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RG⁺ formation following photolysis of NO–RG via the $\tilde{A}$ – $\tilde{X}$ transition: A velocity map imaging study

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Kr⁺ and Xe⁺ formation following photodissociation of NO–RG (RG = Kr or Xe) molecules via the $\tilde{A}$ – $\tilde{X}$ electronic transition in the 44 150–44 350 cm^{−1} region has been investigated using velocity map imaging. Nuclear kinetic energy release (*n*KER) spectra indicate that the NO cofragment is produced in multiple vibrational states of the electronic ground state, with a high degree of rotational excitation. Photofragment angular distributions and *n*KERs are consistent with photo-induced charge transfer at the two-photon level followed by dissociative ionization at the three-photon level. RG⁺ angular distributions showing highly parallel character relative to the laser polarization axis are indicative of a high degree of molecular alignment in the dissociating species. © 2011 American Institute of Physics. [doi:10.1063/1.3610415]

I. INTRODUCTION

Van der Waals complexes of nitric oxide (NO) and rare gas (RG) atoms have been the subjects of numerous studies. Owing to their tractability, both experimentally and theoretically, they have become benchmark systems for the study of dispersion interactions involving open shell–closed shell systems.^{1–3} The NO–Ar complex, in particular, has become the system of choice for high level *ab initio* study within the NO–RG series,^{4–7} although computational investigation has been undertaken for both the ground ($\tilde{X}$) and first excited ($\tilde{A}$) electronic states for RG = He, Ne, Ar, Kr, Xe.⁵

Experimentally, the $\tilde{A}$ – $\tilde{X}$ electronic transition and the associated $\tilde{A}$ state dissociation dynamics of NO–RG (RG = He,^{2,8} Ne,^{9–12} Ar,^{3,7,8,12–18} Kr,^{3,10,13,14,17,19} Xe (Refs. 3, 10, 11, 13, 14, and 17)) have received a great deal of attention. The transition is associated with the $A^2\Sigma^+ - X^2\Pi$ electronic excitation of the NO moiety and occurs between the nominally T-shaped ground state of the complex and the essentially linear excited state.^{5,11} This large change in equilibrium geometries between the $\tilde{X}$ and $\tilde{A}$ states results in significant off-diagonal contributions to the Franck-Condon factors associated with the $\tilde{A}$ – $\tilde{X}$ transition, and for NO–Ar, NO–Kr, and NO–Xe gives rise to a rich spectrum throughout the 44 150–44 350 cm^{−1} region. Interestingly, the $\tilde{A}$ – $\tilde{X}$ spectrum has not been reported for NO–He or NO–Ne – an observation which has been attributed to either very weakly bound (i.e., no vibrational levels supported) or unbound $\tilde{A}$ states in both instances.^{2,5,9–11}

At the high energy end of the NO–RG $\tilde{A}$ – $\tilde{X}$ spectrum, especially in the cases of NO–Kr and NO–Xe, transition intensities drop off abruptly.^{3,10,13} This loss of transition probability has been interpreted as coinciding with the $\tilde{A}$ state dissociation threshold, and has traditionally provided the means by which dissociation energies for the $\tilde{X}$ and $\tilde{A}$ states have

been determined.^{3,10,13} Recent work by Chandler *et al.*, however, suggests that contributions to the spectrum from low-lying vibrationally excited NO–Ar $\tilde{X}$ states introduce a large degree of ambiguity to such measurements.¹⁸ Consequently, Lawrance *et al.* have recently undertaken rigorous velocity map imaging (VMI) (Ref. 2) studies so as to determine unambiguously the dissociation energies of the $\tilde{A}$ state of NO–Ar, and the $\tilde{X}$ states of NO–He, NO–Ne, and NO–Ar.^{2,16} To our knowledge, the VMI technique has yet to be applied to investigating the dissociation dynamics of the heavier NO–RG species, NO–Kr and NO–Xe.

Particularly pertinent to the study described herein is the observation of RG⁺ fragments produced concomitant with [NO–RG]⁺ molecular ions following resonance enhanced multiphoton ionization (REMPI) of NO–Kr and NO–Xe via their respective $\tilde{A}$ – $\tilde{X}$ transitions.^{14,17} The lowest energy pathway by which resonant ionization occurs is a two-photon ionization to produce [NO–RG]⁺ (in which the charge is located on NO), which first involves a $\pi \rightarrow 3s\sigma$ excitation localized on the NO moiety. RG⁺ production is unexpected since energetically it requires at least three photons, and must by necessity involve transfer of electronic excitation from the NO center to the RG center via a super-excited state,²¹ owing to the NO localized excitation of the initial steps. Previous REMPI studies have reported that the relative intensities of the RG⁺ and the [NO–RG]⁺ mass channels are observed to vary as a function of laser pulse energy, with higher photon densities favouring production of RG⁺.^{11,14,17} Such an observation is not surprising given the expected photon dependences of [NO–RG]⁺ versus RG⁺ production (i.e., 2-photon and 3-photon, respectively). Several mechanisms have been postulated for RG⁺ production following NO–RG photodissociation via the $\tilde{A}$ – $\tilde{X}$ transition, including:^{14,17}

1. Photo-induced charge transfer (PICT) dissociative ionization

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FIG. 1. Possible mechanisms of RG^+ production from NO-RG photolysis (see text for details). (Left) Photo-induced charge transfer (PICT) dissociative ionization. (Center) PICT dissociation of the NO^+-Xe molecular ion. (Right) Two-photon dissociation leading to Xe^* production. Photoexcitations are represented by upward pointing arrows (blue), electron kinetic energy (eke) by downward pointing arrows (red) and total kinetic energy release ($n\text{KER}$) by double headed arrows. Relative energies at which PICT occurs are shown with dashed horizontal lines (green). The approximate equilibrium geometries of NO-RG electronic states are displayed in the left hand panel.

