NO(X ²II) ROTATIONAL DISTRIBUTIONS FROM THE PHOTODISSOCIATION OF NOCI AND NOBr AT 450 AND 470 nm

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Received 2 May 1988

The rotational, Λ doublet and spin state distributions of the NO fragment following dissociation from NOCl and NOBr have been measured using a one-colour photolysis analysis laser scheme. Dissociation was by one photon at 450 or 470 nm while twophoton non-resonant LIF at the same wavelength was used to probe the NO fragment. The NO rotational distributions for both precursors are found to be inverted and non-Boltzmann with states up to N=60 populated. Similar Λ doublet ratios of 1.7 and 1.6 for NOCl and NOBr respectively are observed. A statistical F_2/F_1 spin state population has been measured for NO from NOBr photolysis, however, the spin ratio from NOCl is found to be non-statistical with $F_2/F_1=2.1$. Sub-Doppler nascent NO line profiles reveal Cl is formed principally in the lower $P_{3/2}$ state but Br in either $P_{1/2}$ or $P_{3/2}$ depending on the vibrational and rotational state of the NO fragment. In addition, the line profiles demonstrate a predictable perpendicular v-j correlation corresponding to planar dissociation and also allow the assignment of the accessed electronic transitions. Coupled with alignment measurements, $\overline{A}_0^{(2)}$ and β_{effn} the excited state symmetries are assigned.

1. Introduction

In a previous publication [1], we have demonstrated the use of polarisation spectroscopy to determine fragment quantum state distributions generated by one-photon dissociation of NOCl and detecting two-photon absorption laser induced fluorescence (LIF) of nascent NO(X $^{2}\Pi$). The same laser pulse was employed for both dissociation and probing (onecolour experiment). The visible and near UV part of the NOCl electronic spectrum was assigned from an analysis based on the vector correlations between the velocity of the fragment and the transition dipole moment of the parent. In addition, and from the width of selected NO rotational transitions, it was found that at the available energies explored (up to $\approx 9500 \text{ cm}^{-1}$) the Cl fragment appears predominantly in the lower ${}^{2}P_{3/2}$ spin-orbit state. The Λ doublet populations of the NO fragment were also determined. In the present study we carry out similar types of measurements on NOBr and from their analysis we hope to obtain a complete picture of the dissociation of nitrosyl halides from the excited states

accessed by ≈ 455 and ≈ 475 nm light. Both molecules are bent in their ground and lower excited states [2] thus the primary focus of the present study is the NO rotational distributions. Considerable information about the dynamics of a dissociation process can be gained from the shape of the fragment rotational distribution following the dissociation of small molecular systems [3-5].

Photodissociation of triatomics has proved to be the most convenient in terms of theoretical and empirical models as well as experimental studies [5-9]. Indeed NOCl was among the first of such molecules to be studied in the novel work of Busch and Wilson [10] which led to the derivation of the impulsive photofragmentation model. Comparison of the photolysis products of NOCl and NOBr should help elucidate the change in dissociation dynamics induced by the heavier atom.

Most recently attention has focused on the vector properties v, j of the dissociation products [11-14] rather than the traditional scalar quantities such as fragment internal distributions. Linearly polarised excitation preferentially excites molecules whose transition moments are aligned parallel to the electric vector E_p (where the subscript p refers to the

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photolysis laser). Upon fast dissociation this alignment is transferred to the velocity [15] and to the lab frame molecular alignment of the products:

$$f(\vartheta) = (1/4\pi) [1 + \beta P_2(\cos \vartheta)],$$

$$\vartheta = \angle E_p \cdot \text{recoil velocity}.$$
(1)

The former is described by eq. (1), where P_2 is a second-order Legendre polynomial, and the latter can be detected by polarised fluorescence from excited state fragments or as for nitrosyl halides by employing a narrow band linearly polarised analysis laser. Sub-Doppler nascent NO line shapes will therefore be functions of the correlations of the recoil velocity described by the parameter β and the alignment with the electric vector. The magnitude of β will be determined by the symmetry of the transition; $A' \rightarrow A''$ yields $\beta = -1$ and A' \rightarrow A' yields $\beta = -1$ to 2 depending on the position of the transition moment vector in the molecular plane. Other factors such as excited state lifetime and parent rotation will reduce the correlation of $\mu - v$ and $\mu - j$ and hence also the size of β [16,17]. However, as the dissociation of a triatomic must be a planar process the rotational vector j of the fragment at the time of bond rupture will be perpendicular to this molecular plane hence v and j will be perpendicular. Thus a third correlation, independent of E, occurring only at the instant of fragmentation, the v-j correlation is expected. In these experiments all the above vector correlations have been observed. The alignment of the NO photofragments has been determined but we have only qualitatively measured the μ -v and v-j correlations and have made no attempt to deconvolute and extract the exact magnitude of these terms. In section 4 we discuss how for a one-colour LIF experiment all the vector correlations could be measured separately.

