**Rotational and Angular Distributions of NO Products from NO-Rg
(Rg = He, Ne, Ar) Complex Photodissociation**

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ABSTRACT

We present the results of an investigation into the rotational and angular distributions of the NO $\tilde{A}$ state fragment following photodissociation of the NO-He, NO-Ne and NO-Ar van der Waals complexes excited via the $\tilde{A} \leftarrow \tilde{X}$ transition. For each complex the dissociation is probed for several values of E_a , the available energy above the dissociation threshold. For NO-He the E_a values probed were 59, 172 and 273 cm⁻¹; for NO-Ne they were 50 and 166 cm⁻¹; and for NO-Ar they were 44, 94, 194 and 423 cm⁻¹. The NO $\tilde{A}$ state rotational distributions arising from NO-He are cold, with most products in low angular momentum states. NO-Ne leads to broader NO rotational distributions but they do not extend to the maximum possible given the energy available. In the case of NO-Ar the distributions extend to the maximum allowed at that energy and show the unusual shapes associated with the rotational rainbow effect reported in previous studies. This is the only complex for which a rotational rainbow effect is observed at the chosen E_a values. Product angular distributions have also been measured for the NO $\tilde{A}$ photodissociation product for the three complexes. NO-He produces nearly isotropic fragments, but the anisotropy parameter, β , for NO-Ne and NO-Ar photofragments shows a surprising change in sign from negative to positive as E_a increases within the unstructured excitation profile. Franck-Condon selection of a broader distribution of geometries including more linear geometries at lower excitation energies and more T-shaped geometries at higher energies can account for the changing recoil anisotropy. Two-dimensional wavepacket calculations are reported to model the rotational state distributions and the bound-continuum absorption spectra.

1.0 INTRODUCTION

As a consequence of their experimental accessibility, the van der Waals complexes of NO with rare gases (NO-Rg) have come to serve as benchmarks for dispersion interactions between open shell and closed shell systems.[1, 2] The relatively small number of electrons associated with the complexes involving the three lightest rare gases, He, Ne and Ar, facilitate high level *ab initio* calculations and hence the opportunity for strong interplay between theory and experiment in advancing our understanding of these weakly bound systems. While transitions to various excited electronic states have been studied, the $\tilde{A}^2\Sigma \leftarrow \tilde{X}^2\Pi$ electronic transition is particularly interesting because spectra for the NO-He and NO-Ne complexes have not been reported, while the NO-Ar complex has revealed a number of surprises.

The $\tilde{A}^2\Sigma \leftarrow \tilde{X}^2\Pi$ transition of NO-Ar was first observed more than 30 years ago via fluorescence from the NO photodissociation product.[3] This spectrum showed a broad, structureless feature some 300-400 cm^{-1} wide peaking near 44 550 cm^{-1} , 600 cm^{-1} to the blue of the monomeric NO band origin, indicating a significant change in the van der Waals potential between the two electronic states. Because of the large geometry change between the $\tilde{X}$ and $\tilde{A}$ states, transitions to the bound region near the origin are very weak and it was some time before they were observed. The first investigation of the bound-bound $\tilde{A}^2\Sigma \leftarrow \tilde{X}^2\Pi$ transition was of quite low resolution, but nonetheless revealed structure.[4] Subsequent studies with increased resolution[5, 6] revealed several bands assignable to vibrational modes,[6] with the origin being determined as 44 242.4 cm^{-1} .[7] The identification of almost all of the features observed in the

bound-bound $\tilde{A} \leftarrow \tilde{X}$ spectrum was achieved through the enhanced quality of later resonance enhanced multiphoton ionization (REMPI) experiments.[8, 9] Although a recent report found some major discrepancies in the accepted assignments, these have, for the most part, been rectified and the bound-bound $\tilde{A} \leftarrow \tilde{X}$ spectrum is now well understood.[10, 11] Thuis *et al.*[12] originally suggested that the $\tilde{X}$ state of the complex is T-shaped and this was subsequently confirmed by Mills *et al.*[13] from radiofrequency and microwave spectra. In contrast, the $\tilde{A}$ state is linear, [8] with the most recent results revealing that the argon is situated adjacent to the nitrogen atom.[10]

Tsuji *et al.* made the first experimental determination of the NO-Ar binding energy by measuring action spectra for several NO N product states.[5] (N is the diatomic angular momentum excluding spin). Interestingly, resonance features were observed above the dissociation limit for $N = 1$ and 2. Roeterdink *et al.*[7] reported on a velocity map ion imaging (VMI) investigation of dissociation following excitation of the resonance features. They propose that the resonances are due to a type of vibrational Feshbach effect and are not the result of a centrifugal barrier to dissociation, as originally proposed by Tsuji *et al.*[5] Significantly, they found that the translational energy of the products following excitation of pre-dissociative resonances was higher than expected and determined that this was because the features are associated with excitation from thermally populated levels within the $\tilde{X}$ state. Their results implied a need to revise the dissociation energies in the $\tilde{A}$ and $\tilde{X}$ states reported by Tsuji *et al.*, and we have recently measured the dissociation energy afresh, finding values of 93.5 ± 0.9 and 50.6 ± 0.9 cm⁻¹ in the $\tilde{X}$ and $\tilde{A}$ states, respectively, taking advantage of ion imaging to discriminate against the products of hot band photodissociation.[14] In the course of these ion imaging measurements to determine the binding energies, some peculiar

angular distributions were observed, whose full reporting has been deferred to the present work.

Several studies of the NO-Ar dissociation dynamics have been reported. Sato *et al.* [15] reported the first NO $\tilde{A}$ product state distributions following photodissociation of NO-Ar $\tilde{A}$ in a series of experiments with available energies, E_a (*i.e.* the energy above dissociation), in the range 200-500 cm⁻¹. The distributions showed two maxima at high N , with the N states at which these maxima appear being proportional to the square root of the excess energy. The authors ascribed this behaviour to a rotational rainbow effect.[16-18] Parsons *et al.*[19] subsequently extended the investigation of Sato *et al.* to lower available energy, acquiring NO($\tilde{A}$) N distributions for E_a in the range 25 - 400 cm⁻¹. The rainbow effect was observed in the distributions down to $E_a = 50$ cm⁻¹. Unexpectedly, the distributions for $E_a < 100$ cm⁻¹ revealed population in product states that are not accessible with the energy available. We subsequently showed that excitation from levels up to the dissociation threshold in the $\tilde{X}$ state are contributing to the dissociation.[20, 21] It was proposed that this results from a significant increase in the Franck Condon factors for excitation from these levels, which compensates for their very low population.

