# PHOTOFRAGMENTATION LIF SPECTROSCOPY OF NOCI AT DISSOCIATION WAVELENGTHS > 450 nm. PARENT ELECTRONIC SPECTRUM AND SPIN STATE AND Λ-DOUBLET POPULATIONS OF NASCENT NO AND CI FRAGMENTS

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The primary photodissociation of nitrosyl chloride, NOCl +  $h\nu \rightarrow$  NO+Cl, has been investigated at selected excitation wavelengths > 450 nm. By means of a one-colour (1+2)-photon experiment, i.e. one-photon absorption for parent dissociation and two-photon absorption for LIF to probe NO, the vibrational and rotational state distributions of nascent NO(X <sup>2</sup>Π) were measured and in combination with polarized Doppler spectroscopy also the translational energy obtained. Based on the anisotropy parameter  $\beta$  the visible and near-UV part of the electronic absorption spectrum of NOCl was assigned. After excitation at 475 nm the energy partitioning of both, the NO and Cl fragments, reveals that the dissociation proceeds in the molecular plane of the parent preferring ( $\approx 65\%$  efficiency) the channels which lead to NO(<sup>2</sup>Π<sub>-</sub>) and Cl(<sup>2</sup>P<sub>3/2</sub>). The NO  $\Lambda$ -doublet and spin-orbit state population ratios <sup>2</sup>Π<sub>-3/2</sub>: <sup>2</sup>Π<sub>+3/2</sub>: <sup>2</sup>Π<sub>-1/2</sub>: <sup>2</sup>Π<sub>+1/2</sub> were found to be 4.9:3.6:3:1.

# 1. Introduction

The relatively strong absorption over a wide spectral region in combination with a weak N–Cl bond make nitrosyl chloride an attractive model system for the photodissociation of bent triatomic molecules [1–4]. Indeed, NOCl has been the subject of continued interest since 1930 when Kistiakowsky [5] measured a dissociation quantum yield close to 2 at incident wavelengths ranging from 635 to 365 nm. In 1962, Basco and Norrish [6] observed in UV flash photolysis experiments vibrationally excited NO(X <sup>2</sup>II,  $v'' \leq 11$ ) which they concluded to originate from the primary process

$$NOCl + h\nu \to NO(X^{2}\Pi, v'' \leq 11) + Cl$$
(1)

and/or from a secondary process involving collisional energy transfer to nascent NO. The appearance of vibrationally hot NO in (1) was later

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attributed [7] to the increase of the NO bond length upon electronic excitation.

In their pioneering work on photofragmentation, Busch and Wilson [8] studied the translational energy distribution of the NO and Cl fragments using the second harmonic of a ruby laser (347.2 nm) as photolysis source. At this wavelength approximately 70% of the available energy is channeled into translational recoil of the fragments. It was indirectly inferred that the NO fragment is vibrationally excited with  $v'' \leq 3$ paralleling the prediction from an impulsive model. Furthermore, from the angular anisotropy measured at different incident polarizations, a dissociation time < 80 fs was found for the A' electronic state of the parent. More recently, Werner et al. [9,10] measured the kinetic energy of the photofragments produced at 248 and 193 nm in a molecular beam. The analysis of the time-of-flight (TOF) spectra is consistent with a narrow vibrational distribution of the NO fragment for both dissociation energies.

Infrared fluorescence detection was utilized by Grimley and Houston [11] to study vibrationally

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excited NO emerging from the primary and secondary photochemistry of NOCl after excitation at 355 nm as well as in the 480–650 nm range. The secondary process proposed by Basco and Norrish [6] was characterized by these authors [11] to be:

$$NOCI + CI \rightarrow NO(X^{2}\Pi, v'' \ge 0) + CI_{2}.$$
 (2)

In addition, at photolysis wavelengths > 480 nm the primary step was found to produce "little if any" vibrationally excited NO. A similar investigation of the primary process (1) was performed by Moser et al. [12,13]. For excitation at 308 and 337 nm they report a vibrational excitation of NO up to v'' = 5 and, for 193 and 248 nm a very broad distribution with v'' up to 14 and 16, respectively. These latter results contradict the findings of Werner et al. [9,10].

Laser-induced fluorescence (LIF) in combination with Doppler polarization spectroscopy [14,15], recognized as one of the most powerful contemporary techniques to investigate molecular photodissociation processes, has already been used to study several R–NO-type molecules [1,2,15–20]. The major difficulties encountered with NOCI, which precluded the use of this technique in its conventional form, relates to the fact that owing to the broad continuous absorption of the parent, both the pump and probe laser pulse induce dissociation. The resulting mixture of two different NO fragment distributions limits the value of such an experiment.

In the present work we circumvent this experimental difficulty by designing a one-colour experiment in which the dissociation and probing wavelengths are identical and thus only nascent NO from the primary process is probed. (Close to completion of this work we learnt about a similar experimental design used by Pfab et al. [19] to explore features of the CH<sub>3</sub>SNO photodissociation.)