Br and Cl, at the dissociation energies used in the experiment, can be produced in either of the 3/2 or 1/2 spin-orbit states which lie 3685 and 880 cm⁻¹ apart respectively. Line profiles would then be a superposition of two-fragment translational distributions resulting in a complex line profile that cannot be fitted by a single average translational energy. The results show that Cl is formed predominantly in the ground state Cl_{3/2} independent of the NO vibrational and rotational state but Br can be produced in either

state depending on the E_{avl} and the NO rovibrational state.

The NO molecule has four sublevels, two Λ doublet levels which at high *j* can be described by orbitals in or out of the plane of rotation and two spin-orbit states. The analysis of these internal states has been shown to provide further information on the excited state. NOCl and NOBr exhibit non-statistical sublevel distributions revealing the symmetry of the orbital excitation and the influence of the increased spin-orbit coupling of Br.

It is important when the dissociation and probe laser originate from the same laser pulse that the absorption spectrum of the parent molecule is uniform and shows only broad structure. For NOBr the electronic absorption spectrum begins at ≈ 650 nm and rises monotonically and smoothly to the near UV, hence in the range of only 2-3 nm, as used for measuring rotational populations, the absorption is constant. The absorption spectrum of NOCl is similar [18] with the exception of discernible broad electronic structure. Although it is accurate to measure rotational distributions by this so-called one-colour method it is likely that measured vibrational distributions are complicated by the unequal dissociation energies exciting different, or at least a different mixture, of electronic states. These electronic states may even have slightly uneven absorption cross sections. Consequently exact vibrational populations cannot be determined but a qualitative picture of the distribution has been obtained.

2. Experimental

The experimental arrangement and the methods employed have been described previously [1,19]. Briefly, fragmentation of NOCl and NOBr and LIF probing of the NO product were performed with the same laser pulse (fwhm \leq 7 ns) at the tunable wavelength of a dye laser (Lambda Physik FL002E) operated with coumarine dyes and pumped by an excimer laser (Lambda Physik EMG 101MSC). In these one-colour experiments the parent molecule was photolysed by one-photon absorption, whilst the NO fragment was excited in a two-photon absorption process,

NO(A² Σ^+ ; v=0)→NO(X² Π ; v=0, 1, 2).

The undispersed fluorescence was detected by a photomultiplier (Hamamatsu R166UH), integrated in a boxcar averager (Stanford Research Systems SR 250) and corrected for shot-to-shot laser intensity fluctuations. The laser was linearly polarised with the electric vector parallel to the observation axis. The laser linewidth was ≈ 0.2 and ≈ 0.05 cm⁻¹ when spectra and Doppler broadened line profiles were recorded, respectively. The laser pulse energy was kept as low as possible, typically 0.9–1.3 mJ, to avoid saturation and additional multiphoton absorption effects.

NOCl and NOBr were synthesised and purified according to published procedures [1,20]. The room temperature gases were flowed through a sample cell at a pressure of ≤ 150 mTorr with a flow rate sufficiently high to avoid product build-up at the pulse cycle of 6–8 Hz.

3. Results

The two-photon LIF spectra of nascent NO can be converted to rotational populations through the following equation [19]

$$I_{fl} = [KS(j, \Delta j) n/(2j+1)] \times [q^{(0)}(j, \Delta j) + q^{(2)}(j, \Delta j) \bar{A}_{0}^{(2)} P_{2}(\cos \kappa)];$$

$$\kappa = \angle E_{p} \cdot E_{a}, \qquad (2)$$

where S is the rotational line strength, K is an experimental constant, $q^{(0)}$ and $q^{(2)}$ are angular momentum geometrical factors, $\bar{A}_0^{(2)}$ is the molecular alignment, E_a the analysis laser electric vector, and n is the important population term. Figs. 1 and 2 depict the normalised rotational population distributions for v=0 and 1 of NOCl and NOBr. The results have not been corrected for alignment as, in the high j limit and assuming the alignment is independent of j, it will not alter the relative distributions.

It should be noted, because of the nature of the experiment, each rotational distribution corresponds to a slightly different dissociation energy making comparisons more than trivial. The rotational distributions are thus accompanied by both a change in $E_{\rm vib}$ and E_{hv} . Tables 1 and 2 contain a summary of the results of the v=0 and 1 rotational populations (in-



Fig. 1. Rotational distributions of the lowest and first vibrational states of NO(X $^{2}\Pi$) following dissociation of NOCl. Peak heights have been normalised and fitted curves are drawn as guidelines.