In contrast, there is little experimental information concerning the $\tilde{A}$ states of NO-He and NO-Ne. We have recently reported the $\tilde{X}$ state binding energies of these complexes[14] but were unable to observe bound states associated with the $\tilde{A} \leftarrow \tilde{X}$ transition in either. This is consistent with earlier reports for NO-Ne.[22, 23] When reporting NO $\tilde{A}$ rotational distributions associated with dissociation of NO-Ar $\tilde{A}$, Sato *et al.*[15] noted that the rotational distributions of the NO $\tilde{A}$ product following

dissociation of NO-Ne also exhibited a rotational rainbow, with a double maximum in the NO $\tilde{A}$ N state distribution. Although the complete rotational distributions for NO-Ne were not published, the N value of the higher maximum in the rotational distribution was reported to increase linearly with $\sqrt{E_a}$ between about 200 and 440 cm^{-1} . [15]

Further investigation into the rotational distributions of the NO photodissociation products of each of the NO-Rg complexes is warranted for several reasons. First, the rotational rainbow effect reported for the NO-Ar and NO-Ne systems was unexpected given the low energies involved. [15] With the effect having subsequently been observed to occur at even lower available energy in NO-Ar, there is the question of whether it also continues to lower energy in NO-Ne. Furthermore, the NO-Ar distributions for $E_a \sim 100 \text{ cm}^{-1}$ and below need to be reassessed to take into account the significant contribution that comes from excitation of thermally populated levels in the $\tilde{X}$ state. The rotational rainbow effect is predicted to show a dependence on the reduced mass of the system, and this was tested for NO-Ar and NO-Ne by Sato *et al.* [15] It is clearly of interest to determine if the rainbow effect is seen in the products of NO-He dissociation and, if so, whether the predicted dependence on the reduced mass of the system holds. Finally, direct photodissociation experiments provide a different test, in addition to bound state spectroscopy [5, 6, 8, 9, 11, 24-26] and bimolecular scattering, [27-30] to validate the improving and increasingly well-validated *ab initio* calculations of ground state and excited state interaction potentials of NO-Rg systems. [10, 22, 25, 26, 31-34]

The early measurements of rotational state distributions preceded the availability of high quality potential energy surfaces and the dynamical computations to evaluate their consequences. For excited state surfaces without bound states, or with bound states that are inaccessible to spectroscopic investigation because of poor Franck-Condon overlap, the photodissociation dynamics can provide a useful verification of the potential energy surfaces. From another perspective, the calculations on trustworthy surfaces can serve to explain the main features of the observed product state distributions. The rare gas series He, Ne, Ar displays a range of interaction potentials in both $\tilde{X}$ and $\tilde{A}$ states as well as a large variation in kinematics, making the comparison interesting and not obvious without theoretical support.

We have undertaken a series of experiments to investigate the rotational distributions of the NO $\tilde{A}$ product following photodissociation of the NO-Rg (Rg = He, Ne, Ar) complexes, excited via the $\tilde{A}^2\Sigma \leftarrow \tilde{X}^2\Pi$ transition. Distributions were obtained over a range of excitation energies (see Table I). The product rotational distributions provide information about the energy and angular momentum of the recoiling fragments. To gain further insight into the photolysis process we have also measured the angular distributions of the dissociating fragments.

Little is known concerning the angular distributions of the products following photolysis of NO complexes. The NO dimer[35-37] has attracted more attention in this regard than have the rare gas complexes, although the bonding in this complex differs markedly from that of the NO-Rg complexes. Among the NO-Rg complexes excited to the $\tilde{A}$ state, fragment anisotropy has only been reported for NO-Ar. Parsons *et al.*[19] note that the (1+1) REMPI velocity-mapped ion (VMI) image (their Fig 4) of the NO

product resulting from $44\,495\text{ cm}^{-1}$ photodissociation of NO-Ar displays little or no recoil anisotropy. Subsequent work in the same laboratory[7] acquired VMI images of the NO $\tilde{A}$ products following excitation of eight resonant structures, ranging in energy from 3 cm^{-1} below to 17 cm^{-1} above the $\tilde{A}$ - $\tilde{X}$ dissociation threshold of NO-Ar. The images for $N = 0, 1$ and 2 showed a small degree of anisotropy, with β values in the range -0.06 to -0.23 . An essentially isotropic ion image of NO $\tilde{A}$ $N = 0$ from NO-Ne at $E_a = 167\text{ cm}^{-1}$ was published from the work in this laboratory[21] in a study of the binding energies of the ground state complexes. In the present report, we examine the recoil anisotropies as well as product state distributions of photodissociation fragments from the bound-continuum excitation of NO-Rg complexes with the aim of gaining further insight into the photoexcitation and dissociation processes.

2.0 EXPERIMENTAL DETAILS

The experimental apparatus[38] and technique[21] have been detailed previously. In overview, the experiments involve excitation of the NO-Rg $\tilde{A} \leftarrow \tilde{X}$ transition, which leads to dissociation of NO-Rg $\tilde{A}$ into NO ($\tilde{A}$) and Rg. A second, delayed laser probes the NO ($\tilde{A}$) products using 1+1 REMPI via either the forbidden $\tilde{F}^2\Delta \leftarrow \tilde{A}^2\Sigma$ or allowed $\tilde{E}^2\Sigma \leftarrow \tilde{A}^2\Sigma$ transition. The results presented here were generally obtained using the R branch of the $\tilde{E} \leftarrow \tilde{A}$ transition to monitor NO ($\tilde{A}$) because the selection rules allow all NO N states to be probed, whereas for the $\tilde{F} \leftarrow \tilde{A}$ transition $R(0)$ is forbidden, but avoids interfering background signals at some excitation wavelengths. [21] The ions are detected using a time of flight mass spectrometer (ToFMS), yielding REMPI spectra or NO N -specific velocity map images (VMI). Both photolysis and probe lasers are polarised parallel to the face of the detector.

3.0 COMPUTATIONAL METHODS

Time-dependent wavepacket calculations have been performed to explore the bound-continuum photodissociation dynamics of the experimentally investigated systems, using best currently available *ab initio* potential energy surfaces for He, Ne and Ar interacting with NO $\tilde{X}$ and $\tilde{A}$ -states.[10, 31, 33, 34] Details of the calculations are included as Supplemental Material. Notable approximations used in the calculations include fixing the NO bond length at its equilibrium value, thus treating the body-fixed dynamical problem in just two dimensions, the Jacobi coordinates, R and γ . R is the distance from the atom to the NO centre of mass, and γ is the angle between R and the third Jacobi coordinate, r , the fixed NO bond length, with $\gamma = 0$ corresponding to the linear Rg-NO geometry. The unpaired electron spin in the NO $\tilde{A}$ state is neglected in the dynamics of a pseudo-closed-shell model, where integer values of j are used to represent the rotational states N of the $\tilde{A}^2\Sigma$ state, and the effect of electron spin is only included as a degeneracy factor. The initial wavefunction in the $\tilde{X}$ state complexes is computed as the lowest energy bound state in Jacobi coordinates of the average potential $\frac{1}{2}(A' + A'')$. To investigate the total cross sections and energy-dependent product state distributions, the excitation to the upper surface is modelled with a scalar transition moment, producing a total $J = 0$ wavepacket on the dissociative surface. This suppression of the vector properties of the excitation precludes a quantum treatment of the fragment angular distributions, a simplification that can be remedied by a more complete treatment of the angular coordinates, parities and selection rules for the optical excitation step[39-41] in subsequent work.

4.0 RESULTS

4.1 Product Rotational Distributions

Rotationally resolved spectra of the NO product were acquired at several photon energies for each complex. The photolysis photon energies and corresponding available energies, E_a , at which product distributions were measured, are listed in Table I. The spectra were fit to a sum of Gaussians, with the coefficient of the Gaussian for each peak providing the contribution of the corresponding rotational transition to the spectrum. An example spectrum and fit are shown in Fig. 1. The relative populations in each N state were estimated from the Gaussian amplitudes, correcting for the rotational line strengths (the Hönl-London factors),[42, 43] but neglecting any corrections for rotational alignment. [27, 44-46] The resulting rotational population distributions are shown in Figs. 2-4 for NO-He, NO-Ne and NO-Ar, respectively. In the case of NO-Ar, the contribution due to excitation from states above the zero point level was subtracted from the distributions, as discussed previously.[20, 21] For NO-Ne, our study focused on E_a values below those previously investigated[15] to determine whether the structured rotational distribution extends to lower energies. Only a single peak in the rotational state distribution was observed at the relatively low energies measured in this work.