We report here results on the primary photodissociation of NOCl (1) for dissociation wavelengths of  $\approx 455$ ,  $\approx 475$ , and  $\approx 495$  nm. The NO fragments were probed by a two-photon absorption LIF method [21] taking the rotational line strength given in the literature [22]. We obtained state population distributions, in particular  $\Lambda$ -doublet and spin populations in order to elucidate possible spin correlation effects of the fragments. Furthermore, Doppler profile measurements provided recoil translational energy distributions for both NO and Cl fragments as well as anisotropy parameters to assign the longer wavelength part of the electronic absorption spectrum of NOCl.

# 2. Experimental

The experiment was performed in a flow cell at room temperature keeping the total pressure of NOCl below 150 mTorr. These conditions guaranteed that only nascent NO exclusively from the primary process (1) was monitored during the time between the dissociation and fragment detection of  $\leq 8$  ns as given by the laser pulsewidth. Tunable laser radiation in the 450-520 nm region (coumarin dyes) was provided by an excimer (XeCl) pumped dye laser system (Lambda-Physik EMG 101 MSC + FL2002E) operated at 10 Hz. The rotational structure of NO(X  $^{2}\Pi$ ) vibronic bands were recorded at resolutions of  $\approx 0.2 \text{ cm}^{-1}$ while scans over selected rovibrational lines were carried out at  $0.05 \pm 0.02$  cm<sup>-1</sup> depending on the wavelength and laser power. Actual bandwidth values, required in the convolution step of the Doppler profile fitting procedure, were obtained by recording simultaneously the interference fringes of a thermally stabilized confocal etalon (Tecoptics, finesse 20-30) with each measurement. The laser beam was slightly focused by a silica lens (f = 750 mm) about 5 cm before the viewing zone of the photomultiplier tube (PMT Hamamatsu R166UH). Power levels did not exceed 1.5 mJ to avoid saturation effects or power broadening and to minimize resonant multiphoton ionization processes which are known to compete with fluorescence [23] thus introducing intensity distortions in rotational lines of the NO excitation spectrum. Fluorescence reaching the PMT was integrated in a boxcar averager (Stanford Research System SR-250) and was corrected for shot-to-shot intensity fluctuations. The experiment was controlled by a MINC 11 computer.

Nitrosyl chloride was prepared by allowing a mixture of  $Cl_2$  and NO in excess to react at about

-100 °C. The product is at thermal equilibrium with the reactants according to  $2NO + Cl_2 \rightleftharpoons$ 2NOCl. Although the chlorine and nitric oxide concentrations are <1% at room temperature, an excess of NO was left in the sample to supress the spectroscopically interfering Cl<sub>2</sub> except when probing NO(v'' = 0). In the latter case the sample was degassed at low temperature (-60 °C) prior to use.

## 3. Results

### 3.1. Spectral data

Some features of NOCl are well suited for a one-colour laser experiment (i.e.  $\lambda_{diss} = \lambda_{probe} = \lambda$ ) which warrant a single NO vibrational distribution. The absorption spectrum of NOCl is smooth thus reducing fluctuations in the NO productions to a negligible amount when scanning over a vibrational band of the fragment to obtain the rotational spectrum. The lifetime of the lower electronic states [8] is  $\approx 10^5$  times shorter (vide infra) than the laser pulsewidth of  $\approx 8$  ns. Furthermore, from previously reported data [11,12] on the NOCl photodissociation it was expected that using photolysis wavelengths > 450 nm, the NO vibrational distribution will involve only lower v'' levels.

The energetics of the experiment is depicted in fig. 1. Following one-photon absorption, NOCl dissociates and nascent NO(X  $^{2}$ II) is probed with the same laser pulse by LIF detection utilizing two-photon absorption to the A  ${}^{2}\Sigma \leftarrow X {}^{2}\Pi$  electronic band system [21,22]. The wavelengths used in the present experiment were those of two-photon transitions which originate from the v'' = 0, 1, and 2 vibrational states of NO(X  $^{2}\Pi$ ) and terminate in the v' = 0 level of NO(A  ${}^{2}\Sigma$ ). At the red edges the dissociation wavelengths were 454.6, 474.7 and 496.6 nm. The  $v' = 0 \leftarrow v'' = 3$  transition (520 nm) was not observed (even at higher photon intensities than used for the v'' = 0 and 1 levels) and the fluorescence intensity was strongly decreasing with increasing v''. The rotational distributions of the three vibrational levels examined were quite different. For v'' = 0 and v'' = 1 the



Fig. 1. Energy level diagram pertinent to the NOCl photodissociation performed by a one-colour (1+2)-photon experiment. Photon energies (nm) correspond to the red edges of the  $v' = 0 \leftarrow v'' = 0$ , 1 and 2 transitions of NO(<sup>2</sup>II). At these wavelengths the NOCl absorption is a continuum while the two-photon spectrum of NO is discrete. Note that with  $\lambda_{diss} = \lambda_{prob}$  only those vibrational levels which satisfy the condition  $E_{avl} - E_{vib}(NO) > 0$  are energetically accessible. Therefore  $v'' \ge 4$  levels were not considered.  $D_0$  is given in cm<sup>-1</sup>.

rotational distributions show population maxima at  $J_{\text{max}}^{"'} \approx 34$  and  $J_{\text{max}}^{"'} \approx 29$ , respectively. The rotationally "coldest" NO was produced in v'' = 2where  $J_{\text{max}}^{"'} \approx 11$ . The spectrum of NO(X <sup>2</sup> II, v''= 1), recorded at a resolution of  $\Delta \tilde{\nu} \approx 0.2 \text{ cm}^{-1}$ , is shown in fig. 2. Using an intracavity etalon ( $\Delta \tilde{\nu}_{\text{laser}} \approx 0.05 \text{ cm}^{-1}$ ) we obtained the spectrum displayed in fig. 3 for the O<sub>12</sub> branch of NO(X <sup>2</sup> II, v'' = 2).