Fig. 2. Rotational distributions of the lowest and first vibrational states of NO(X $^{2}\Pi$) following dissociation of NOBr. Peak heights have been normalised and fitted curves are drawn as guidelines.

tegrated) for NOCl and NOBr. Clearly, probing of the v=1 NO fragment channel is accompanied by a decrease in laser frequency and a subsequently lower $E_{\text{avl}}^{\text{NO}}$.

After photolysis the rotational vectors of the NO fragment should, assuming prompt dissociation of the triatomic, be spatially anisotropic. Conventionally, lab frame $(z || E_p)$ rotational alignment $\overline{A} \langle 2^2 \rangle$ has been measured by comparing results taken with the photolysis and analysis laser electric vectors parallel and perpendicular, respectively [21–23]. However, in a one-colour experiment this is impossible and the alignment has been derived from the intensities of two rotational branches originating from the same Λ and spin-orbit ground state. For example, O_{12} and $Q_{12}P_{12}$ can be used because the Q_{12} transition is negligible at large *j*. Equating rotational populations of two transitions originating from the same level, eq. (2) be-

Table	e 1				
NO($X^2\Pi$)	from	NOCI	photodissociation	a)

λ(nm)	v	E _{avl}	E^{\ddagger}_{avl}	$\bar{E}_{\rm rot}$	$E_{\rm trans}^{\rm NO}$ b)	$E_{\rm trans}^{\rm Cl}$	$ar{E}_{ m rot}/E^{ m t}$	$E_{\rm trans}^{\rm total}/E^{\ddagger}$
≈450	0	9490	9490	1940	4080	3470	0.20	0.80
≈470	1	8500	6620	1350	2850	2430	0.20	0.80

^{a)} Energy in cm⁻¹; $D_0^0 = 13030 \pm 100$ cm⁻¹. ^{b)} Assuming $E_{el}^{Cl} = 0$.

Table 2 NO($X^{2}\Pi$) from NOBr photodissociation ^{a)}

λ (nm)	v	Eavt	E_{avl}^{\ddagger}	\bar{E}_{rot}	$\bar{E}_{ m rot}/E^{\ddagger}$		
≈450	0	13080	13080	2890	0.22		
≈470	1	11930	10000	2100	0.18		

^{a)} Energy in cm⁻¹; $D_0^0 = 9700 \pm 100$ cm⁻¹.

comes after rearrangement, remembering $\kappa = 0$,

$$\bar{A}_0^{(2)} = (I_s q_1^{(0)} - q_2^{(0)}) / (q_2^{(2)} - I_s q_1^{(2)}), \qquad (3)$$

where

 $I_{\rm s} = I_2 S_1 / S_2 I_1$.

The q factors are angular momentum geometrical factors where the subscripts refer to transition 1 or 2 and $\bar{A}_0^{(2)}$ has the theoretical limits $-2/5 \leq \bar{A}_0^{(2)} \leq 4/5$. (The value of I_s for $\bar{A}_0^{(2)} = 0$ is $q_2^{(0)}/q_1^{(0)}$ because the detector is spatially fixed and there is no angular integration of the unresolved fluorescence.) The values of the alignment were for NOCl v=1, $\bar{A}_0^{(2)} = 0.66 \pm 0.15$ and $\bar{A}_0^{(2)} = -0.13 \pm 0.2$ for NOBr v=0, averaged over J, A and spin states.

Laser wavelengths \approx 450, 470 and 490 nm probe the v=0, 1 and 2 levels of NO thereby allowing us to measure its vibrational content. At wavelengths \approx 510 nm, corresponding to (NO(A² Σ^+ ; v=0) \leftarrow NO(X² Π ; v=3), no LIF signal was observed indicating $v \leq 2$ were populated at this excitation wavelength. Below 510 nm it was established that the majority of NO was produced in v=0 and 1 with a small proportion in v=2. These results are obviously not exact vibrational distributions because of the distortions generated by the change in the dissociation laser frequency (energy). Nevertheless, as the laser energy is altered by merely ≈ 2000 cm⁻¹ the vibrational distributions can be regarded as an adequate representation of the photodissociation of NOCl and NOBr at ≈ 470 nm.

²II state molecules possess both Λ doublet and spin state splitting thus the NO is formed in one of four sublevels and although spectroscopically the spin-orbit states can be separated the Λ doublets are not resolved. In two-photon absorption by monitoring the intensity of four rotational branches, O₁₁, O₁₂, S₂₁ and S₁₂ all four sublevel populations can be measured. Figs. 3 and 4 display the distributions found for NOCI



Fig. 3. Sub-level populations of NO(X ${}^{2}\Pi$; ν =1) from the dissociation of NOCl. The *y*-axis scale is in arbitrary units. Fitted curves are drawn only as guidelines.