(formation of a super - excited Rydberg state),

(dissociative ionization).

2. Photodissociation of the molecular ion produced in the (1+1) REMPI process

(photoexcitation; charge transfer),

3. Multiphoton dissociation to form RG^* followed by ionization

(excitation of a super - excited Rydberg state),

(charge transfer; ion core switch),

(ionization of excited RG^*).

All of the above proposed mechanisms, shown schematically in Fig. 1 and tabulated with approximate energetics in Table I, involve production of RG^+ via a three-photon process, and thus accord with the observed photon dependence of the mass spectrum signal intensities. Here we report a VMI study that investigates the mechanism by which Kr^+ and Xe^+ are formed following excitation via the NO-Kr and NO-Xe $\tilde{A}-\tilde{X}$ transitions.

II. EXPERIMENTAL

The experiments described within this article were carried out using a custom-built VMI spectrometer. The apparatus consists of three vacuum chambers: source, imaging, and detection. Within the source chamber, NO-RG is produced by expanding a gas mixture of 1% NO (BOC, >99.9%) and 5% RG (Kr or Xe ; BOC, >99.9%) in 2 bar Ar (BOC, >99.9%) into high vacuum via a pulsed solenoid valve (Parker Hannifin, series 9) operating at 10 Hz. 40 mm downstream of the nozzle orifice the molecular beam is skimmed before entering the differentially pumped imaging chamber that contains the velocity mapping ion optics assembly. The ion optics consist of repeller, extractor, and ground electrodes, each of which are 90 mm in diameter, 2 mm thick, and are spaced apart by 15 mm. The repeller electrode has a central 1 mm diameter, conically shaped aperture to admit the molecular

TABLE I. Possible pathways and energetics for production of RG⁺ following photolysis of NO–RG.

Mechanism	Photon absorption level			Predicted	
	1st photon E ≈ 44 200 cm ⁻¹	2nd photon E ≈ 88 400 cm ⁻¹	3rd photon E ≈ 132 600 cm ⁻¹	Max nKER (cm ⁻¹)	Max eKE (cm ⁻¹)
1		i. NO – Kr($\tilde{A}$) $\xrightarrow{\nu}$ NO** – Kr	NO – Kr* $\xrightarrow{\nu}$ Kr ⁺ + NO(X, ν) + e ⁻	~2000 ^a	Kr ⁺ (² P _{3/2}) ≈ 17 580 ^a
		ii. NO** – Kr $\xrightarrow{\text{PICT}}$ NO – Kr*			Kr ⁺ (² P _{1/2}) ≈ 12 210 ^a
2	NOKr($\tilde{A}$)	NO – Kr($\tilde{A}$) $\xrightarrow{\nu}$ NO ⁺ – Kr + e ⁻	i. NO ⁺ – Kr $\xrightarrow{\nu, \text{PICT}}$ NO – Kr ⁺	Kr ⁺ (² P _{3/2}) ≈ 4820 ^b	~14 870 ^b
	↑		ii. NO – Kr ⁺ → RG ⁺ + Kr(X, ν)	Kr ⁺ (² P _{1/2}) ≈ N/A ^b	
3	NOKr($\tilde{X}$)	i. NO – Kr($\tilde{A}$) $\xrightarrow{\nu}$ NO** – Kr	Kr* + NO(X, ν) $\xrightarrow{\nu, -e^-}$ Kr ⁺ + NO(X, ν)	Kr*5s ² [3/2] ₂ ≈ 8320 ^c	Kr*5s ² [3/2] ₂ ≈ 11 260 ^c
		ii. NO** – Kr $\xrightarrow{\text{PICT}}$ NO – Kr		Kr*5s ² [3/2] ₁ ≈ 7370 ^c	Kr*5s ² [3/2] ₁ ≈ 12 200 ^c
		iii. NO – Kr* → Kr* + NO(X, ν)		Kr*5s ² [1/2] ₀ ≈ 3100 ^c	Kr*5s ² [1/2] ₀ ≈ 11 110 ^c
				Kr*5s ² [1/2] ₁ ≈ 2440 ^c	Kr*5s ² [1/2] ₁ ≈ 11 760 ^c
1		iii. NO – Xe($\tilde{A}$) $\xrightarrow{\nu}$ NO** – Xe	NO – Xe* $\xrightarrow{\nu}$ Xe ⁺ + NO(X, ν) + e ⁻	~4000 ^d	Xe ⁺ (² P _{3/2}) ≈ 30 650 ^d
		iv. NO** – Xe $\xrightarrow{\text{PICT}}$ NO – Xe*			Xe ⁺ (² P _{1/2}) ≈ 20 110 ^d
2	NOXe($\tilde{A}$)	NO – Xe($\tilde{A}$) $\xrightarrow{\nu}$ NO ⁺ – Xe + e ⁻	iii. NO ⁺ – Xe $\xrightarrow{\nu, \text{PICT}}$ NO – Xe ⁺	Xe ⁺ (² P _{3/2}) ≈ 19 230 ^e	~15 530 ^e
	↑		iv. NO – Xe ⁺ → Xe ⁺ + NO(X, ν)	Xe ⁺ (² P _{1/2}) ≈ 8700 ^e	
3	NOXe($\tilde{X}$)	iv. NO – Xe($\tilde{A}$) $\xrightarrow{\nu}$ NO** – Xe	Xe* + NO(X, ν) $\xrightarrow{\nu, -e^-}$ Xe ⁺ + NO(X, ν)	Xe*7p ² [1/2] ₁ ≈ 360 ^f	Xe*7p ² [1/2] ₁ ≈ 34 290 ^f
		v. NO** – Xe $\xrightarrow{\text{PICT}}$ NO – Xe*		Xe*7s ² [3/2] ₁ ≈ 2850 ^f	Xe*7s ² [3/2] ₁ ≈ 31 810 ^f
		vi. NO – Xe* → Xe* + NO(X, ν)		Xe*7s ² [3/2] ₂ ≈ 3100 ^f	Xe*7s ² [3/2] ₂ ≈ 31 560 ^f
				Xe*5d ² [3/2] ₁ ≈ 4400 ^f	Xe*5d ² [3/2] ₁ ≈ 30 260 ^f