### 3.2. Doppler profiles

Fast photodissociation of a gas phase molecular ensemble with polarized light results in a non-isotropic recoil velocity distribution. The center-of-



Fig. 2. Two-photon absorption LIF spectrum of the  $\tilde{A}^2 \Sigma^+ (v'=0) \leftarrow \tilde{X}^2 \Pi(v''=1)$  rovibronic band of nascent NO fragments from dissociation of NOCl.



Fig. 3. Spectrum of the  $O_{12}$  branch in the (0-2) vibronic band of nascent NO recorded with a resolution of 0.05 cm<sup>-1</sup>. The line profiles shown in the upper part of the figure were recorded with a higher S/N ratio than the spectrum.

mass normalized angular distribution of fragments is [14]

$$f(\theta) = (1/4\pi) [1 + \beta P_2(\cos \theta)], \qquad (3)$$

where  $\theta$  is the angle between the polarization direction of the photolysis light and the recoil direction.  $P_2(\cos \theta) = (3 \cos^2 \theta - 1)/2$  and  $\beta$  is the anisotropy parameter which has to be determined experimentally [24–28]. Since the present experiment is constrained to only one polarization orientation between the dissociation "d" and probe "p" laser light,  $k^p || k^d$  and  $e^p || e^d$  where k and e are the propagation and polarization vectors.

By means of Doppler spectroscopy with LIF detection one measures the recoil velocity of nonisotropically distributed fragments (3) with respect to a specific direction  $k^{p}$ . For a single recoil velocity v, eq. (3) gives an inhomogeneously broadened line profile of the form [16]

$$G(v_{k}, \chi) = (1/2v_{k})[1 + \beta P_{2}(\cos \chi) P_{2}(v_{k}/v)],$$
  

$$v_{k} \leq v;$$
  

$$G(v_{k}, \chi) = 0, \quad v_{k} > v,$$
(4)

where  $v_k$  is the projection of the fragment velocity onto the direction of the probing laser beam and  $\chi$  denotes the angle between  $e^d$  and  $k^p$ . The fragment velocity is related to the absorption frequency by  $\tilde{v} = \tilde{v}_0(1 - v/c)$  [29] where  $\tilde{v}_0$  denotes the center frequency (i.e. zero-velocity component along  $k^p$ ). Integration of eq. (4) over  $v_k$ for the one-colour experiment results in [30]

$$G(\tilde{\boldsymbol{\nu}}, \tilde{\boldsymbol{\nu}}_{0}) \approx 1 + \frac{1}{2}\beta - \frac{3}{4}\beta [\tilde{\boldsymbol{\nu}} - \tilde{\boldsymbol{\nu}}_{0}/\Delta \tilde{\boldsymbol{\nu}}_{D}]^{2},$$
  
for  $|\tilde{\boldsymbol{\nu}} - \tilde{\boldsymbol{\nu}}_{0}| \leq \Delta \tilde{\boldsymbol{\nu}}_{D}.$  (5)

Here  $\Delta \tilde{v}_D$  is the Doppler width. Figs. 4, 5 and 6 show high-resolution rotational line profiles of v'' = 0 and 1 vibrational levels of nascent NO (curves a). The smooth line in each case corresponds to the best  $\chi^2$ -fit of the experimental data to eq. (5) upon convolution with the Gaussian function

$$D(\tilde{\mathbf{v}}, \tilde{\mathbf{v}}_{con}) \sim \exp\left\{-4(\ln 2)\left[(\tilde{\mathbf{v}} - \tilde{\mathbf{v}}_{con})/\Delta \tilde{\mathbf{v}}_{con}\right]^2\right\}.$$
(6)

 $\Delta \tilde{\nu}_{con}$  refers to an effective convolution width



Fig. 4. Doppler profile of the  $P_{22}(21.5)$  rotational line in the (0-1) vibronic transition of nascent NO from photodissociation of NOCl.The dissociation energy (center frequency) corresponds to 21151 cm<sup>-1</sup>. (a) refers to the experimental and fitted (smooth line) results, (b) shows the corresponding residuals and (c) is the theoretical profile for an ideal laser resolution. The anisotropy parameter (uncorrected for v-J correlation effects) and the translational energy obtained from the best fit are  $\beta(2A'') = -0.92$  and  $E_{trans} = 3140$  cm<sup>-1</sup>, respectively.

which takes into account the laser bandwidth  $\Delta \tilde{v}_{\text{laser}}$  and the parent motion in terms of  $\Delta \tilde{v}_{\text{parent}}$ . At room temperature the parent motion amounts merely to  $\Delta \tilde{v}_{\text{parent}} = 3.4 \times 10^{-2} \text{ cm}^{-1}$ .