Fig. 4. Sub-level populations of NO(X ${}^{2}\Pi$; v=0) from the dissociation of NOBr. The y-axis scale is in arbitrary units. Fitted curves are drawn as guidelines.

and NOBr. Intriguingly, in each case the $\Pi(A'')$ is the most favoured dissociation channel but there then appears to be an inversion of the next most populated state.

Finally, by employing the intracavity etalon and scanning the dye laser frequency through a rotational transition high-resolution Doppler broadened line shapes were obtained. These Doppler profiles will be complex functions of the recoil velocity correlation $(\mu \cdot v)$, the correlation of the optical transition moment and j $(\mu \cdot j)$ and the correlation of the recoil velocity and j $(v \cdot j)$. In general such a line profile can be expressed, when $E_p || E_a$ and $k_p || k_a$, by the simple function below

$$g(\nu) = (1/2\Delta\nu_{\rm D}) [1 + \beta_{\rm eff} P_2(\cos\vartheta') P_2(x_{\rm D})];$$

$$\vartheta' = \angle E_{\rm p} \cdot k_{\rm a} = 90^{\circ},$$

$$g(\nu) = (1/2\Delta\nu_{\rm D}) [1 - \frac{1}{2}\beta_{\rm eff} P_2(x_{\rm D})];$$

$$x_{\rm D} = (\nu - \nu_0)/\Delta\nu_{\rm D},$$
(4)

where ν is the frequency, ν_0 the transition frequency and $\Delta \nu_D$ the Doppler width from which the translational energy can be obtained. The anisotropy parameter, β_{eff} , is a function of all the correlations mentioned above but a further complication arises due to the two spin-orbit states of the halogen atoms. Consequently, experimentally measured profiles could be a combination of two translational energies correlating to the 3/2 and 1/2 spin states of the halogen atom. The splitting $\Delta E(Cl_{1/2}-Cl_{3/2})$ is only $\approx 880 \text{ cm}^{-1}$ resulting in a difference of the Doppler widths of 5-8% whereas $\Delta E(Br_{1/2}-Br_{3/2})$ is 3685 cm⁻¹ thus the apparent Doppler width difference would be $\approx 20\%$.

The fitting procedure must also incorporate the finite resolution of the laser ($\approx 0.05 \text{ cm}^{-1}$) and the parent molecule Doppler motion. A Gaussian function (the fwhm was obtained by measuring thermal NO) was used to replicate accurately this sum of the laser linewidth and Doppler motion. Although this experimental convolution lowers the resolution, both parameters β_{eff} and Δv_D can be deconvoluted easily from the fitting procedure.

In ref. [1] we have shown that the Doppler profiles of NO resulting from NOCl photodissociation at ≈ 470 nm exhibit large *v*-*j* correlation and for the first vibrational state show β_{eff} varying from -0.9 to 0 depending on the probed rotational branch. By energy balance, Cl was calculated to be formed principally in the lower $Cl_{3/2}$ level. Unfortunately, the resolution of the experiment did not allow a more quantitative analysis.

Two NO line profiles, S_{22} and R_{11} from the dissociation of NOBr are shown in figs. 5b and 6b. There is clearly, as expected, a large v-j correlation as can be seen by the strikingly different forms of the two line shapes proving v and j are perpendicular. Figs. 5a and 6a display a single translational energy fit to a simulated profile containing a mixture of NO arising







Fig. 6. (a) As in fig. 5a except $\beta_{eff}=0.3$. (b) As in fig. 5b for the R₁₁(36.5) branch.

from the $Br_{3/2}$ and $Br_{1/2}$ formation. The residuals display the characteristic "fingerprint" of a line shape having two translational energy components but fit-

Table 3 NOBr photodissociation energy partitioning ^{a)}

ted with the assumption of a single translational energy. Figs. 5b and 6b display two experimental line profiles of NO in v=0 from NOBr which have been fitted again with the assumption of a single translational energy. The residuals show a very similar pattern to figs. 5a and 6a indicating a fragmentation process composed of $Br_{3/2}$ and $Br_{1/2}$ channels. The line profiles of v=1 did not exhibit the same pattern proving almost exclusive production of the lower Br spin state with a branching ratio $Br_{3/2}/Br_{1/2} > 0.9 \pm 0.1$. Any $Br_{1/2}$ production could not be experimentally resolved.