^aBased on measured nKER and predicted value of D₀''(NOKr) = 112 cm⁻¹ given in Ref. 5. See text for details.^bBased on predicted values of D₀''(NOKr) = 112 cm⁻¹ given in Ref. 5 and D_e⁺ = 1310 cm⁻¹ given in Ref. 33.^cBased on predicted value of D₀''(NOKr) = 112 cm⁻¹ given in Ref. 5 and known excited states of Kr (ref NIST).^dBased on measured nKER and predicted values of D₀''(NOXe) = 117 cm⁻¹ given in Ref. 5. See text for details.^eBased on predicted values of D₀''(NOXe) = 117 cm⁻¹ given in Ref. 5 and D_e⁺ = 1980 cm⁻¹ given in Ref. 33.^fBased on predicted value of D₀''(NOXe) = 117 cm⁻¹ given in Ref. 5 and known excited states of Xe (ref NIST). There are 17 additional channels to higher nKER that yield Xe*.

beam, and extractor and ground electrodes have 20 mm apertures to allow ion extraction. The ground electrode is fitted with a shielding tube (50 mm long, 50 mm diameter, 2 mm thick) at the output to limit electric field penetration into the field free drift region. To achieve velocity mapping conditions, the ratio of potentials applied to the extractor and repeller electrodes is maintained at ~0.71.

Midway between the repeller and extractor electrodes, the molecular beam is crossed orthogonally by the laser beam. In the experiments reported here, a single UV beam is used for both photolysis of the parent molecule and for resonant ionization of the nascent photofragments. The laser system

consists of a tunable linearly polarized, frequency-doubled pulsed dye laser (Sirah Cobra Stretch, ~600 μJ per 8 ns pulse, Δν ≈ 0.3 cm⁻¹) operating with Coumarin 450 laser dye and pumped by the third harmonic of a Nd:YAG laser (Continuum Surelite II). The laser beam was focused into the ion optics region using a fused silica lens to yield an energy density of ~7.5 × 10⁸ W/cm² at the point of intersection with the molecular beam. The electric field of the laser is oriented so as to be parallel to the plane of the microchannel plate (MCP)/phosphor screen detector assembly.

The resulting Newton spheres of ionized photofragments are accelerated by the velocity mapping field and pass through

the apertures in the extractor and ground electrodes into the field free flight tube. After a total flight distance of 482 mm from the laser interaction region the ions impinge upon a 2D position sensitive detector. The detector assembly consists of 40 mm diameter chevron MCPs coupled to a P47 phosphor screen. By directing a small fraction of the light from the phosphor through a liquid light guide to a photomultiplier tube coupled to a digital oscilloscope (Tektronix TDS 2024B), time-of-flight (TOF) mass spectra for the parent ions and fragment ions formed in the photodissociation process can be monitored. The mass-resolution of the VMI spectrometer is sufficient to observe the four highest naturally occurring isotopologues of NO–Kr and Kr, and the seven highest naturally abundant isotopologues of NO–Xe and Xe. The detector is gated to the arrival time of the specific ion of interest by pulsing the rear MCP from +1000 V to +1500 V. The light from the phosphor screen is imaged by an intensified charge-coupled device (CCD) camera (Photonic Science Mini IDI), controlled via a LABVIEW interface. The data acquisition software captures a 691×691 pixel subarray of the CCD array on each TOF cycle. Images are acquired over 5000 laser shots, and are subsequently analyzed using a purpose built LABVIEW routine employing the Polar Onion Peeling algorithm.²²

III. RESULTS AND DISCUSSION

A. General comments

Photoionization across the $44\,150\text{--}44\,400\text{ cm}^{-1}$ region produced ion signals from four chemical species: NO^+ , $[\text{NO-Ar}]^+$ (from NO complexation with the Ar carrier gas), RG^+ , and $[\text{NO-RG}]^+$, where RG refers to either Kr or Xe depending on the gas mixture employed. Monitoring the signal intensity of a given mass species as a function of laser excitation wavenumber yields the REMPI spectrum for that species. The spectra observed for the krypton mixture are shown in Fig. 2. The peaks observed in the NO^+ mass channel arise from (1+1) REMPI of uncomplexed NO in the molecular beam via the $\text{NO } A^2\Sigma^+ \leftarrow X^2\Pi$ transition.^{23,24} The rotational profile of the NO band suggests a molecular beam temperature of approximately 5 K. Peak positions and relative intensities observed in the $[\text{NO-Ar}]^+$, Kr^+ , and $[\text{NO-Kr}]^+$ mass channels are in an excellent agreement with those reported previously for the NO–Ar and NO–Kr $\tilde{A} \leftarrow \tilde{X}$ transitions.^{3,10,13}