Since the laser wavelength, which probes the v'' = 1 level after exciting the parent into the 2A" state, turned out to be most favorable regarding line profile measurements, we studied profiles in v'' = 1 more extensively than those in v'' = 0 and 2. From v'' = 1 we selected for analysis lines with J'' = 21.5, 28.5, 29.5, 35.5 and 39.5 of the P<sub>22</sub>Q<sub>12</sub>, P<sub>11</sub>O<sub>21</sub> and S<sub>21</sub> branches in order to probe the different states of nascent NO. The combination branches have been chosen because the transition strength ratio  $S^{(2)}(P_{22})/S^{(2)}(Q_{12})$  are  $\gg 10^3$  at  $J'' \ge 5$  making the Q<sub>12</sub> contributions to the P<sub>22</sub>Q<sub>12</sub> line intensity negligible [22,31]. The  $S^{(2)}(P_{11})/V$ 

(a) <del>WWM</del>

(Ъ)

0.6

0.3

Fig. 5. Doppler profile of the  $S_{21}(21.5)$  rotational line in the (0-1) vibronic transition of nascent NO from photodissociation of NOCl at 21358 cm<sup>-1</sup>. (a), (b) and (c) are as explained in caption of fig. 4. The "dip" at the zero fragment velocity region of this profile is significantly less pronounced than that of the profile shown in fig. 4, in spite of the fact that both correspond to NO molecules having the same J'' quantum number. This difference is the result of  $J-\nu$  correlation which is manifested more strongly in  $\Delta J = \mp 2$ , 0 than in  $\Delta J = \mp 1$  transitions [16,32]. The "dip" more pronounced in P or R than in O or S profiles indicates that  $\nu$  tends to be perpendicularly oriented with respect to J. The best fit provided  $\beta(2A'') = -0.1 \pm 0.05$  (uncorrected for correlation) and  $E_{trans} = 3220$  cm<sup>-1</sup>.

0.0

Frequency Shift [cm<sup>-1</sup>]

 $S^{(2)}(O_{21})$  ratio is, at the J'' values here studied, close to 4.

The anisotropy parameter determined from  $P_{22}$ lines is, within experimental error, J'' independent and it averages to  $\beta = -0.92 \pm 0.05$  (see fig. 4). In contrast, the  $\beta$  value determined from the  $S_{21}(21.5)$  line is rather small, i.e.  $\beta = -0.15 \pm 0.05$ (see fig. 5) clearly indicating that the recoil velocity v and the angular momentum J of the NO fragment are correlated [16,32]. The anisotropy parameter determined from  $P_{11}O_{21}$  lines is expected to be free of J-v correlation effects. Both



Fig. 6. Doppler profile of the  $P_{22}(29.5)$  rotational line in the (0-0) vibronic transition of nascent NO from photodissociation of NOCl at 22139 cm<sup>-1</sup>. (a), (b) and (c) are as explained in caption of fig. 4. At this energy, NOCl is excited into superimposed parallel and perpendicular transitions giving rise to a Doppler profile composed of two components indicated in (c) (see text). The best fit (uncorrected for  $\nu - J$  correlation) provided  $\beta(2A') = 1.8$  and  $\beta(2A'') = -0.92$ , and  $E_{trans} = 4190$ cm<sup>-1</sup>.

individual transitions of this combination branch have opposite polarization behavior [16,31] and their contributions to the line intensities are very close to the weights (according to eq. (19) of ref. (16)) required to completely eliminate  $J_{-\nu}$ -type effects. The more accurate anisotropy parameter thus determined and averaged over three  $P_{11}O_{21}$ lines is  $\beta = -0.7 \pm 0.05$ .

The translational energy for the various rotational lines here studied are reported in table 1. They were calculated from

$$E_{\rm trans}(J^{\prime\prime}) = \frac{1}{2}m_{\rm NO}(c\Delta\tilde{\nu}_{\rm D}/\tilde{\nu}_{\rm laser})^2, \qquad (7)$$

where  $\Delta \tilde{\nu}_{\rm D}$  was obtained from the fitting procedure.

(c)

-0.3

- 0.6

$NO(v'', J'', F''(\Pi^-))$	ν <sub>laser</sub>	E <sub>avl</sub>	$E_{\rm rot}$ $E_{\rm vib}$ $E_{\rm el}({ m NO})$	$E_{\rm trans}({\rm NO})$	E <sub>trans</sub> (Cl) <sup>a)</sup>	$E_{\rm cl}({\rm Cl})^{\rm b)}$
$(0, 29.5, F_2(\Pi^-))$	22139	9420	1463 0 124	4190	3540	100
$(1, 39.5, F_2(\Pi^-))$	21295	8580	2572 1876 124	2140	1810	60
$(1, 28.5, F_2(\Pi^-))$	21196	8480	1344 1876 124	2830	2390	- 80
$(1, 21.5, F_2(\Pi^-))$	21151	8430	736 1876 124	3140	2650	- 100
$(1, 21.5, F_1(\Pi^-))$	21358	8640	757 1876 0	3220	2720	60
$(1, 29.5 F_1(\Pi^-))$	21229	8510	1441 1876 0	2890	2440	- 140
$(1, 35.5, F_1(\Pi^-))$	21275	8560	2091 1876 0	2510	2120	- 40