In order to confirm the predictions of the v=0 state, the line profiles were fitted, using conservation of energy, with a double profile fit, $\Delta \nu_{\rm D}({\rm Br}_{1/2})$ and $\Delta \nu_{\rm D}({\rm Br}_{3/2})$ were fixed according to eq. (4). Best fits, in terms of χ_r^2 , were obtained by assuming a β_{eff} corresponding to $Br_{3/2}$ production was equal to the β_{eff} values for the v=1 state and letting the β_{2eff} vary. However, in all cases simply by using a double profile a better fit to the data was obtained demonstrating the problematic nature of fitting these types of line profile with only limited resolution. Thus it is unclear whether there are two states with $\beta_{1\text{eff}} \neq \beta_{2\text{eff}}$ or simply one β_{eff} , however, the value of the Br spinorbit branching ratio did not alter appreciably for the two fitting procedures. Thus from the results shown in table 3 we can certainly conclude the v=0 state of NO correlates predominantly with $Br_{1/2}$ production whereas the v=1 with $Br_{3/2}$.

Branch	Quantum	ν ₀	Eavl	E ^{NO}	$E_{\rm trans}^{\rm NO+Br}$	$E_{\rm trans}^{\rm NO}$	β_{eff}	% Br _{1/2}	E ^{NO} trans	Theoretical
	state	-				1 profile		$\beta_1 \neq \beta_2$	Br _{3/2}	Br _{1/2}
	() $v = 0$, <u>, , , , , , , , , , , , , , , , , , </u>
S ₂₂	j = 34.5 A'	22390	12980	2106	10874	5160	2.0	72	7905	5226
S	j = 34.5 A'	22402	12992	2151	10841	6050	2.0	61	7881	5202
R ₁₁	j = 36.5 A''	22355	12945	2395	10550	5600	0.4	54	7670	4991
R ₁₁	j = 45.5 A''	22477	13067	3658	9409	5540	0.3	33	6840	4161
NO(Х ² П	() $v = 1$									
0,1	j = 34.5 A'	21202	11792	3997	7795	5350	2.1		5667	2988
P11	j = 37.5 A''	21294	11884	4363	7521	5250	0.6		5468	2789

a) Energy in cm⁻¹

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4. Discussion

Andresen et al. [24,25] and Schinke et al. [26,27] studied experimentally and theoretically the photodissociation of H₂O at 157 nm. The main thrust of their analysis is the separation of the dissociation process into two steps

$ABC \rightarrow ABC^* \rightarrow AB + C$.

The first step, the instantaneous absorption of the photon, leaves the atomic nuclei in their ground state positions and is essentially the Franck-Condon (FC) limit. The second step describes how the nuclei begin to move under the influence of the potential and at this point a large torque can be exerted leading to the final state product distributions. This latter step is termed the final state or exit channel interaction. The fragment distributions will then be governed depending on which of the above stages dominate, but, there is no reason to suppose that vibrational and rotational modes will be affected equally. In the case of H₂O, Andresen et al. [24,25] and Schinke et al. [26,27] observed rotationally cold OH at 157 nm which could be satisfactorily explained in the FC limit but vibrational excitation was due to final state interaction coupling of the translation to vibration.

NOCl and NOBr both display highly inverted non-Boltzmann NO(X $^{2}\Pi$) rotational distributions populating states up to N=60 with no population below N=10-15. In the situation of the FC limit and no exit channel coupling of the translational and rotational degrees of freedom, rotationally "cold" fragments as have been observed in the dissociation of H_2O and H_2S [28], would be expected. For NOCI and NOBr the converse is true. Coupling of the rotational and translational motions induces a large torque on the separating atom and diatom to produce high rotational excitation. If indeed this coupling were the dominant force of the dissociation mechanism. NOBr should have, in comparison with NOCl, higher rotational states populated because of the smaller dissociation energy and thus larger E_{avl} . This effect is quite evident in fig. 2 although it may be due in part to the increased reduced mass and slightly different potential surfaces. Hence it is apparent that the form of rotational distributions is controlled by the final state interactions.

In contrast to the rotation, the NO fragment was

found to be vibrationally "cold". Moser et al. [29] and Grimley and Houston [30] observed that at wavelengths of \ge 350 nm NOCl was produced in $v \le 5$ with the majority in the v=0 and 1 levels. In the present experiment, NO was found to be predominantly in v=0 and 1 with very little population of the v=2state. As it was necessary to alter the dissociation wavelength to probe each vibrational level no exact populations could be calculated. Listed in tables 1 and 2 are the fractional energies in translation and rotation for both vibrational modes, where we have redefined $E_{avl}^{\ddagger} = E_{avl} - E_{vib}$ with $E_{avl} = E_{h\nu} - D_0 +$ $E_{int}^{NOCI, NOBr}$. The rotational content remains approximately equal for both NOBr and NOCl suggesting the vibrational mode evolves independently and is decoupled from all others.