Qualitatively, it is clear that in going from He to Ne to Ar, the NO rotational distributions at a comparable E_a become broader and shift towards higher N , reaching a larger fraction of the available energy in rotation for the heavier rare gases. One may seek an explanation in changes in the ground state structure, the excited state potentials or in a kinematic effect due primarily to the mass ratios. Within this series of Rg partners, changes in all three factors are significant and will be addressed in the

discussion below. Included for comparison in Figs. 2-4 are the results of two-dimensional time-dependent wavepacket calculations, discussed below, which provide a simplified means of understanding the rotational state distributions and how they follow from the ground state structure and the excited state potential.

4.2 Time-Dependent Wavepacket Calculations

The time-dependent wavepacket calculations contain dynamical information about all energies within the energy bandwidth of the bound-continuum absorption. Analysing the asymptotic wavepacket gives partial cross sections for each product rotational state as a function of wavevector k . When plotted as a function of k and j , the partial cross sections give a global overview of the energy-dependent state distributions, as shown in Fig. 5 for NO-He, NO-Ne and NO-Ar. The rotational state distributions can be read along curves of fixed total energy, $E_a = B j(j+1) + k^2 \hbar^2 / 2\mu$. These (approximately) elliptical curves shown on Fig. 5 indicate the energies at which the experimental and calculated state distributions are compared in Figs 2-4. Smooth contour plots have been prepared to illustrate the structures in the final state distributions, but it needs to be recognized that while the translational energy is evaluated from a dense grid in R , the rotational states are strictly integers in the calculation.

The total cross section for absorption can be obtained from the Fourier transform of the wavepacket autocorrelation function,[47] as described in more detail in the Supplemental Material. Figure 6 illustrates the calculated absorption spectra for the three NO-Rg systems studied. The bound-continuum structure dominates in all cases. Only NO-Ar shows a sharp feature corresponding to a bound-bound transition, and several $J = 0$ resonance features at photon energies just above the dissociation threshold.

4.3 Product Angular Distributions

The dependence of the product angular distributions on the initial available energy, E_a , was first investigated by examining the variation of β with E_a for the $N = 0$ NO $\tilde{A}$ photodissociation product using the $R(0)$ line of the $\tilde{E} \leftarrow \tilde{A}$ transition. $N = 0$ was chosen because this state is accessible from all values of E_a , and the apparent anisotropy of the images cannot be affected by rotational polarization effects.[48] Images were acquired for NO-He in the range $E_a = 59 - 273 \text{ cm}^{-1}$, NO-Ne in the range $E_a = 50 - 220 \text{ cm}^{-1}$ and NO-Ar in the range $E_a = 44 - 220 \text{ cm}^{-1}$. The values of β extracted from the resulting ion images are shown in Fig. 7.

In the case of NO-He dissociation, β values are close to isotropic at all energies. For both NO-Ne and NO-Ar, β values are negative at low E_a , but exhibit a change in sign to positive values at increasing E_a . The negative anisotropy at low energies is consistent with previous measurements near the dissociation threshold in NO-Ar by Roeterdink *et al.* [7], but the transition to positive anisotropy at higher E_a has not been previously reported. The sign change is quite abrupt and occurs at *ca.* 170 and 110 cm^{-1} for NO-Ne and NO-Ar, respectively.

To further probe this change and confirm that it is a function of the products and not an artefact of the particular probe transition used, we have acquired a series of ion images for the NO(A) $N=1$ products from NO-Ar dissociation observed via the $R(1)$ line of the $\tilde{F} \leftarrow \tilde{A}$ transition. (The $\tilde{F} \ ^2\Delta \leftarrow \tilde{A} \ ^2\Sigma$ transition has no rotational lines originating in $N=0$). Images were obtained following the dissociation of NO-Ar at increasing energies

above the dissociation threshold (i.e. increasing E_a), repeating the region covered by the $N=0$ experiments and extending the range to $E_a = 423 \text{ cm}^{-1}$. A plot of the data is shown in Fig. 8. The β parameters show the same trend as is observed for $N=0$ monitored via the $\tilde{E} \leftarrow \tilde{A}$ transition, being negative at low available energy, but increasing rapidly as E_a increases, becoming positive above $E_a \sim 150 \text{ cm}^{-1}$ before reaching a plateau for E_a above approximately 200 cm^{-1} . The energy at which the fragment anisotropy changes sign appears to be shifted to higher energy for $N=1$.

Ion images as a function of rotational state at a few selected values of E_a were measured and showed diverse anisotropy patterns for NO-Ar. The contributions of rotational polarization to the observed image anisotropy are expected to be significant,[36] and we have not done the comprehensive probe polarization studies required to analyse these images in detail.[46] A more complete study of the coupled velocity anisotropy and rotational polarization in the $\tilde{A}$ state photodissociation of NO-Ne and NO-Ar complexes would provide a good exercise in direct photodissociation theory for a case where the transition moment in the body-fixed frame is a strong function of the large amplitude bending coordinate, and non-axial recoil effects may be significant. The simplicity of a ^1S atom and $^2\Sigma$ electronic state of the vibrationally inactive diatomic co-fragment removes most other complexity from the problem.

5.0 DISCUSSION

5.1 NO product rotational distributions and the effect of the Rg partner

A comparison of distributions for the three complexes at selected E_a reveals interesting trends in the partitioning of available energy between recoil translational energy and rotational excitation. At $E_a \sim 50 \text{ cm}^{-1}$, where rotational states up to $N = 4$ are

energetically accessible, NO-He shows population only up to $N=2$, while NO-Ne show population up to $N = 3$ and NO-Ar shows population up to $N = 4$. Similarly, at $E_a \sim 180 \text{ cm}^{-1}$, where rotational states up to $N = 8$ are energetically accessible, the rotational distribution from NO-He extends to $N = 5$, NO-Ne extends to $N=7$ and NO-Ar extends to its energetic limit. Thus, the extent to which energetically accessible N states are populated appears to depend on the mass of the Rg partner. An increase in Rg mass is accompanied by an increase in the population of higher N states, although as we see below, it is the potential and not the mass that is the primary factor leading to these differences.