Table 1 Energy  $(cm^{-1})$  partitioned into the NO and Cl fragments in the photodissociation of NOCl

<sup>a)</sup>  $E_{\text{trans}}(\text{Cl}) = (m_{\text{NO}}/m_{\text{Cl}})E_{\text{trans}}(\text{NO}).$ 

<sup>b)</sup>  $E_{el}(Cl) = E_{avl} - E_{total}(NO) - E_{trans}(Cl)$ , where  $E_{total}(NO) = E_{rot} + E_{vib} + E_{el}(NO) + E_{trans}(NO)$ .

The experimental line profile shown in fig. 6 corresponds to the  $P_{22}(29.5)$  line of the v'' = 0 vibrational level. Because the absorptions of the 2A' and 2A'' states overlap at this wavelength (see section 4.1), they are simultaneously excited. Therefore, the line profile has been fitted to a sum of two weighted functions (5). The fitting parameters for this profile are the Doppler width,  $\Delta \tilde{\nu}_D$ , the weights w(A') and w(A''), and the anisotropy parameter  $\beta(A')$ . The best fit was obtained with  $\beta(A') = 1.8 \pm 0.1$  and  $\beta(A'') = -0.9 \pm 0.1$ , weights w(A') = 0.78 and w(A'') = 0.22, and  $E_{trans}(29.5) = 4190$  cm<sup>-1</sup>.

Three line profiles belonging to the v'' = 2 of the O<sub>12</sub> single branch are shown in the upper part of fig. 3. The  $\Delta \tilde{\nu}_D$  values of the fit for J'' = 5.5, 11.5, and 25.5 are included in the figure. The slow fragments produced under these conditions give rise to narrow Doppler linewidths making the profile analysis less accurate.

# 3.3. Spin state and $\Lambda$ -doublet populations of nascent NO

Spin-orbit interactions split the  ${}^{2}\Pi$  ground electronic state of NO into the two spin states  ${}^{2}\Pi_{1/2}$  and  ${}^{2}\Pi_{3/2}$  according to the coupling scheme  $J'' = N'' \mp \frac{1}{2}$ . The  $F_{2}(3/2)$  level lies  $\approx 124 \text{ cm}^{-1}$ above the  $F_{1}(1/2)$  one [21,22]. They are the only two electronic states energetically accessible when using the present dissociation wavelengths. Each F level is further split into an antisymmetric  $\Pi_{-}$ and a symmetric  $\Pi_{+}$  sublevel owing to interactions between rotation and orbital angular momentum. Although the spacing between the  $\Lambda$ states is too small to be resolved at our laser resolution, the four resulting sublevels,  $F_2(\Pi_{-3/2},$  $\Pi_{+3/2}$ ) and  $F_1(\Pi_{-1/2}, \Pi_{+1/2})$ , can be probed separately in different branches of the two-photon absorption spectrum. The rotational distributions of the four sublevels in the three NO vibrational levels v'' = 0, 1 and 2 examined are non-Boltzmann. In the v'' = 1 case, which allows clean excitation into the 2A'' electronic state, the Adoublet and spin-orbit state population ratios  $\Pi_{-3/2}: \Pi_{+3/2}: \Pi_{-1/2}: \Pi_{+1/2}$  were found to be 4.9:3.6:3:1 at  $J''_{max} = 29.5$ . The populations were calculated using a previously described procedure [16] with the exception that the alignment factor  $A_0^{(2)}$ , required to correct raw line intensity data, was determined by comparing line intensities of differently polarized transitions. It is noted that the  $\Pi_{-}/\Pi_{+}$  ratio is J dependent [33,34]; for  $J'' < J''_{\text{max}}$  it is smaller, for  $J'' > J''_{\text{max}}$  greater. The value taken at  $J''_{\text{max}}$  represents about the average value of the rotational distribution. A detailed account of the properties of the rotational distributions will be given in a forthcoming publication [35].

# 4. Discussion

### 4.1. Electronic absorption spectrum of NOCl

The visible and near-UV part of the absorption spectrum of NOCl is reproduced in fig. 7. Four maxima are clearly discernable at 330, 436, 472 and 610 nm which were labeled B, C, D and E, respectively [36,37]. A preliminary assignment has been given by Mitchell and Simons [7] who used arguments based on Walsh's molecular orbital rules [38] and SCF calculations. More recently, an ab initio study of the potential energy surfaces for the ground and excited singlet states of NOCl has been performed by Solgadi et al. [39]. The results pertinent to this work are included in table 2. Although the calculated transition energies are too high with respect to the observed maxima, the ordering of the lower singlet states is consistent with our findings (vide infra).

The NOCl molecule belongs to the  $C_s$  point group (see fig. 8). Electric dipole transitions from the ground state to excited electronic states,  $A' \leftarrow$ 



Fig. 7. Visible and near-UV part of the NOCl absorption spectrum as reported by Goodeve and Katz [36]. The dissociation wavelengths used in this study are indicated by arrows ( $\varepsilon$  is given in units  $\ell$  mol<sup>-1</sup> cm<sup>-1</sup>).