The peak progressions observed in the spectra of NO–Ar and NO–Kr (separated by approximately 30 cm^{-1}) have been attributed to a vibrational progression in the NO–RG coordinate.¹⁰ However, recent theoretical calculations suggest that these assignments are incorrect and that the NO–RG $\tilde{A} \leftarrow \tilde{X}$ band system is a highly complex series of transitions owing to the strongly anharmonic and mixed nature of energy levels in both the $\tilde{A}$ and $\tilde{X}$ states.⁵ It has been postulated that, owing to the relatively soft and shallow potentials of the NO–RG $\tilde{A}$ states, increasing amounts of internal rotation of the NO moiety are accessed at higher excitation energies, thus leading to more complex and dense REMPI spectra.¹⁰ This is exemplified in the $\tilde{A} \leftarrow \tilde{X}$ REMPI spectrum of NO–Xe, shown in Fig. 3, in which spectral density makes it difficult to identify

FIG. 2. REMPI spectra observed for NO, NO–Ar, Kr, and NO–Kr in the region of the NO–RG $\tilde{A} \leftarrow \tilde{X}$ transition ($44\,150\text{--}44\,375\text{ cm}^{-1}$). Progressions observed in $[\text{NO-RG}]^+$ (and Kr^+) species arise due to excitation of the $\tilde{A}$ state NO–RG local mode (Ref. 10).

any vibrational progression. It is thought that the abrupt ending of the NO–Xe $\tilde{A} \leftarrow \tilde{X}$ spectrum at $\sim 44\,320\text{ cm}^{-1}$ coincides with the dissociation threshold for the $\tilde{A}$ state, with the weaker transitions observed up to $\sim 44\,330\text{ cm}^{-1}$ being attributed to transitions involving quasi-bound states lying above the $\tilde{A}$

FIG. 3. REMPI spectra observed for Xe and NO–Xe in the $44\,125\text{--}44\,375\text{ cm}^{-1}$ region. Peaks marked with an asterisk (*) arise from (2+1) REMPI of Xe via the $5p^5(^2P^{\circ}_{3/2})7p^2[{}^5/2]_2 \leftarrow 5p^6(^1S_0)$ and $5p^5(^2P^{\circ}_{3/2})7p^2[{}^3/2]_2 \leftarrow 5p^6(^1S_0)$ atomic transitions (Ref. 25).

state dissociation threshold.¹⁰ Two additional, very intense features in the Xe^+ mass channel at $44\,175.8\text{ cm}^{-1}$ and $44\,344.1\text{ cm}^{-1}$ may be assigned to (2+1) REMPI of Xe via the $5p^5(^2P^{\circ}_{3/2})7p^2[5/2]_2-5p^6(^1S_0)$ and $5p^5(^2P^{\circ}_{3/2})7p^2[3/2]_2-5p^6(^1S_0)$ atomic transitions, respectively.²⁵

B. RG^+ images

1. Kr^+ images

Figure 4 shows the reconstructed Kr^+ image and nuclear kinetic energy release ($n\text{KER}$; i.e., total kinetic energy release excluding electron kinetic energy) spectrum recorded following excitation via the NO-Kr transition at $44\,260.5\text{ cm}^{-1}$. This region correlates with an $\tilde{A}-\tilde{X}$ transition wherein a mixed Σ bend/stretch combination is excited.⁵ Images of both NO-RG species showed only a central molecular beam spot indicating that these species were not generated by fragmentation of larger NO-RG_n or NO_n-RG clusters. In the case of NO-Kr photolysis, there was no Kr^+ production off-resonance with NO-Kr $\tilde{A}-\tilde{X}$ transitions, showing that Kr^+ was only produced following photolysis of the NO-Kr parent molecule. The angular distributions obtained for the Kr^+ images were fitted to the expression $I(\theta) = 1 + \beta_2 P_2(\cos\theta) + \beta_4 P_4(\cos\theta) + \beta_6 P_6(\cos\theta)$, where $P_n(\cos\theta)$ are Legendre polynomials, β_n are the associated expansion coefficients and θ is the angle between the laser polarization axis and the fragment recoil direction. Kr^+ photofragment angular distributions are characterized by beta parameters of $\beta_2 \approx 1.2$, which were observed to increase across the band system from $\beta_2 \approx 0.5$ at $44\,202.0\text{ cm}^{-1}$ to $\beta_2 \approx 1.6$ at $44\,298.0\text{ cm}^{-1}$. Higher order expansion coefficients were zero within experimental error. Product angular distributions were also observed to correlate with product velocity, with low $n\text{KER}$ products typically displaying higher values of β_2 . The origin of these angular distributions is discussed below (see Sec. III B 2). The $n\text{KER}$ spectrum is dominated by two