Comparison of the shapes of the NO rotational distributions for the Rg partners also shows interesting trends apparent at both $E_a \sim 50$ and 180 cm^{-1} . The distributions arising from NO-He are uni-modal, biased to low N , with all but the lowest N states sparsely populated. The rotational population distributions arising from NO-Ne reveal a broader, but still uni-modal distribution, while those resulting from the photodissociation of NO-Ar appear to comprise both a low energy uni-modal distribution, and a high energy bimodal distribution, resulting in three peaks. The two high energy peaks are separated by a single N state node. The distributions for NO-Ar are similar in features to those observed by Sato *et al.*[15] and Parsons *et al.*[19] The double peak at high N is characteristic of the rotational rainbow phenomenon in heteronuclear diatomics. The rotational population distributions resulting from the photodissociation of NO-He displays no evidence of a rotational rainbow. In the case of NO-Ne, our measurements at E_a up to 166 cm^{-1} show only a low energy peak and a shoulder at higher rotational levels. At E_a between ~ 200 and 440 cm^{-1} Sato *et al.*[15] reported double maxima, with the higher N_{max} values scaling with $\sqrt{E_a}$, a trend that

evidently does not continue much below 200 cm^{-1} . In contrast, the rainbow structure in the NO $\tilde{A}$ state distributions from NO-Ar persists to lower energies.[19, 21]

5.2 Potential Energy Surfaces and Partial Cross Sections

For molecules with little pre-existing rotational energy, the excitation of final rotational states during photodissociation can be considered in two steps: a rotational Franck-Condon mapping of the parent molecule's bending or torsional motion onto the separated fragment rotational coordinates, and an inelastic redistribution among these rotational states, driven by the anisotropy of the excited state potential.[18, 49, 50] For cold van der Waals molecules, the pre-existing angular momentum is not expected to contribute significantly to product rotational excitation. After years of improvements and testing against spectroscopic and scattering measurements, the interaction potentials of NO $\tilde{A}$ and $\tilde{X}$ with the rare gases are now known well enough to expect predictive validity for photodissociation calculations.

The differences in the energy-dependent NO $\tilde{A}$ rotational distributions among the three investigated NO-Rg complexes become quite clear from an inspection of the two-dimensional potential energy surfaces and the dynamics they mediate. The ground state interaction potentials are similar for the three investigated rare gas complexes, leading to similar average structures, near the symmetric T-shaped geometry. The main difference among the complexes is in the floppiness, due to variations in the depth of the attractive region and the mass of the rare gas atom. The zero-point wavefunction of NO-He is substantially more diffuse in both γ and R coordinates than either NO-Ar or NO-Ne. When projected onto the free rotor states, the large amplitude bend projects mostly onto $j = 0$ in all cases, with some additional amplitude in $j = 2$ and 4 for NO-Ar,

not present in NO-He. (We note in passing that symmetric T-shaped geometries will have non-zero expansion coefficients for only even j states.) The rotational Franck-Condon limit does not, however, account for much, if any, of the additional rotational excitation in NO-Ne and NO-Ar. Illustrations of the initial wavefunctions in the R, j basis can be seen in the Supplemental Material associated with this paper.

The most intuitively useful representation of the differences among the NO-Rg systems is perhaps in Figs 9-11. These figures show the location and extent of the ground state wavefunction in R, γ coordinates, along with a contour plot of the $\tilde{A}$ state interaction potential. Contours of the $\tilde{A}$ state potential are labelled in cm^{-1} relative to its own dissociation limit. The distribution of vertical transition energies, weighted by the squared ground state wavefunction, gives a good representation of the bound-continuum absorption spectrum, and the potential gradients in the γ direction, that will drive the rotational excitation, can be visualized easily. In the case of NO-He, in Fig. 9, the excited state is nearly purely repulsive in the R coordinate, with little anisotropy, particularly at the larger values of R corresponding to the lower energy portion of the excitation spectrum. The product rotational distribution starts out in a Franck-Condon distribution strongly peaked at $j = 0$ and undergoes little inelastic scattering in a nearly isotropic, repulsive exit channel. A product rotational distribution described by the rotational Franck-Condon limit would be approximately independent of E_a and produce a nearly horizontal band in the k, j plots, as seen in Fig. 5a for NO-He. The cold product rotational distribution and the absence of rotational rainbow structures are not surprising.

The experimental observation of substantial population in $N = 1$ does, however, contrast with the calculations, which predict very little $N = 1$ population, since the initial expansion in rotor states is primarily $N = 0$, and what inelastic scattering there is on the $\tilde{A}$ state potential strongly favours even ΔN . This discrepancy may be one consequence of the simplifications inherent in our total $J = 0$ calculation, which neglects the disappearing electronic angular momentum in the $\Sigma \leftarrow \Pi$ transition and the angular momentum transfer during excitation.

The NO-Ne ground state wavefunction and its dissociative $\tilde{A}$ state potential are shown in Fig. 10. The initial wavefunction is more tightly confined than in NO-He, although still represents a floppy structure. The repulsive $\tilde{A}$ state, however, displays substantially more anisotropy than for NO-He, with gradients in the γ coordinate away from the T-shaped structure and toward the two linear structures in the $\tilde{A}$ state: Ne-NO and NO-Ne. The early bifurcation of the initial R, γ wavepacket in the γ coordinate may be associated with the interference structures in the final state distributions depicted for NO-Ne in Fig. 5b. The tendency for peaks in the rotational state distribution to scale with $\sqrt{E_a}$ corresponds to ridges of probability along lines through the origin on the k, j plots (Figs. 5b and 5c). The slope of these ridges increases with the fraction of E_a expressed as rotational energy for those product channels. The time-dependent wavepacket calculations are in accord with the structured rotational distributions reported by Sato[15] at E_a above 200 cm^{-1} , as well as the decreased visibility of the rainbow structures at lower energies, observed in the present work.

Qualitatively different features can be seen in the NO-Ar system, illustrated in Fig. 11. The attractive well in the linear geometry of Ar-NO $\tilde{A}$ has a poor overlap with the T-

shaped, but diffuse ground state wavefunction. Vertical excitation to the $\tilde{A}$ state samples a repulsive surface in the R coordinate, and addresses a strongly γ -dependent anisotropy, influenced by the attractive linear well. Intuition is sufficient to anticipate mischief in the dynamics, and the time-dependent wavepacket dynamics bear out this expectation. A look at the animated wavepacket propagation, available as Supplemental Material, is recommended for the interested reader. The complex structure of energy-dependent rotational state distributions depicted in Fig. 5c is in remarkably good agreement with the present experiments, as seen particularly in Fig. 4.

5.3 NO product angular distributions

The product angular distributions are defined in terms of an anisotropy parameter, designated β , which indicates the distribution relative to the polarisation direction of the photolysis laser. Zare and Herschbach[51] have shown that for a simple one photon dissociation, as appropriate for our experiment, the angular distribution is described by

$$F_{\theta} = \frac{1}{4\pi} [1 + \beta P_2(\cos \theta)],$$

where β is the recoil anisotropy parameter, θ is the angle

between the recoil velocity vector, $\mathbf{v}$, and the laser polarisation direction, and $P_2(x) = \frac{1}{2}(3x^2 - 1)$. In the simplest case of direct dissociation, β depends only on the angle, α , between the transition moment $\boldsymbol{\mu}$ and the recoil direction $\mathbf{v}$, according to $\beta = 2P_2(\cos \alpha)$, so that $\beta = 2$ and $\beta = -1$ correspond respectively to recoil parallel and perpendicular to the molecular transition moment, with $\cos^2 \theta$ and $\sin^2 \theta$ distributions, respectively. Numerous classical and quantum treatments have been presented to explain intermediate values of β for systems more complex than direct dissociation of linear molecules, including simultaneous transitions to multiple excited states of

different symmetry, non-axial recoil, predissociation and rotational averaging.[49, 52-57] A combination of large amplitude bending or hindered internal rotation in the NO-Rg complexes, as well as possible non-axial recoil effects makes the interpretation of the present fragment anisotropy measurements challenging, in spite of the availability of trustworthy potential energy surfaces and transition dipoles.