A' and A''  $\leftarrow$  A', are allowed by transition dipole moments  $\mu_{f,i}(\Gamma(A'))$  and  $\Gamma(A'')$ , respectively) lying in the plane or perpendicular to it. Moreover, all vibrational modes are totally symmetric and therefore do not affect the symmetry of the electronic transitions [8]. For a planar molecule which undergoes prompt dissociation from an A'' state,  $\mu$ of the parent is perpendicular to the recoil velocity of the fragment v. The anisotropy parameter  $\beta$  is then found negative with a limiting value  $\beta = -1$ . In case of an A' state dissociation,  $\mu$  and v are in the plane of the parent and  $\beta$  becomes positive with a limiting value of  $\beta = +2$  [14].

At an excitation wavelength of about 450 nm, close to the absorption valley between C and D, the fitting procedure described above rendered two P<sub>22</sub> anisotropy parameters  $\beta(A') = 1.8$  and  $\beta(A'') = -0.9$  which thus correspond to a parallel and a perpendicular transition in the parent. At this excitation wavelength two electronic states of A' and A'' symmetry are prepared. According to the fit of the line profile (see fig. 6) which, however, was performed without consideration of J-vcorrelation effects, the A'  $\leftarrow$  A' transition contributes  $\approx 78\%$  and the A''  $\leftarrow$  A' one  $\approx 22\%$  to the

State (symmetry)	Dominant electronic configuration <sup>a)</sup>	Type <sup>b)</sup>	Spectroscopic region <sup>c)</sup>	Spectral energy maximum (nm)	Estimated energy range (nm)	Calculated vertical transition energy <sup>a)</sup> (nm)	
$\overline{S_0(1 A')}$	$\dots (6a')^2 (2a'')^2 (7a')^2$	_	_		_		
$S_1(1 A'')$	$\dots (7a')(3a'') \leftarrow (7a')^2$	$(\pi^* \leftarrow n_N)$	E	610	650-560	498	
$S_2(2 A'')$	$\dots (6a')(3a'') \leftarrow (6a')^2$	$(\pi^* \leftarrow n_{Cl})$	D	472	580-410	364	
$S_{3}(2 A')$	$\dots (2a'')(3a'') \leftarrow (2a'')^2$	$(\pi^* \leftarrow n_{Cl})$	С	436	460-400	359	
S <sub>4</sub> (3 A')	$\dots (8a') \leftarrow (6a')^2$	$(\sigma^* \leftarrow n_{Cl})$	В	330	435-280	292	

Table 2								
Absorption maxima and	assignment c	of the	visible	and tl	he UV	electronic	spectrum	of NOCl

<sup>a)</sup> Solgadi et al. [39]. <sup>b)</sup> Mitchel and Simons [7]. <sup>c)</sup> Goodeve and Katz [36].

total absorption. The interpretation of two overlapping transitions is corroborated by the finding that excitation into the D maximum at 472 nm resulted in single valued anisotropy parameters of  $\beta(A'') = -0.9 \pm 0.05$  when P<sub>22</sub> lines were probed. Finally, Busch and Wilson [8] who used 347.2 nm laser excitation into the B absorption found  $\beta =$ 1.78 which implies an excited state of A' symmetry.

These results in conjunction with the ab initio calculations [39] allow assignments of the electronic states in the B, C and D absorption regions of NOCl. The D continuum arises from absorption to the 2A" antisymmetric state, the C region corresponds to the 2A' state and the B continuum with a maximum absorption at 330 nm is assigned



Fig. 8. Equilibrium configuration of nitrosyl chloride in the ground electronic state [40,41]. The a and b principal axes are indicated, c is perpendicular to the plane.

to the 3A' state. The distinct absorption band E is predicted by the calculations [39] to arise from a  $1A' \leftarrow A'$  transition. In table 2 we summarize the results and include the dominant electronic configurations involved in the transitions. Within the simple MO picture, excitation from the ground state to the 2A", 2A' and 3A' excited states promotes an electron from the 6a' to the 2a" molecular orbital localized mainly at the Cl atom. This behavior is different from the one in the S<sub>1</sub> photodissociation of HONO [15], (CH<sub>3</sub>)<sub>2</sub>N-NO [16], CH<sub>3</sub>ONO [17] and CH<sub>3</sub>SNO [19] where the excitation process is localized on the N=O group.