low-kinetic-energy-release product channels. $n\text{KER}$ peak separations accord well with the vibrational interval of the NO cofragment, and the $n\text{KER}$ spectrum can be reasonably well reproduced by employing known NO molecular parameters to calculate product internal energies.²³ Peak separations between the $n\text{KER}$ distributions of $\sim 2000\text{ cm}^{-1}$ indicate that low energy vibrational levels of the $\text{NO}(X^2\Pi)$ state are populated in the fragmentation process. By assuming that the highest $n\text{KER}$ peak observed correlates with $\text{NO}(X^2\Pi, v'' = 0) + \text{Kr}^+$ products, we may then calculate the $n\text{KER}$ for each energetically accessible rotational state, bin the results to match the experimental $n\text{KER}$ scale, and thereby fit the experimental $n\text{KER}$ curve by assuming a Gaussian distribution of rotational levels within each vibrational state. The rotational distributions were truncated such that the highest state populated generated $n\text{KER} \geq 0\text{ cm}^{-1}$ (i.e., negative $n\text{KER}$ s were not allowed). The resulting best-fit simulated $n\text{KER}$ spectrum shown in Fig. 4 corresponds to Gaussian rotational distributions described by mean J values of $J_v = 0 = 28.5$ and $J_v = 1 = 20.5$, with standard deviations in J of $\sigma_{v=0} = 7$ and $\sigma_{v=1} = 4$, respectively, and an available energy, $E_{\text{avail}} \approx 2400\text{ cm}^{-1}$. Here, E_{avail} refers to the amount of energy available to the dissociating nuclear fragments above the dissociation threshold. These distributions correspond to an average rotational energy of $\langle E_{\text{rot}} \rangle \approx 621\text{ cm}^{-1}$. Product channel intensities have a $v = 1:v = 0$ branching ratio of approximately 0.72:0.28. The relative intensities of the two Kr^+ production channels were not observed to vary as a function of laser energy.

Figure 5 shows the $n\text{KER}$ spectra obtained from the Kr^+ images acquired from selected NO-Kr $\tilde{A}-\tilde{X}$ transitions across the absorption band. With increasing photolysis wavenumber, the $n\text{KER}$ peaks move to higher kinetic energies. The relative intensities of the two product channels are also observed to evolve as a function of photolysis wavenumber, with the lower kinetic energy peak (associated with an increased degree of vibrational excitation of NO) gaining in relative intensity with increasing excitation wavenumber. Product state distributions (PSDs) and anisotropy parameters for Kr^+ production from NO-Kr photodissociation are given in the electronic supplementary material.²⁶

FIG. 4. (Top right) Reconstructed Kr^+ image recorded following Kr·NO photolysis via the $\tilde{A}-\tilde{X}$ transition at $44\,260.5\text{ cm}^{-1}$. The electric field vector (E) of the photolysis laser is vertical with respect to the plotted image. (Top left) $n\text{KER}$ spectrum extracted from the Kr^+ image shown. (Bottom left) Simulated $n\text{KER}$ spectrum for $\text{NO}(X^2\Pi)$ cofragment produced with 2400 cm^{-1} (see text for details).

2. Xe^+ images

Figure 6 shows the reconstructed Xe^+ image and $n\text{KER}$ spectrum recorded following excitation via the NO-Xe transition at $44\,303.1\text{ cm}^{-1}$. As this corresponds to the higher energy region of the $\tilde{A}-\tilde{X}$ band system, it is likely that several quanta in mixed bending/stretching modes are excited in the NO-Xe coordinate, however, the complexity of the spectrum precludes definitive assignment of the individual bands.^{5,10} In common with the $n\text{KER}$ spectra extracted from Kr^+ images recorded following excitation of NO-Kr, Xe^+ $n\text{KER}$ spectra are also dominated by low kinetic energy release product channels. In this instance, product angular distributions are slightly more anisotropic, with $\beta_2 \approx 1.5$. Interestingly, in contrast with Kr^+ formation from NO-Kr, low $n\text{KER}$ Xe^+ product channels consistently have angular distributions described by β_2 parameters that are less than

FIG. 5. n KER spectra extracted from Kr^+ images acquired following NO–Kr photolysis via the four members of the $\tilde{A}$ – $\tilde{X}$ band system. $\bar{\nu}_{\text{photolysis}} = 44\,297.9\text{ cm}^{-1}$, $\bar{\nu}_{\text{photolysis}} = 44\,260.5\text{ cm}^{-1}$, $\bar{\nu}_{\text{photolysis}} = 44\,230.1\text{ cm}^{-1}$, and $\bar{\nu}_{\text{photolysis}} = 44\,202.0\text{ cm}^{-1}$. The experimental data are plotted as black squares, while the solid curve (red) shows a 5-point smooth of the data.

those of the higher n KER product channels. In addition to this, Xe^+ product angular distributions are not observed to vary as a function of laser excitation wavenumber. Whether these trends in product angular distributions are a result of changing transition dipole moments across the $\tilde{A}$ band, or arise due to dynamical differences in the evolution of products on the dissociative potential energy surface, or indeed for other reasons, is not clear, and will likely require a detailed theoretical analysis to disentangle. It is, however, interesting to note that RG^+ ions are produced highly aligned parallel (i.e., $\beta_2 \approx 1.5$) with the laser electric field vector via three

FIG. 6. n KER spectrum extracted from the Xe^+ image recorded following photolysis of NO–Xe at $44\,303.1\text{ cm}^{-1}$. Weaker product channels observed at $\sim 20\,000\text{ cm}^{-1}$ are due to photolysis of Xe_2 at the two-photon level. The electric field vector (E) of the photolysis laser is vertical with respect to the plotted image.