Interestingly, at wavelengths $\approx 190 \rightarrow 250$ nm NO is formed highly vibrationally excited, up to v=16[29,31]. In fact 40% or greater is channelled into the vibration of the diatomic fragment implying a radically different dissociation mechanism occurs below 300 nm. Experimentally two laser LIF probing of the excited vibrational states could be performed at ≈ 210 nm as in this region the analysis laser, despite photolysing the precursor, would solely produce non-interfering low-lying vibrational states.

A recent ab initio calculation of the S₁ excited state of NOCl [32] illustrates that we would expect similar NO internal distributions as experimentally observed for the S_2 state. The qualitative nature of the potential surface indicates the amount of diatom vibrational excitation should be dependent on the initial excitation position on the S1 surface. A mapping of the ground state equilibrium geometry on the excited state surface indicates vibrationally cold products would be expected. The potential shows more complex behaviour when the O-N-Cl angle is varied and rotational excitation will be inevitable on this anisotropic surface. It is unreliable to infer results and conclusions from the comparison of two potential surfaces of the same molecule as one has to make the rather gross assumption of similar potential surfaces. Nevertheless with this assumption the analysis and calculations are in good agreement.

Focusing our attention on the highly selective Λ doublet populations more information can be gained about the excited electronic states being accessed. In ref. [1], excitation of NOCl ≈ 474 nm gave $\beta \approx -0.7$

(partially corrected for v-j correlation) and $\bar{A}_0^{(2)} = 0.66$ establishing transitions at this wavelength are $A' \rightarrow A''$. Furthermore, from the calculations of Solgadi et al. [2] it must be $S_0 \rightarrow S_2(2A'')$ with the excited state orbital localised on the NO group. Under these circumstances, if the NO fragment molecule had a "memory" of its parent configuration and the dissociation was planar, which it must be in a triatomic, then the $\Pi(A'')$ state would be preferentially populated, exactly as observed.

The situation of NOBr is not quite so transparent. $\beta_{\rm eff}$ is positive thus the transition must be $S_0(A') \rightarrow A'$ which could mean electron excitation from either $a'' \rightarrow a''$ or $a'' \rightarrow a''$. However, a planar dissociation and strong $\Pi(A'')$ state preference limit the transition to $a'' \rightarrow a''$. Hence despite the forces involved in generating the rotationally hot distributions, the Λ doublet ratio demonstrates the nascent fragment retains a strong memory of the parent electronic distribution at the time of dissociation. If the spin-orbit populations are averaged over rotational states the final Λ doublet ratios of NOCl and NOBr are $\Pi(A'')/$ $\Pi(A') = 1.7$ and 1.56, respectively, suggesting the dissociation mechanisms are similar. The degree of electron alignment (DEA) is defined by $[\Pi(A'') \Pi(A')]/[\Pi(A'')+\Pi(A')]$ and according to the theory of Andresen and Rothe [33] would have an average (for N=15-60) theoretical value of ≈ 0.65 . The DEA of NO from NOCl and NOBr are 0.22 and 0.26 respectively. Clearly, even though there is obvious preferential population of one Λ doublet it is by no means close to the theoretical limit. The Λ doublet yield, in contrast to the alignment and β (excluding v-j correlation), is independent of the excited state lifetime as creation occurs only at the instant of fragmentation. If there was considerable parent rotation during the break up of the excited state then the "orthogonality" of the Λ doublet states, with respect to the dissociating parent, would be broken. In this situation a preferential Λ doublet distribution below theoretical would be observed. However, in the limit of fast dissociation as is expected in the nitrosyl halides, this mechanism is unlikely to lower the Λ doublet propensities significantly. We are therefore unable, at present, to ascribe a reason to the discrepancy between the theoretical and experimental measured DEA.

Joswig et al. [34] and Brühlmann and Huber [35]

have addressed the question of unequal spin-orbit populations of CN from ICN photodissociation and NO from CH₃ONO respectively. Different models are invoked to explain the observed propensities. The present experiment averaging the Λ doublets furnishes the result $F_2/F_1 = 2.1$ for NOCl but $F_2/F_1 = 0.9$ for NOBr. Thus NOBr exhibits no preference and total randomisation of NO spin-orbit states but NOCl photodissociation yields 68% of the upper $\Pi_{3/2}$ level. This supports our claim of NOCl photodissociation proceeding through a primarily adiabatic path which evolves into specific spin states of $Cl_{3/2}$ and $\Pi_{3/2}$ [1]. It is reasonable to conclude that the increased spinorbit coupling of the Br atom disrupts this adiabatic picture effectively generating a statistical distribution of NO spin states. An analysis similar to Joswig et al. [34] may prove useful in NOCl and NOBr but a careful N dependence of the effect would be required and due to the intrinsic experimental uncertainties has not been attempted. A considerably more detailed analysis would be needed to even qualitatively explain these effects.