# 4.2. Fragment energy partitioning and channel efficiencies

The available energy for distribution among the degrees of freedom of the NO and Cl fragments is given by  $E_{avl} = h\nu + E_{int}(NOCl) - D^0$ . The internal energy  $E_{int}$  of the parent at room temperature is essentially  $E_{\rm rot} = \frac{3}{2}kT = 310$  cm<sup>-1</sup>. The dissociation energy  $D^{0}(ON-Cl)$ , which has been calculated from heats of formation of  $Cl(^{2}P_{3/2})$ , NO( ${}^{2}\Pi_{1/2}$ ) and NOCl [40], is 13030 ± 100 cm<sup>-1</sup>. Given these data  $E_{avl}$  amounts to  $\approx 9400$ , 8300, 7400, and 6300 cm<sup>-1</sup> at the four laser light energies  $(h\nu)$  employed for dissociation of NOCl and probing of the v'' = 0, 1, 2, 3 vibrational levels of NO. The energies of the NO vibrational levels are 0 (v''=0), 1876 (v''=1), 3724 (v''=2) and 5544 (v'' = 3) cm<sup>-1</sup> [41,42]. With excitation wavelengths of 455 (2A', 2A" states) and 475 nm (2A" state), corresponding to  $E_{avi}$  of 9400 and 8300 cm<sup>-1</sup>, respectively, the v''=0 and v''=1 levels

are probed as illustrated in fig. 1. They show a high rotational excitation with population distribution maxima at  $J_{\max}''(v''=0) \approx 34.5$  and  $J_{\text{max}}^{''}(v''=1) \approx 28.5$ . At 496 nm (2A' state) and  $E_{\rm avl} = 7400 {\rm ~cm^{-1}}$ , the weak fluorescence signal observed indicates that the v'' = 2 level is only weakly populated. The rotational excitation appeared downward shifted with  $J''_{\max}(v''=2) \approx$ 11.5. Finally, at a wavelength of 519.5 nm ( $E_{avl} =$ 6300 cm<sup>-1</sup>) no LIF signal of the probed v'' = 3level could be detected. Based on these observations it is very likely - an extremely inverted vibrational distribution excluded - that following a 520 nm excitation of NOCl the primary photodissociation produces NO fragments populated appreciably only in the v'' = 0 and v'' = 1 levels. This result is consistent with the findings of Grimley and Houston [11].

The energy partitioning after dissociation was examined in detail for NO fragments in selected rotational, vibrational,  $\Lambda$ -doublet and electronic states. Having measured the translational energy of these state selected fragments their energy content is completely known. The results are summarized in table 1. Apart from translational energy, the Cl fragment may also possess electronic energy depending whether it is created in the <sup>2</sup>P<sub>3/2</sub> or <sup>2</sup>P<sub>1/2</sub> state whose energies are  $E_{\rm el}(\rm Cl) = 0$  and 881 cm<sup>-1</sup>, respectively. While the translational energy of Cl is readily obtained from  $E_{\rm trans}(\rm NO)$  by linear momentum conservation,  $E_{\rm trans}(\rm Cl) = (m_{NO}/m_{Cl}) E_{\rm trans}(\rm NO)$ , the electronic energy is given by the energy conservation

$$E_{\rm el}(\rm Cl) = E_{\rm avl} - E_{\rm tot}(\rm NO) - E_{\rm trans}(\rm Cl), \qquad (8)$$

where

$$E_{\text{tot}}(\text{NO}) = E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}}(\text{NO}) + E_{\text{trans}}(\text{NO}).$$
(9)

Thus, with the exception of the distribution of the electronic energy between the  ${}^{2}P_{3/2}$  and  ${}^{2}P_{1/2}$  states of Cl, all energy data are basically available for the selected rotational lines.

In determining  $E_{\rm el}(\rm Cl)$  we relied on the accuracy of the  $E_{\rm avl}$  and  $E_{\rm trans}(\rm NO)$  values. Due to the parent internal energy,  $E_{\rm avl}$  is subject to a distri-

bution with fwhm of  $\approx 200 \text{ cm}^{-1}$ . This is mainly due to  $E_{rot}(\text{NOCl})$  as shown in fig. 3 of ref. [8] and is accounted for in the convolution procedure (see section 3.2). Furthermore, the error range in  $E_{trans}(\text{NO})$  is less than  $\pm 100 \text{ cm}^{-1}$ .  $E_{trans}(\text{NO})$ determined from P and S lines having the same J''(cf. table 1) agree with those calculated on energy conservation basis within 4% indicating that J-vcorrelation produces only small effects on the translational energy. Hence, in spite of the uncertainties, the  $E_{el}(\text{Cl})$  values given in table 1 suggest a preferential population of the lower  ${}^{2}\text{P}_{3/2}$  state of Cl, i.e.  $E_{el}(\text{Cl}) = 0 \text{ cm}^{-1}$ .