The product angular distributions associated with the $N = 0$ NO $\tilde{A}$ photodissociation products for the three complexes show distinctive behaviour as a function of photolysis photon energy. The β values resulting from NO-He dissociation are close to zero at all dissociation energies probed but those of NO-Ne and NO-Ar are negative at low E_a and switch to positive at *ca.* 110 and 170 cm^{-1} for NO-Ne and NO-Ar, respectively.

A rigorous quantum calculation of the recoil anisotropy is beyond the scope of the present report, but we can make some qualitative arguments that likely capture the main factors responsible for the observations.

The interaction of the rare gas with NO is weak enough that the transition moment in the complex should closely resemble that for the perpendicular $\tilde{A}^2\Sigma \leftarrow \tilde{X}^2\Pi$ transition in the body frame of NO, independent of the position of the Rg, which serves only to perturb the cylindrical symmetry of the NO and resolve the degenerate Π state into a weakly split Renner-Teller pair of A' and A'' states with only weak quenching of the electronic angular momentum.[1, 2, 58] It is in the spirit of this weak coupling that we have represented the ground state as the zero-point wavefunction on the average $(A' + A'')/2$ potential. In the molecular frame of the complex, there will be two equal components to the transition moment, the $A' \leftarrow A''$ component μ_y perpendicular to the

molecular plane, and the $A' \leftarrow A'$ component μ_x perpendicular to NO in the plane of the complex, with a projection $\mu_x \sin \gamma$ along the Jacobi vector $\mathbf{R}$. If the complex had a sharply defined geometry, and the recoil proceeded promptly along the direction $\mathbf{R}$ selected at the time of excitation, classical arguments[53, 59] lead to an anticipated variation in the anisotropy parameter with γ in the form $\beta(\gamma) = -P_2(\cos \gamma)$. Linear complexes have $\mathbf{R}$ perpendicular to both μ_x and μ_y , so both $A' \leftarrow A'$ and $A' \leftarrow A''$ components of the $\tilde{A}^2\Sigma \leftarrow \tilde{X}^2\Pi$ transition contribute to a limiting perpendicular anisotropy parameter $\beta = -1$. For T-shaped complexes, when $\gamma = 90^\circ$, $\mathbf{R}$ is perpendicular to μ_y but parallel to μ_x . Equal weighting of a parallel $A' \leftarrow A'$ component and the perpendicular $A' \leftarrow A''$ components of the $\tilde{A}^2\Sigma \leftarrow \tilde{X}^2\Pi$ transition leads to an anisotropy parameter of $\beta = +0.5$ in this limit.

The ground states of the NO-Rg complexes have a wide range of γ represented in its zero-point wavefunction, but there can be a Franck-Condon bias in the selection of γ through vertical transitions to the excited state at different excitation energies. In NO-Ar, for example, we can see in the arrangement of the $\tilde{A}$ state potential contours and their alignment with the ground state wavefunction in Fig. 11 that at transition energies corresponding to $E_a \approx 400 \text{ cm}^{-1}$, the most heavily weighted vertical transitions occur from regions where γ is close to 90° . The regions of coordinate space with vertical transitions leading to $E_a \approx 100 \text{ cm}^{-1}$ are most strongly weighted by the ground state wavefunction near 50° . This Franck-Condon selection of γ at different transition energies is qualitatively consistent with the experimentally observed trends in β . A simple weighted average of $-P_2(\cos \gamma)$ over a region of coordinate space where the vertical energy matches the desired available energy within a small tolerance gives a

more quantitative treatment of the large amplitude motion problem, still within the axial recoil approximation:

$$\beta(E_a) \approx \sum \frac{-P_2(\cos \gamma) |\psi(R, \gamma)|^2 \delta(E_a, E(R, \gamma))}{|\psi(R, \gamma)|^2 \delta(E_a, E(R, \gamma))}.$$

In practice, the delta functions selecting the vertical regions were replaced by Gaussian weights with a width (σ) of 10 cm^{-1} , and the sum is over the normalized grid in R and γ used in the TDWP calculations. The normalization function in the denominator is the sum of the wavefunction squared along the energy contours, the energy dependence of which is proportional to the absorption spectrum according to the two-dimensional reflection principle.[50] The results of this model calculation are shown in Fig. 12 for each of the three investigated NO-Rg complexes. The trends in β are encouragingly similar to the observations of Fig. 7, given the simplicity of the model. The transition from negative to positive occurs at about the right energy for NO-Ne and NO-Ar, and NO-He is much more isotropic. The absorption spectra estimated in this way are in good qualitative agreement with the more precise total cross sections obtained from the wavepacket time autocorrelation function, and shown in Fig. 6.

A pleasing correspondence can be seen between the Franck-Condon selection of initial coordinates near the regions of vertical transitions and the energy filtered scattering wavefunctions, computed by a direct Fourier transform of the time-dependent wavepackets. Illustrations of several of these energy-resolved wavefunctions are included in the Supplemental Material for the NO-Ar system at the values of E_a studied experimentally, as well as at energies near a resonance feature 18 cm^{-1} above the dissociation threshold, for comparison with the experiments of Roeterdink et al.[7]

Still not included in this calculation are corrections for non-axial recoil. For the low total angular momentum states present in the jet-cooled complex, the transverse velocity corresponding to pre-existing rotation of the complex will not be significant, but the re-orientation of R required by angular momentum conservation as the diatomic fragment rotates under the influence of the angular potential[54] can contribute to the observed anisotropy in a way that will increase for lighter rare gases, and for higher rotational states of the product.

The rotational state dependence of the anisotropy is also not explicitly addressed with this simple model. In the same way that energy resolved products can be tagged with the distribution of γ at the time of excitation, there can be an analogous reflection principle that maps different initial values of γ onto final j states that would modulate the anisotropy among rotational levels,[60] an effect also not addressed in the present study, but amenable to future work, either by semiclassical trajectory analysis, or by a more rigorous treatment of the vector properties of the photodissociation. The effects of the difference potential $(A' - A'')/2$ on the ground state wavefunctions will also need to be considered in a rigorous treatment of the photodissociation anisotropy from specific initial rotational states of the NO-Rg complexes.

6. CONCLUSIONS

We have presented the results of an investigation into the rotational and angular distributions of the NO $\tilde{A}$ state fragment following photodissociation of the NO-He, NO-Ne and NO-Ar van der Waals complexes excited via the $\tilde{A} \rightarrow \tilde{X}$ transition. The dissociation has been probed for several values of the available energy within the bound-continuum spectra for each of these complexes.

The NO $\tilde{A}$ rotational distributions arising from NO-He dissociation are cold, reflecting the rotational Franck-Condon projection of large amplitude motion in the Jacobi γ coordinate onto low rotational states only, and little subsequent redistribution in the nearly isotropic repulsive exit potential. NO-Ar differs in every possible way. A less floppy ground state projects onto a wider range of initial rotational states in the Franck-Condon limit. The repulsive excited state interaction includes a strong anisotropy, through the influence of an attractive well in the linear Ar-NO geometry that drives extensive inelastic redistribution among the rotational levels in the exit channel. NO-Ne is an intermediate case, with no strong well in the excited state, but more anisotropy in the interaction potential than for NO-He.

Time-dependent wavepacket calculations treating in two dimensions the excited state dynamics, starting with a wavepacket computed on the average ground state potential, projected onto the excited state reproduce quite well the range of structured and unstructured rotational distributions observed in this work and previously reported at various energies within the unstructured excitation spectrum.