There are four influences on the measured line profiles, β depending on the symmetry and position of the transition moment vector, $\overline{A}_0^{(2)}$ the molecular alignment referenced to E_p , the correlation of the recoil velocity with the rotational vector \mathbf{j} and finally, the superposition (if any) of the two translational energies arising from the halogen spin-orbit splitting.

Perhaps the easiest of these to discuss is the v-j correlation. As all torques and forces must lie in the plane of the parent triatomic the rotational vector will be perpendicular to v. Put slightly more formally

 $j_{\text{photon}} + j_{\text{NOCl}} = L_{\text{Cl}} + j_{\text{NO}} + L$,

where L is the orbital angular momentum, $L_{Cl} = 1$ and assuming j_{NOCl} to be small

 $\mathbf{j}_{\rm NO} \approx -L$ (antiparallel).

Thus, because $L \perp v, j \perp v$. (Deviation could be caused by the non-zero value of j_{NOCI} in the thermal cell.) The effect on a two-photon Doppler broadened transition will be to increase β_{eff} for S or O and decrease it for P or R branch excitation. Examination of the Doppler profiles data in ref. [1] and figs. 5 and 6 shows dramatic changes of β_{eff} indicating high v-jcorrelation. In the final paragraph of this section we show, using the theory of Dixon [36], how to obtain the exact values of this correlation for a common dissociation analysis experimental scheme but the rather predictable nature of this correlation in this experiment did not warrant a more in-depth analysis.

Table 3 lists the $\beta_{\rm eff}$ parameters obtained from a one-profile fit to several line shapes and reveal the "true" β are in the range ≈ 1 to 1.5 for both v=0 and v=1 states of NOBr and from ref. [1] ≈ -0.4 to -0.8 for NOCl v=1. These results coupled with the alignment values of $\bar{A}_0^{(2)} = -0.13$ for NOBr v = 0 and $\bar{A}_0^{(2)} = 0.66$ for NOCl v = 1 allows us to assign the electronic states being accessed. A negative β value can be obtained under two circumstances: (a) If the transition moment vector $\boldsymbol{\mu}$ is in the plane of the molecule but perpendicular to the recoil velocity $(A' \rightarrow A')$ transition). (b) If μ is perpendicular to the molecular plane $(A' \rightarrow A'' \text{ transition})$. The alignment provides the distinguishing factor in the two cases. For (a) as j is perpendicular to the molecular plane in a triatomic, $j \perp \mu$, E_p and z thus the alignment will be negative. For (b) the converse is true, $j \parallel \mu$, E_p and z and will attain a positive value. Hence, dissociation of NOCl at 470 nm is via an $A' \rightarrow A''$ transition which from the previous section was already ascribed to the $S_0 \rightarrow S_2(A'')$ verifying the conclusions made earlier.

The β_{eff} value measured in the fragmentation process of NOBr indicates an A' excited surface with an orbital excitation of $a'' \rightarrow a''$ (section 3). The low value of the alignment suggests two states may be involved in the excitation process but it would be impossible to identify this from the Doppler profiles.

The Doppler profiles also provide a gauge to the yield of halogen spin-orbit channels for each rovibrational state. The small energy gap of ≈ 885 cm⁻¹ for Cl made it feasible to measure the preferential population of the two Cl spin-orbit states. For all v, j states probed the lower Cl_{3/2} level was favoured, in good agreement with the photodissociation results of Tiemann et al. [37] (193 nm) who measured a Cl_{1/2} :Cl_{3/2} ratio of $\approx 1:2$ for a range of Cl containing compounds.

The simulations of Br branching provide the necessary technique of pin-pointing when a line shape consists of a combination of fragmentation channels but does not provide the exact magnitude of the branching ratio. The values quoted for the $Br_{3/2}$: $Br_{1/2}$ ratio can only be regarded as a guideline for the reasons mentioned in section 3 and the possibility of the two Br spin-orbit states correlating with different excited state surfaces cannot be ruled out. Despite the intrinsic problems of the Doppler profile analysis several conclusions are apparent. The total $Br_{1/2}$ production, averaged over rotational states, is $\ge 50\%$ in v=0 but falls to $\le 10\%$ in v=1. The processes occurring can be summarised below