To further look into a possible selectivity of the channels leading to  ${}^{2}P_{3/2}$  and  ${}^{2}P_{1/2}$  states of Cl with respect to the  $F_{1}$  and  $F_{2}$  state production of NO, we recoursed to a correlation diagram [43]. NOCl contains 18 valence electrons and it is bent in both the ground and excited states examined here. The electronic configuration of NOCl in the ground state is  $6a'^2 2a''^2 \overline{7}a'^2$  while those of the 2A" and 2A' states are 6a'3a" and 2a"3a", respectively (cf. table 2). In a Walsh diagram, the configurations of these two excited states are  $\pi^3\pi^3$ , i.e. a core  $\pi^3$  with tight spin-orbit coupling plus three outer electrons  $\pi^3$  (Hund's case (c) [44]). Under  $(\Omega, \omega)$  coupling, where  $\Omega$  designates the total angular momentum for the core and  $\omega$  for the outer electrons, two pairs of states arise,  $\{(3/2, 3/2), (3/2, 1/2)\}$  and  $\{(1/2, 3/2), (3/2, 1/2)\}$ (1/2, 1/2), which further split to generate a total of 10 states [44,45]. Connecting these states with those of the separate NO and Cl fragments by using the appropriate non-crossing rules [43], the correlation diagram shown in fig. 9 was constructed. Furthermore, dipole-allowed parallel and perpendicular transitions resulting from the  $\Delta \Omega =$ 0 and  $\Delta \Omega = 1$  selection rules are indicated in fig. 9. According to the correlation diagram it is expected that dissociation from the 2A' and 2A" states, accessed by parallel and perpendicular transitions, correlate with both NO(X  ${}^{2}\Pi_{1/2}$ ) and NO(X  ${}^{2}\Pi_{3/2}$ ) while only the ground state  ${}^{2}P_{3/2}$  of the Cl fragment is expected if the NOCl dissociation process proceeds adiabatically.

Albeit adiabatic conditions are not always prevailing, the present result conforms with the prediction of the correlation diagram. Therefore, we



Fig. 9. Correlation diagram for the NOCl  $\rightarrow$  NO(<sup>2</sup>II) + Cl(<sup>2</sup>P) dissociation system assuming a  $\pi^{3}\pi^{3}$  electronic configuration for the excited states of NOCl. Parallel and perpendicular transitions are denoted by full and dashed arrows, respectively.

may conclude that NOCl excited into the D state at 475 nm results in photodissociation proceeding mainly adiabatically and producing preferentially correlated fragments. Though this was examined only for the antisymmetric  $\Lambda$ -state ( $\Pi_{-}$ ) in both F levels of NO, an extension to the  $\Pi_{+}$  component is allowed since no symmetry restrictions due to the NO  $\Lambda$ -doublet is involved in this correlation. The 475 nm photolysis with LIF probing of the v'' = 1 level generates a sublevel population distribution of NO given by the  $\Lambda$ -doublet and spin-orbit state population ratios  $\Pi_{-3/2}$ :  $\Pi_{+3/2}$ :  $\Pi_{-1/2}$ :  $\Pi_{+1/2}$  of 4.9: 3.6: 3.0: 1.0 measured at the maximum of the rotational population  $J''_{max}(v'' = 1) = 28.5$ . These findings provide now the following picture of the spin-state channel

efficiencies for NO(v'' = 1) fragments when NOCl is excited into the 2A'' state at 475 nm:

$$NOCl^{*}(475 \text{ nm}) \xrightarrow{\approx 39\%} NO(^{2}\Pi_{-3/2}) + Cl(^{2}P_{3/2})$$
  
$$\xrightarrow{\approx 29\%} NO(^{2}\Pi_{+3/2}) + Cl(^{2}P_{3/2})$$
  
$$\xrightarrow{\approx 24\%} NO(^{2}\Pi_{-1/2}) + Cl(^{2}P_{3/2})$$
  
$$\xrightarrow{\approx 8\%} NO(^{2}\Pi_{+1/2}) + Cl(^{2}P_{3/2}).$$
  
(10)

The preferred population of the antisymmetric  $\Lambda$ -doublet state in the  $F_1$  and  $F_2$  spin states parallels the behaviour observed in the  $S_1$  photodissociation of CH<sub>3</sub>ONO [17] and implies a fast and planar dissociation process.

#### 5. Conclusions

The photofragmentation of NOCl(2A', 2A'')  $\rightarrow$  $NO(^{2}\Pi) + Cl(^{2}P)$  at excitation wavelengths of 455 and 475 nm has been studied under collision-free conditions. With an available energy of 9500 to  $7300 \text{ cm}^{-1}$  the NO fragment carries a high degree of rotational excitation and the translational energy of individual lines is J''-dependent. Appreciable vibrational population is confined to states with  $v'' \leq 2$ . When probing selected NO fragment states  $(v'', J'', F'', \Lambda)$  by measuring the translational energy, the energy partitioning into the fragments is obtained which revealed that, irrespective of the spin state  $\Pi_{1/2}$  or  $\Pi_{3/2}$  of NO, the Cl fragment is preferentially produced in the  ${}^{2}P_{3/2}$ state. This selectivity is consistent with symmetry correlations following electronic excitation into the 2A' and 2A" states of NOCl.

According to the measured  $\beta$  values and in conjunction with a previous ab initio calculation the transitions in the spectral regions E, D, C and B correspond to  $S_1(1A'') \leftarrow S_0(1A')$ ,  $S_2(2A'') \leftarrow S_0(1A')$ ,  $S_3(2A') \leftarrow S_0(1A')$  and  $S_4(3A') \leftarrow S_0(1A')$ , respectively.

#### Note added in proof

In order to avoid confusion a new nomenclature will be proposed (M.H. Alexander et al.) for  $\Lambda$ -doublet levels of linear molecules with non-zero electronic angular momentum:  $\Lambda(A')$  and  $\Lambda(A'')$ . These levels correspond to  $\Pi_+$  and  $\Pi_-$ , respectively, in the present paper.

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