perpendicular electronic transitions ($\pi \rightarrow \sigma \rightarrow p$ -Rydberg $\rightarrow s/d$ wave electron; see below). This result is unexpected since prompt dissociation following such an excitation should yield photofragments with β_2 parameters approaching a limiting value of $-5/3$.³¹ Further to this, despite the multiple photon nature of the dissociation process, β_4 and β_6 were observed to be zero (within experimental error). The observed angular distributions are likely to be a result of the localized excitation on the NO center and the three body nature of the dissociation process. Owing to the fact that the first and second photons absorbed promote electronic excitation within the NO moiety, a subset of NO–RG molecules is prepared wherein the NO bond axis is aligned perpendicular to the laser electric field vector at the two-photon level (see Fig. 1, left panel). Since the prepared molecular state (*viz.* super-excited Rydberg state) is T-shaped, this results in a NO–RG bond with highly parallel alignment. In the dissociative ionization process initiated by the third photon, the electron then leaves as either an s - or a d -wave and the NO–RG bond promptly dissociates along the direction of the laser polarization. β_2 parameters are tabulated as a function of excitation wavenumber in the journal supplementary electronic information and are discussed in more detail below.²⁶

Unlike with NO–Kr, off-resonant Xe^+ production was observed throughout the spectral region studied. These contributions were easily assigned to 2-photon photodissociation of ArXe and Xe_2 , also present in the molecular beam, and will be the subject of a future publication.²⁷ Xe^+ images acquired in the absence of NO (i.e., using a molecular beam comprised of 5% Xe in 2 bar Ar) were used to perform a background subtraction on the Xe^+ images, thus removing contributions from Xe_2 and ArXe photolysis. The resulting images contain only contributions from NO–Xe photodynamics.

The low n KER region for images recorded at several excitation wavenumbers is shown on an expanded scale in Fig. 7. Closer inspection shows that the low n KER region consists of structured peaks extending up to approximately 6000 cm^{-1} . The relative intensities of the observed n KER peaks were not observed to vary as a function of laser energy. Owing to the lack of structure within each n KER peak and degree of convolution of the observed peaks, extraction of individual rotational level populations was not attempted. Instead, the measured experimental data were reconstructed using a simplified sum of Gaussians model (Fig. 7, solid curves; red online). This modeling procedure indicates that the observed n KER peaks are a composite of several distributions, most likely rotational envelopes, separated by vibrational intervals in the NO cofragment. As was the case with Kr^+ , the product state distributions for NO–Xe photolysis as extracted from the Xe^+ images are observed to vary as a function of excitation wavenumber and are provided in the supplementary information.²⁶ The topmost spectrum in Fig. 7 shows the Xe^+ n KER distribution recorded following excitation of NO–Xe via a member of the $\tilde{A}$ – $\tilde{X}$ transition near the high energy end of the band system, while the bottom-most spectrum shows the Xe^+ n KER distribution recorded following excitation via the transition assigned as the $\tilde{A}$ – $\tilde{X}$ origin band. At low excitation energies the product state distributions are dominated by the product channel at $\sim 2800\text{ cm}^{-1}$, while at higher

FIG. 7. n KER spectrum of the Xe^+ photofragment produced via photolysis of NO–Xe at various excitation wavenumbers with the $\tilde{A}$ – $\tilde{X}$ transition. Experimental data are plotted as black squares, while fitted Gaussian peaks are plotted as dashed blue lines. A sum of the Gaussian curves is plotted as a thick red line. The separations between the fitted Gaussian curve peak maxima corresponds to vibrational intervals in the NO cofragment.

excitation energies the 2800 cm^{-1} product channel loses relative intensity in favour of populating those at other kinetic energy releases (see Fig. 7). Interestingly, the maximum n KER is observed to increase by approximately 2300 cm^{-1} across the band system, a significantly larger change than the $\sim 143\text{ cm}^{-1}$ increase in excitation wavenumber. We interpret this result as arising from accessing successively higher energy regions of the dissociative curve leading to Xe^+ production (see below).

C. RG^+ formation mechanism

One of the most intuitive mechanisms by which RG^+ might be formed from NO–RG is via single-photon dissociation of the molecular ion produced in the REMPI process (mechanism 2; see Sec. I). Similar photodissociative charge-transfer half-collisions have been reported for systems such as $\text{Kr} \cdot \text{O}_2^+$, $\text{Kr} \cdot \text{H}_2\text{O}^+$, and AuXe^+ .^{28,29} In contrast with the observations for AuXe^+ , however, neither the (neutral) Kr/Xe, nor the NO^+ moiety, have electronic states near $\sim 44\,200\text{ cm}^{-1}$ to which the molecular ion could be excited prior to undergoing photo-induced charge transfer (PICT).^{23,25} Photoexcitation would therefore have to drive charge transfer to directly access a dissociative potential energy surface correlating with $\text{RG}^+ + \text{NO}$ products, as