Product angular distributions have also been presented for the NO A photodissociation product for the three complexes. NO-He dissociation produces nearly isotropic fragments at all dissociation energies probed. In contrast, NO-Ne and NO-Ar produce fragments characterized by negative β at low E_a , switching to positive β as E_a increases. This switch can be attributed to a Franck-Condon bias in the complex geometry, with the low energy excitation favouring a wide distribution of geometries including more linear geometries, while higher energy excitation favours more rigidly T-shaped

geometries. In the axial recoil limit, this causes the $A' \leftarrow A'$ component of the excitation to switch from perpendicular to parallel, while the $A' \leftarrow A''$ component remains equally weighted and strictly perpendicular. The energy-resolved and final-state-resolved anisotropy measurements across this series of NO-Rg complexes provides a well-posed challenge to an exact quantum treatment of a triatomic direct photodissociation when large-amplitude motion is important, and deviations from the axial recoil limit may play a variable role.

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Table 1: The photolysis photon energies and corresponding available energies, E_a , at which product distributions were measured. The dissociation energies used to determine the E_a values are those reported in Ref. [14].

Complex	Photon energy / cm^{-1}	E_a / cm^{-1}
NO-He	44 261	59
	44 374	172
	44 475	273
NO-Ne	44 278	50
	44 394	166
NO-Ar	44 337	44
	44 387	94
	44 487	194
	44 716	423

Fig. 1 The R branch of the NO $E \leftarrow A$ rotational spectrum measured for the NO product of NO-Ar photodissociation at $44\,487 \text{ cm}^{-1}$ (black line). The least squares fit of a sum of Gaussians to the spectrum is shown in red. The photolysis photon energy corresponds to an available energy of 194 cm^{-1} .

Fig. 2 Rotational population distributions for the NO A photodissociation product for NO-He excited at the indicated available energies. Filled black squares are experimental values; open red triangles are calculated values. The maximum N states that can be populated at these E_a values are 11 (273 cm^{-1}), 8 (172 cm^{-1}) and 5 (59 cm^{-1}).

Fig. 3 Rotational population distributions for the NO A photodissociation product for NO-Ne excited at the indicated available energies. Filled black squares are experimental values; open red triangles are calculated values. The maximum N states that can be populated at these E_a values are 8 (166 cm^{-1}), and 4 (50 cm^{-1}).

Fig. 4 Rotational population distributions for the NO A photodissociation product for NO-Ar excited at the indicated available energies. The distribution at $E_a = 423 \text{ cm}^{-1}$ was acquired via the forbidden NO $F \leftarrow A$ transition and so $N = 0$ is absent. Filled black squares are experimental values; open red triangles are calculated values. The maximum N states that can be populated at these E_a values are 14 (423 cm^{-1}), 9 (194 cm^{-1}), 6 (94 cm^{-1}) and 4 (44 cm^{-1}).

Fig. 5 Calculated partial cross sections for (a) NO-He, (b) NO-Ne, and (c) NO-Ar dissociations in the $\tilde{A}$ state. Contours indicate relative probabilities of forming rotational state j with translational energy $k^2\hbar^2/2\mu$. White curves, labelled in cm^{-1} , indicate lines of constant total energy, E_a , at the energies used in the experiments of this work.

Fig. 6 Total cross sections for NO-Rg photodissociation in the $\tilde{A}$ state, calculated from the time-dependent wavepacket autocorrelation function. Experimental[14] dissociation energies to NO ($\tilde{A}$) + Rg of 44202, 44228 and 44293 cm^{-1} for He, Ne and Ar, respectively, are indicated by vertical arrows. The computed spectra are referenced to these experimental values.

Fig. 7 A plot of the β values for the NO $N = 0$ product as a function of the available energy above the dissociation threshold, E_a , for NO-He (open circles), NO-Ne (filled squares) and NO-Ar (filled circles). The NO product was monitored via the $E \leftarrow A$ transition. The error bars correspond to one standard deviation.

Fig. 8 A plot of the β values for the NO $N = 0$ (diamonds) and $N = 1$ (circles) products as a function of E_a for NO- Ar. The NO $N = 0$ product was monitored via the $\tilde{E} \leftarrow \tilde{A}$ transition; the NO $N = 1$ product via the $\tilde{F} \leftarrow \tilde{A}$ transition. The error bars correspond to one standard deviation.

Fig. 9 Ground state wavefunction and $\tilde{A}$ state potential for NO-He. The filled contours map the square of the wavefunction with logarithmic contour intervals, three per decade. The labelled contour lines are the $\tilde{A}$ state interaction energy, in cm^{-1} relative to separated He + NO $\tilde{A}$.

Fig. 10 Ground state wavefunction and $\tilde{A}$ state potential for NO-Ne. The filled contours map the square of the wavefunction with logarithmic contour intervals, three per decade. The labelled contour lines are the $\tilde{A}$ state interaction energy, in cm^{-1} relative to separated $\text{Ne} + \text{NO } \tilde{A}$.

Fig. 11 Ground state wavefunction and $\tilde{A}$ state potential for NO-Ar. The filled contours map the square of the wavefunction with logarithmic contour intervals, three per decade. The labelled contour lines are the $\tilde{A}$ state interaction energy, in cm^{-1} relative to separated Ar + NO $\tilde{A}$.

Fig. 12 Absorption spectra and fragment velocity anisotropy calculated with two-dimensional reflection principle, Franck-Condon model with axial recoil approximation for the $\tilde{A}$ state dissociation of NO-Rg complexes.

SUPPLEMENTAL MATERIAL

Supplemental material is available online, consisting of a pdf file describing computational methods in more detail than the main text, including illustrations of the initial wavefunctions and potentials in (R, γ) as well as (R, j) representations, and animation files depicting the time evolution of the wavepackets in each representation. Total absorption cross sections and selected time-independent, energy-resolved scattering wavefunctions are illustrated, including an investigation of the resonance states in NO-Ar. The animation files are available in mp4 format.

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NO distribution vs E_a : He

NO distribution vs E_a : Ne

NO distribution vs E_a : Ar

He+NO(A)

Ne+NO(A)

Ar+NO(A)

Absorption Spectra **$\langle -P_2(\cos \gamma) \rangle$**

Supplemental Material

Rotational and Angular Distributions of NO Products from NO-Rg

(Rg = He, Ne, Ar) Complex Photodissociation

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S1. COMPUTATIONAL METHODS

A time-dependent wavepacket (TDWP) method[1] is used to study rotational dynamics in the photodissociation processes of NO-Rg. The TDWP calculations are performed in two dimensions, solving a simpler model problem in atom-diatom Jacobi coordinates $(R, \gamma; r)$ with r , the NO diatomic bond length, fixed at the equilibrium distance. R is the distance from the Rg atom to the NO center of mass, and γ is the angle between R and r , defined with $\gamma = 0$ corresponding to the Rg-NO geometry. Dynamical effects of the unpaired electron spin are also ignored, treating the problem as a pseudo-closed-shell NO molecule, but interacting with a rare gas according to accurate *ab initio* interaction potentials.[2-5] These potential energy surfaces have generally given excellent agreement with an assortment of inelastic scattering and bound-state spectroscopic experiments, confirming that treating the NO vibrational coordinate as frozen or adiabatic with respect to the van der Waals coordinates is an appropriate simplification for problems that do not involve vibrational excitation of NO.