NOBr
$$\xrightarrow{> 50\%}$$
 NO + Br_{1/2}
 $\stackrel{< 50\%}{\longrightarrow}$ NO + Br_{3/2}, $v=0$ (≈ 450 nm),
NOBr $\xrightarrow{> 90\%}$ NO + Br_{3/2}, $v=1$ (≈ 470 nm),

which is very similar to the results obtained by Russell et al. [38] for BrCN dissociation at 248 nm. Furthermore, the $Br_{1/2}$ yield is inversely proportional to the rotational state of NO, implying the governing force for excited state Br production is the energy available after partitioning into vibrational and rotational modes. The electronic excitation is therefore a spectator in the fragmentation process absorbing energy only when available, hence at shorter wavelengths the v=0 state of NO would be expected to generate 100% $Br_{1/2}$. This would be in complete contrast to the low Cl_{1/2} from NOCl. Thus an important correlation exists between the quantum state of NO and Br and there are two pathways by which this process can occur. The fragmentation process can be pictured as having a reservoir of energy to be disposed of among the products. If NO is ejected rotationally excited Br is formed principally in its ground state and vice versa. Alternatively, two closely spaced and overlapping rotational distributions corresponding to $Br_{1/2}$ and $Br_{3/2}$ are superimposed. Thus a particular j state contains contributions from both distributions appearing to be a correlation of fragments. This latter argument is supported by the "shoulder" evident in the rotational distribution for v=0 in fig. 2.

In this paragraph we describe briefly how, for a common photolysis analysis laser two-photon absorption LIF experiment, all three vector correlations could be measured. This method can be employed when the analysis laser dissociates the parent molecule. The theory involves describing the photodissociation LIF detection scheme in terms of bipolar spherical harmonics and the respective moments thereby decoupling the vector correlation effects [36]. The analysis of Doppler broadened line shapes is achieved by fitting the line profiles with only two parameters β_{eff} and $\Delta \nu_{\text{D}}$ but β_{eff} can be decomposed thus

$$\beta_{\rm eff} = [x_1 \beta_0^2(20) + x_2 \beta_0^0(22) + x_3 \beta_0^2(22) + x_4 \beta_0^2(24)] / [x_6 + x_5 \beta_0^2(02)],$$

into five variables and their respective weights $(x_1 \rightarrow x_5)$ depending on the transition geometry, polarisation and rotational branch. Conventionally for one-photon LIF detection $\beta_0^2(24)$ can be ignored because of the negligible value of x_4 . Thus for a onecolour 1+1 LIF experiment the bipolar moments $\beta_0^2(20), \beta_0^2(02), \beta_0^0(22)$ and $\beta_0^2(22)$ can be extracted by measuring four line profiles, two different branches with laser polarisations parallel and perpendicular to the detection axis [36]. In contrast, for two-photon LIF x_4 is comparable in magnitude to all other terms and moreover, it converges slowly to its high j limit [39]. Thus two-photon absorption has the advantage that all the abovementioned bipolar moments can be measured including $\beta_0^2(24)$ and indeed this bipolar moment could be measured by comparison of β for O and S (or P and R) branches. Clearly more details of photodissociation vector correlations can be achieved using two-photon detection.

5. Conclusions

Photolysis of NOBr and NOCl between 450 and 470 nm has been shown to yield inverted Gaussianlike rotational distributions. From the extent of the rotational excitation it can be concluded that there must be strong final state interactions of the translational and rotational modes on the dissociating potential hypersurface. In contrast little NO vibrational excitation was observed implying fragmentation proceeds uninfluenced by the NO stretch, v_3 , of the excited state surface. This simple picture suggests the lower electronic states of NOCl and NOBr are similar which can be attributed to the large contribution of the halogen electrons to the highest occupied orbitals.

Analysis of the line profiles revealed a correlation

of the Br spin-orbit state with the rotational and vibrational state of the ejected NO molecule. Unexcited Br was always formed in parallel with vibrationally or highly rotationally excited NO. Diatomic fragments in low rotational states correlated directly with the higher spin-orbit state $Br_{1/2}$.

The rotational sublevels were measured allowing assignment of the NOBr orbital excitation. Equal propensities were observed for the $\Pi(A'') \Lambda$ doublet level in both NOCl and NOBr confirming the dissociation mechanisms are similar. The spin-orbit levels of NO illustrated the possible randomising effect of the large spin-orbit coupling of the Br atom as a statistical spin-orbit ratio was observed for NOBr but a ratio of 2:1 ($F_2:F_1$) was measured for NOCl dissociation.

Finally we would like to emphasise the power and economy of experimental effort of the one-colour technique. An almost complete description of the internal state populations resulting from the photodissociation of NOCl and NOBr has been achieved and with relatively little experimental sophistication all the vector correlations can be deconvoluted and measured exactly.

Acknowledgement

Support for this work by the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung is gratefully acknowledged. We thank Dr. M. Nonella and H. Suter for the ab initio potential surface calculations of NOCl and R. Pfister for preparing the NOCl and NOBr samples. AT would like to thank Dr. M.P. Docker for many helpful discussions during the preparation of this manuscript.

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