was observed for $\text{Kr} \cdot \text{O}_2^+$ and $\text{Kr} \cdot \text{H}_2\text{O}^+$.²⁹ Such a mechanism is inconsistent with the observed RG^+ n KER spectra following photolysis of NO–RG. In the case of NO–Kr, production of $\text{NO}^+ \text{--} \text{Kr}$ via (1+1) REMPI can potentially generate molecular ions at energies ranging from $\sim 73\,531\text{--}74\,831\text{ cm}^{-1}$ above that of the neutral ground state.^{6,10} Single photon charge transfer dissociation to yield $\text{Kr}^+(^2P_{1/2}^\circ) + \text{NO}(X, v=0, J=0.5)$ would generate a maximum n KER of $\sim 635\text{ cm}^{-1}$, approximately 1400 cm^{-1} less than the maximum n KER observed (see Fig. 5). Alternatively, should dissociation occur via the $\text{Kr}^+(^2P_{3/2}^\circ) + \text{NO}(X, v=0, J=0.5)$ product channel, one would expect to observe product state distributions reflecting the internal energy structure of the NO cofragment up to a maximum n KER of $\sim 6000\text{ cm}^{-1}$, more than 4000 cm^{-1} higher than the maximum n KER observed. In principle, it is possible that a significant portion of the available energy is partitioned as high internal energy states of the NO cofragment; however, it seems unlikely that the dissociation process should have a propensity to yield exclusively $\text{NO}(X, v=2, 3, J)$ products. Similar arguments can be made for NO–Xe, where single photon charge transfer dissociation would yield $\text{Xe}^+ + \text{NO}(X, v, J)$.

Mechanism 3 (see Sec. I) involves neutral dissociation at the two-photon level to generate excited $\text{RG}^* + \text{NO}(X, v, J)$. In the case of NO–Xe, 16 product channels may be accessed which are predicted to yield n KERs of $\sim 6500\text{ cm}^{-1}$ or less. As such, mechanism 3 is energetically consistent with the observed n KERs. The observed product state distributions, however, are indicative of a product channel involving only a single $\text{Xe}^{0/+}$ internal energy state and several $\text{NO}(X, v, J)$ states. Given the density of Xe^* states at the two-photon level, and the fact that 15 of the 16 accessible product channels are expected to involve coupling of molecular states with $\text{NO}(X, v, J)\text{--}\text{Xe}^+(^2P_{3/2}^\circ)$ ion core configurations, dynamically it seems unlikely that only one of these thresholds would be accessed. For NO–Kr the situation is somewhat simplified owing to the lower density of Kr^* states at the two-photon level. In this instance, only four thresholds correlating with Kr^* are available, all with predicted n KERs of $\sim 8400\text{ cm}^{-1}$ or less. Production of $\text{Kr}^* 4p^5(^2P_{1/2}^\circ)5s^2[1/2]_1^\circ + \text{NO}(X, v, J)$ via two-photon dissociation of neutral NO–Kr would produce photofragments with a maximum n KER of $\sim 2500\text{ cm}^{-1}$, in good agreement with those measured. However, as is the case with $\text{Xe} \cdot \text{NO}$, it seems unlikely that the super-excited $\text{NO}^{**}\text{--}\text{Kr}$ Rydberg state would couple exclusively with a single super-excited NO– Kr^* potential energy surface. Moreover, in both the NO–Kr and NO–Xe cases, RG^+ angular distributions are observed to be highly anisotropic with $\beta_2 \approx 2$, which is inconsistent with a process involving a two-photon $\pi \rightarrow \sigma \rightarrow \pi$ excitation followed by prompt predissociation. Dixon has shown that the limiting β_2 value for such a process is $\beta_2 = -10/7$.^{30,31}

Taking all these factors into account, we favour mechanism 1, as proposed by Wright *et al.*, for RG^+ production via NO–RG photolysis.¹⁴ In the initial excitation step NO–RG is promoted to the $\tilde{A}$ state via an NO localized transition based on the free NO $A^2\Sigma^+(3s\sigma)\text{--}X^2\Pi$ transition. Absorption of a second photon then excites this Σ -like (s -character) intermediate state to a short-lived (perhaps virtual) super-excited

Rydberg NO⁺–RG state. Here, owing to conservation of the absorbed photon momentum, the electron may leave either as a *p*-wave thus initiating autoionization to form NO⁺–RG + *e*[−], or may be retained as a Rydberg *p*-electron. As the [RG·NO]⁺ molecular ions are observed, particularly strongly at relatively low laser fluence, it is apparent that the autoionization process does occur at the two-photon level. It should be noted, however, that we are unable to distinguish between NO⁺–RG and NO–RG⁺ in our experiments i.e., we cannot identify the location of the positive charge. Owing to the fact that the Rydberg electron, originally associated with the NO moiety, occupies an orbital large enough to encompass all three nuclei, a NO⁺–RG ion core is created.¹⁴ An ion core switch (i.e., charge transfer) can then occur whereby the RG atom “donates” an electron to the NO⁺ center via coupling between the potential energy surface associated with the super-excited NO⁺–RG state and that of a nearby NO–RG^{*} state in which the excitation is localized on the RG center.¹⁴ In this way, the Rydberg electron originally associated with the NO⁺ moiety thus becomes associated with the RG⁺ center. In the case of NO–Xe, there are numerous candidates for Xe excited states which could lead to NO–Xe^{*} molecular states at the two-photon level. Given that the Rydberg electron is expected to occupy a *p*-orbital, likely candidates for the Xe^{*} states are 5*p*⁵7*p*²[1/2]₀ (88 842.256 cm^{−1}), 5*p*⁵7*p*²[3/2]₁ (88 744.559 cm^{−1}), 5*p*⁵7*p*²[3/2]₂ (88 686.500 cm^{−1}), 5*p*⁵6*p*²[3/2]₁ (88 379.126 cm^{−1}), 5*p*⁵7*p*²[5/2]₃ (88 469.213 cm^{−1}), and 5*p*⁵7*p*²[5/2]₂ (88 351.681 cm^{−1}). Absorption of a photon by the NO–Xe^{*} molecular state would serve to excite NO–Xe^{*} above the dissociation thresholds correlating with Xe⁺(²P_{3/2}) and Xe⁺(²P_{1/2}) products. Dissociative ionization would then generate Xe⁺(²P_{3/2,1/2}), with the remaining available energy being partitioned between kinetic energy release and the internal energy of the NO(*X*, *v*, *J*) cofragment. A similar process has recently been observed for AuXe (Ref. 28) (Au I.E. = 74 408.88 cm^{−1}).²⁵ For NO–Kr, only the Kr^{*} 4*p*⁵(²P_{1/2}^o)5*p*²[1/2]₁ state lies within 3000 cm^{−1} of the excitation energy and could produce a bound NO–Kr Rydberg state. It should be noted that the Kr^{*} Rydberg electron for this excited state occupies a 5*p* orbital.

