which we do not observe for the NO \((v = 0)\)/Ar system nor in the theoretical DCS for NO \((v = 0)\). Aside from this level, the comparison of \(v = 1\) to \(v = 0\) does not reveal significant differences in the scattering distributions within the present signal-to-noise. The results obtained might not be that surprising since we only excite NO to \(v = 1\), and the equilibrium bond length is only \(\sim 1\)% larger. Houston and coworkers observed only a small change in the angle of the rainbow maxima in the scattering of vibrationally excited NO \((v = 5)\) with Ar compared to the scattering of NO in the vibrational ground state with Ar. However, the root-mean-square spread in the N-O distance is \(\sqrt{3}\) times larger for \(v = 1\), suggesting an effect might be observable. It may be that by averaging over the 20 K distribution we obscure small changes in the DCS. Future studies that employ spectroscopic preparation of vibrationally excited levels while maintaining a rotationally very cold beam may have an improved chance of revealing subtle effects.

5. Conclusion

We have used crossed molecular beams coupled to dc slice velocity map imaging to investigate the effect of vibrational excitation on the inelastic scattering for NO with Ar. The inelastic collision process at a collision energy of 3.0 kcal mol\(^{-1}\) for vibrationally excited NO at \(v = 1\) with Ar is examined and compared to that of the vibrational ground state NO with Ar. We observed the expected gradual shift of the rotational rainbow maxima to larger scattering angles as we probed higher rotational levels. Within the signal-to-noise, we did not observe significant scattering differences between the NO \((v = 1)\)/Ar and NO \((v = 0)\).

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