The molecular Hamiltonian is written in atom-diatom Jacobi coordinates $(R, \gamma; r=r_{NO})$ as

$$H(R, \gamma; r) = -\frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial R^2} - \left(\frac{1}{2\mu_R R^2} + \frac{1}{2\mu_r r^2} \right) \frac{\hbar^2}{\sin \gamma} \frac{\partial}{\partial \gamma} \sin \gamma \frac{\partial}{\partial \gamma} + V(R, \gamma; r) - iW(R) \quad (1)$$

where μ_r and μ_R are the reduced masses of NO and NO-Rg. V is the potential energy surface of the system of interest. [2-5] The last term is a negative (imaginary) absorbing potential used to prevent unphysical reflections of the wavepacket from the large R edge of the computational grid, at the dissociation limit.[6] A very smooth onset of the absorbing potential is important for accurate photodissociation product distributions; we use an absorbing potential of the form: [7]

$$W(R) = \frac{V_0}{\cosh^2[(R_{\max} - R)/\lambda]}. \quad (2)$$

The time dependent wavepacket $|\psi(t)\rangle$ is obtained by solving the time dependent Schrödinger equation on the electronically excited $\tilde{A}$ state of NO-Rg. It can be written as

$$|\psi(t)\rangle = e^{-iH(t-t_0)/\hbar} |\psi(t_0)\rangle. \quad (3)$$

Time propagation is performed using a split-operator (SOP) method[8, 9] with a small time step $\Delta t = 0.027$ fs. Here H is the $\tilde{A}$ state Hamiltonian $H(R, \gamma; r)$ with $r = 2.01135 a_0$, i.e., the equilibrium bond length of free NO ($\tilde{A}$).[10] The initial excited state wavepacket $|\psi(t_0)\rangle$ is taken as a product of the transition dipole surface μ_d (approximated as a scalar constant, independent of R and γ in this work) and the ground-state wavefunction $|\psi_{0,X}\rangle$ of the NO $\tilde{X}$ state + Rg complex, namely,

$$|\psi(t_0)\rangle = \mu_d |\psi_{0,X}\rangle. \quad (4)$$

For each rare gas, the initial state $|\psi_{0,X}\rangle$ is approximated as the total $J = 0$ ground state wavefunction, using the average $\frac{1}{2}(A' + A'')$ interaction potential for $V(R, \gamma; r)$, and setting $r = 2.17468 a_0$, the bond length of free NO($\tilde{X}$).[10] The neglect of the difference potential $\frac{1}{2}(A' - A'')$ should be a reasonable approximation, similar in spirit to

its neglect in classical trajectory studies by Aoiz *et al.*[11] in the treatment of fine-structure preserving interactions of Ar with NO($\tilde{X}$).

During the time evolution, the wavepackets are expressed as

$$|\psi(t)\rangle = C_{j\alpha}(t; R_\alpha) |j\alpha\rangle \quad (5)$$

in a mixed basis set $\{|j\alpha\rangle\}$, in which $|j\rangle$ refers to the rotational basis functions of NO in the angular γ coordinate and $|\alpha\rangle$ denotes the Fourier grid DVR basis localized at R_α in the radial R coordinate. The Fourier grids used $N_\alpha = 1024$ values bounded by $[R_{min}, R_{max}]$, and the rotational basis included $N_j = 45$ j states from 0 to 44. In this model that neglects electron spin, the diatomic rotational quantum state j is an integer. In total, 320,000 time steps were propagated for each case, corresponding to 8.64 ps. The energy-resolved wavefunction at a given E can be calculated as

$$|\psi(E)\rangle = \int e^{iEt/\hbar} |\psi(t)\rangle dt. \quad (6)$$

The total photodissociation cross sections are calculated by[1]

$$\sigma_{tot}(\nu) = \frac{2\pi\nu}{3\hbar c \epsilon_0} \int_0^\infty C(t) \exp\left(\frac{i(h\nu + E_0)t}{\hbar}\right) dt \quad (7)$$

with the autocorrelation function

$$C(t) = \langle \psi(t_0) | \psi(t) \rangle, \quad (8)$$

where E_0 is the initial energy on the electronic ground state relative to the asymptotic Rg + NO($\tilde{A}$) energy, and ν is the photon frequency, so that the available energy, $E_a = h\nu + E_0$. Other constants have their usual meanings. The partial cross sections to a final j state of NO are analyzed at a large R_β where the interaction potential between NO and Rg is negligible. It can be written [1, 12] as

$$\sigma_j(\nu) = g_j \frac{\pi^2 \nu k_j}{3c\epsilon_0 \mu_R} \left| \int_0^\infty C_{j\beta}(t; R_\beta) \exp\left(\frac{i(h\nu + E_0)t}{\hbar}\right) dt \right|^2 \quad (9)$$

where $k_j = \sqrt{2\mu_R(E_a - E_j)}/\hbar$ is the wavevector for the rotational j state of NO. An approximate statistical correction to the closed-shell model to account for the effect of electron spin in the NO ($\tilde{A}$) $^2\Sigma$ state is to apply a spin degeneracy factor $g_j = 2$ for all rotational states other than for the rotationless state, which is non-degenerate, having only an F_1 spin component. In this way, the $j = 0$ state in the pseudo-closed-shell calculation represents the non-degenerate $N = 0$ state of NO($\tilde{A}$) and $j > 0$ states in the calculation represent spin-doublets for $N > 0$.

Table S1 lists the computational parameters used in the TDWP calculations. These parameters were confirmed to give well-converged total and partial cross sections for the step size and propagation times used. Each of the three calculations (for He, Ne, Ar) required approximately 2 hours of computer time at the NERSC Computing Center.

Table S1. Parameters for the wavepacket calculations

Molecule	R_{min}/a_0	R_{max}/a_0	R_β/a_0	V_0/eV	λ/a_0	N_α	N_j
He	3.75	47.0	25.0	0.35	4.4	1024	45
Ne	3.50	45.0	25.0	0.25	4.0	1024	45
Ar	4.40	47.0	25.0	0.50	4.2	1024	45

S2. INITIAL WAVEFUNCTIONS AND POTENTIALS

The (R, γ) dependence of the initial ground state wavefunction $|\psi_{0,x}|^2$ is shown in Fig.

S1 for NO-He. The lower panel includes contour lines in white for the NO-He ($\tilde{X}$) average $(A'+A'')/2$ potential that was used to calculate this wavefunction. The contour lines are labeled in cm^{-1} with respect to the asymptotically separated system. The squared wavefunction contour intervals are logarithmic with three contour lines per

Figure S1. Initial wavefunction for He-NO in R, γ coordinates, with contour lines for X state average potential (below) and A state potential (above). Animation file S1.mp4 depicts the subsequent time evolution.

decade in a 1-2-5-10 sequence. The upper panel shows the same van der Waals wavefunction with an overlay of the $\tilde{A}$ state potential contour lines, labeled with respect to the separated $\text{He} + \text{NO}$ ($\tilde{A}$) energy in cm^{-1} . The wavefunction is diffuse in both R and γ coordinates, with a floppy, T-shaped geometry. The $\tilde{A}$ state potential in the Franck-Condon region is purely repulsive, with low anisotropy, particularly so at large R .