Whether dissociative ionization of NO–RG^{*} occurs via the repulsive arm of a bound state or via a purely repulsive state is unknown, as are the internal energies of the RG⁺ cofragments (i.e., RG⁺[²P_{1/2}^o] or RG⁺[²P_{3/2}^o]). Based on the likely RG^{*} states accessed it seems reasonable to assume ion core configurations of NO(*X*, *v*, *J*)–Xe⁺(²P_{3/2}) and NO(*X*, *v*, *J*)–Kr⁺(²P_{1/2}^o). However, given the expectation that configuration mixing should play an important role in molecular states involving RG^{*} (particularly Xe^{*}),³² and the uncertainty in which RG^{*} state(s) is(are) involved in the charge transfer process, definitive assignment of the RG⁺ electronic state is not possible. As such, these measurements would benefit greatly from a complementary photoelectron imaging study.

It is intriguing to note that although the photolysis wavenumber changed by only ~200 cm^{−1} across the $\tilde{A}$ – $\tilde{X}$ band system, the maximum observed *n*KERs are found to increase by several times that amount – by several thousand wavenumber in the case of Xe⁺ formation. The variability in

the structure of the observed PSDs for RG⁺ over the excitation range is not fully understood, but may arise as a result of vertical projection of the NO–RG $\tilde{A}$ state wavefunctions onto the dissociative ion state. Exciting NO–RG at the high energy end of the $\tilde{A}$ – $\tilde{X}$ band system prepares molecules that are highly excited in the NO–RG coordinate. Since the $\tilde{A}$ state potential energy surface is relatively shallow and broad along the NO–RG coordinate, projection of these wavefunctions onto the super-excited NO⁺–RG potential energy surface, and subsequently onto the dissociative NO–RG⁺ surface, likely accesses a much broader range of internuclear distances at the high energy end of the $\tilde{A}$ – $\tilde{X}$ band system than when excitation is nearer the band origin. It is therefore not unreasonable to expect dissociative ionization via the high energy members of the $\tilde{A}$ – $\tilde{X}$ band system to access higher energy regions of the dissociative NO–RG surface (through vertical excitation from inner turning points), thus resulting in higher RG⁺ kinetic energies. Likewise, accessing longer NO–RG internuclear distances (via the outer turning points) could explain the increased propensity for the production of low kinetic energy release products at the high energy end of the $\tilde{A}$ – $\tilde{X}$ band system. Since the form of the NO–RG⁺ potential energy surfaces is unknown, a computational study of the molecular states correlating with RG⁺(²P_{3/2,1/2}^o) + NO(*X*, *v*, *J*) products would be very beneficial for determining overlap integrals and thus predicting *n*KERs and PSDs.

IV. CONCLUSIONS

Velocity map imaging studies of Kr⁺ and Xe⁺ production following photolysis of NO–Kr and NO–Xe have been undertaken across the $\tilde{A}$ – $\tilde{X}$ absorption band. Image anisotropies and *n*KERs are consistent with a mechanism whereby photo-induced charge transfer occurs at the two-photon level, followed by dissociative ionization at the three-photon level. Kr⁺ *n*KER spectra show two product channels which may be assigned as arising due to population of successive NO(*X*²Π) vibrational levels, with peak widths suggesting population of several rotational levels within the vibrational manifold. At low excitation wavenumber, Kr⁺ *n*KER spectra are dominated by the higher kinetic energy product channel, whereas excitation in the high energy region of the NO–Kr spectrum yields *n*KER spectra with a propensity for the lower kinetic energy release product channel. Excitation of NO–Xe via the origin band of the $\tilde{A}$ – $\tilde{X}$ transition yields a *n*KER spectrum that is dominated by *n*KER peaks at ~2800 cm^{−1} and 900 cm^{−1}, with a minor contribution from an additional channel at *n*KER ≈ 4700 cm^{−1}, all assignable to rotational envelopes populated in successive NO(*X*²Π) vibrational levels. These PSDs are observed to vary with increasing photo-excitation wavenumber such that the product channel at 2800 cm^{−1} loses relative intensity in favour of the other two, with a fourth channel (~6500 cm^{−1}) opening at the high energy end of the $\tilde{A}$ – $\tilde{X}$ band system.

A high degree of parallel alignment is observed for RG⁺ angular distributions despite the fact that dissociative ionization is thought to occur via three perpendicular transitions. This is thought to arise as a consequence of the initially localized NO excitations essentially preparing an ensemble of

T-shaped NO–RG Rydberg states wherein the NO–RG bond axis is aligned parallel with the photolysis laser's polarization. It is therefore possible that atypical angular distributions may be observed in other similar systems wherein localized electronic transitions occur within a molecular moiety weakly (i.e., van der Waals) bound to another species.

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