Figure S2 shows the analogous initial wavefunction for NO-Ne, with the $\tilde{X}$ state average $(A'+A'')/2$ potential from which it was calculated in the lower panel, and the $\tilde{A}$ state potential above. The initial state is also T-shaped, but more rigidly confined to a

deeper van der Waals well. The excited state Franck-Condon region is still purely repulsive, but with more anisotropy than the NO-He $\tilde{A}$ state surface. It can immediately be seen that the Franck-Condon region corresponding to 50 cm^{-1} available energy is centered around $R = 7.5$ bohr, $\gamma = 20^\circ$, whereas the Franck-Condon region corresponding to 400 cm^{-1} available energy is centered around $R = 6$ bohr, $\gamma = 100^\circ$.

Figure S2. Initial wavefunction for Ne-NO in R, γ coordinates, with contour lines for X state average potential (below) and A state potential (above). Animation file S2.mp4 depicts the subsequent time evolution.

Figure S3 shows the analogous wavefunction and potentials in the case of NO-Ar. Here the $\tilde{X}$ state van der Waals potential well is deeper still, yet with an anisotropy similar to that in Ne. The ground state wavefunction includes large deviations away from the T-shaped minimum, but is more symmetrically distributed around 90° than in Ne. The

excited state NO-Ar($\tilde{A}$) potential has a minimum, supporting bound states in the linear geometry. The ground state wavefunction extends into this near-linear region and accounts for the weak bound-bound transitions observed in NO-Ar. Vertical transitions from the dominant geometries of the ground state access excited state potential regions with large and γ -dependent anisotropy, which play a major role in the energy-dependent final

Figure S3. Initial wavefunction for Ar-NO in R, γ coordinates, with contour lines for X state average potential (below) and A state potential (above). Animation file S3.mp4 depicts the subsequent time evolution.

S3. INITIAL WAVEFUNCTIONS IN THE (R, j) REPRESENTATION

Throughout the propagation, the two-dimensional wavefunctions are repeatedly transformed between a coordinate representations (R, γ) in which the potential is easily computed, and the conjugate momentum variables (k, j) in which the kinetic energy is

Figure S4. Initial wavefunctions for Rg-NO in R, j coordinates. Animation files S4He.mp4, S4Ne.mp4, and S4Ar.mp4 depict the subsequent time evolution.

most easily computed. The same initial wavefunctions illustrated in Figs. S1-S3 can be viewed instructively in the mixed (R, j) representation. The contour plots of Fig. S4 depict the “initial j distribution” that corresponds to expanding the ground state in-plane bending wavefunction in a free rotor basis, at each R . Note that the wavefunctions are defined on a dense grid in R , but only integer values of j , despite the appearance of the smooth interpolating contour plots of Fig. S4. These j distributions correspond to a Franck-Condon limit of rotational excitation – what would be observed as a final state distribution in the absence of excited state anisotropy.

The very broad distribution of γ for NO-He (Fig. S1) corresponds to an initial wavefunction in the R, j representation (Fig. S4) that is strongly peaked at $j = 0$. In contrast, the initial wavefunction for NO-Ar extends to higher j values, primarily $j = 2$ and 4. The near absence of odd j values is a consequence of the very near symmetry of the wavefunction (and the potential) about $\gamma = 90^\circ$. In the case of NO-Ne, the maximum ground state wavefunction peaks closer to $\gamma = 100^\circ$, and the expansion in j includes larger amplitudes for odd values 1 and 3.

S4. TIME PROPAGATION

We have prepared animations to illustrate the time-evolution of the wavepackets, in both (R, γ) and (R, j) representations for each Rg system studied. Supplemental files S1.mp4 S2.mp4 and S3.mp4 illustrate He, Ne, and Ar respectively, in (R, γ) coordinates, depicting the subsequent evolution starting from the initial conditions depicted in Figs. S1-S3. Files S4He.mp4, S4Ne.mp4, and S4Ar.mp4 show the same calculations in (R, j) coordinates, starting from the initial conditions depicted in Fig S4. The low anisotropy of the He-NO ($\tilde{A}$) potential produces little additional rotational excitation beyond that present in the initial wavepacket, as can be seen in movies S1 and S4He. In the cases of Ne and Ar, the initial time evolution of the wavepacket includes substantial excitation in the γ or j representation, with a division of the wavepacket into regions heading toward Rg-NO and Rg-ON geometries. The effect is more extreme in the case of Ar, but qualitatively similar for Ne. The animations S4He, S4Ne, and S4Ar in the (R, j) representation are a pleasing visualization of the meaning of Eq. S9 for the partial cross sections. Under the influence of the $\tilde{A}$ state potential, the initial j distribution is inelastically redistributed and accelerated outward. Once beyond the range of the

interaction potential, the j distribution is fixed, and each component j has been spread out and accelerated in R . The time-dependent rise and fall of the outgoing amplitude for each j at a dividing surface near the outer limit of the displayed animation is $C_{j\beta}(t;R_\beta)$, the argument of the Fourier transform in Eq. 9 that gives the velocity distribution of the chosen j channel. Note that the actual TDWP calculations included a grid in R about twice as large, and the propagation time was 4-8 times longer than illustrated in the movies. The time step between displayed frames in the movies is over 1000 times larger than the actual time step of the TDWP propagation.

S5. TOTAL CROSS SECTIONS

The Fourier transform of the wavepacket time autocorrelation function gives the total absorption cross sections as a function of excitation energy (Eq. 7-8). Figure S5 shows

Figure S5. Total cross section vs. excitation energy for NO-Rg. Experimental threshold dissociation energies are indicated with vertical arrows.

the total cross sections, computed in this way for NO-He, NO-Ne and NO-Ar complexes. The dominant features correspond to the bound-continuum transitions in each system. A bound-bound transition is evident only in the case of NO-Ar as the feature near 44250 cm^{-1} , corresponding to a small

component of the wavepacket that remains trapped in the NO-Ar ($\tilde{A}$) well, as seen in movie S3. Experimentally observed bound state absorptions in this region have been

observed by multiple research groups.[13-17] The Ar-NO resonance structure evident near 44320 cm^{-1} is likely related to the features investigated experimentally by Roeterdink et al.[18].

S6. TIME-INDEPENDENT SCATTERING WAVEFUNCTIONS

Energy-selected scattering wavefunctions have been calculated for NO-Ar at the experimentally chosen energies and to investigate the lower energy features evident in the total cross sections, by accumulating the Fourier transform of the time-dependent wavepacket at a few selected energies, according to Eq. 6. The squared modulus of the wavefunction $|\psi_E(R, \gamma)|^2$ is illustrated in each of the following plots for the E_a values identified in the titles, and $\tilde{A}$ state potential contours have been added, as before. The first four plots represent the experimental energies investigated in this work. The heavy weighting of initial γ coordinates in regions of vertical transitions is illustrated in the regions of large amplitude within the ground state coordinate distribution.

The bound-bound transition to the zero point in the excited complex is found 47 cm^{-1} below the dissociation threshold:

The resonance feature at $E_a \sim 18 \text{ cm}^{-1}$ shows clearly defined nodal features characteristic of a $j = 4$ rotor and a $v = 1$ van der Waals stretch. The total energy

exceeds the dissociation threshold, but the weak coupling of the dissociative van der Waals coordinate with internal rotation inhibits dissociation in this metastable $J = 0$ complex. In contrast, the quasi-bound character of the scattering wavefunction is strongly suppressed at energies only a few cm^{-1} higher:

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