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# The 355 nm Photolysis of Methyl Nitrite

C. G. ATKINS and G. HANCOCK

*Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, UK*

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Single photon laser induced fluorescence (LIF) has been used to study the NO fragment produced in its ground electronic state from the 355 nm photolysis of CH<sub>3</sub>ONO. Populations of rotational, vibrational, spin-orbit and lambda doublet components have been measured. The results are in broad agreement with previous two photon LIF studies, and confirm the dynamics of the process in which the NO fragment departs from an essentially planar CONO framework with non-statistical energy partitioning in the internal states of the products.

KEY WORDS: Photodissociation, laser induced fluorescence, CH<sub>3</sub>ONO, NO.

## INTRODUCTION

The information that is carried by the fragments of a photodissociation event can be divided into two types: first, scalar information, an example of which is the distribution of molecular photofragments' internal energies, and secondly vector information, such as the alignment of the photofragments' angular momenta with respect to the framework of the dissociating molecule. The second of these, the study of "dynamical stereochemistry" in photodissociation has recently become a topic of considerable interest.<sup>1</sup> The experimental technique which has made the largest impact in this field is that of tunable laser induced fluorescence (LIF) detection of the fragments, and this has enabled a variety of vector correlations to be measured in diatomic photofragments such as OH(*X*<sup>2</sup>Π),<sup>2,3</sup> NO(*X*<sup>2</sup>Π),<sup>4-9</sup> CN(*X*<sup>2</sup>Σ<sup>+</sup>)<sup>10</sup> and CO(*X*<sup>1</sup>Σ<sup>+</sup>).<sup>11</sup>

This report is of LIF measurements of scalar and vector properties of the NO( $X^2\Pi$ ) product of the 355 nm photodissociation of methyl nitrite. An extensive compilation of data now exists on the dynamics of the photolysis of RONO compounds<sup>9</sup> with  $R = H^2$ ,  $CH_3$ ,<sup>4,6,7,12-16</sup>  $C_2H_5$ <sup>17</sup> and  $(CH_3)_3C$ ,<sup>8</sup> in their first absorption bands in the near uv, with results derived either from photofragment spectroscopy<sup>16,17</sup> or from LIF of the NO primary photofragment.  $CH_3ONO$  has been studied by both methods, with the LIF measurements on NO carried out in all cases<sup>4,6,7,12-16</sup> by two photon excitation of the ( $A^2\Sigma^+ - X^2\Pi$ ) transition at wavelengths around 450 nm. Results have been presented for photolysis at 355 nm in a series of papers by Lahmani and co-workers<sup>4,12,13</sup> and both they<sup>13</sup> and the group of Huber and co-workers<sup>6,7,15</sup> have reported photolyses at nearby wavelengths corresponding to peaks in the structured  $\pi^* \leftarrow n$  transition. In the present study we have detected NO by single photon LIF of the same transition between 225–250 nm, and we present results on the rotational, vibrational and spin-orbit state distributions and on the electronic orbital alignment as revealed by the lambda doublet populations. Our results are generally in good agreement with previous two photon LIF studies,<sup>4,6,7,12,13,15</sup> confirming the non-statistical distributions of energy in the internal degrees of freedom of the NO product, and that the molecule dissociates from an essentially planar excited state.

## EXPERIMENTAL

The photodissociation and probe beams required were both derived from a  $Nd^{3+}$ -YAG laser (JK Lasers System 2000). The fundamental output (1.06  $\mu m$ ) was first frequency doubled in KDP. Part of this radiation was used to pump a dye laser, and part mixed with the residual 1.06  $\mu m$  output to produce the third harmonic photolysis beam at 355 nm. This wavelength lies just to the red of a peak in the  $CH_3ONO \tilde{A}^1A'' - \tilde{X}^1A'$  ( $\pi^* \leftarrow n$ ) transition corresponding to excitation of two quanta in the N=O stretch of the parent molecule.<sup>9,12</sup> The dye laser output was frequently doubled and anti-Stokes stimulated Raman shifted in  $H_2$  to produce the wavelengths needed to detect NO by single photon LIF of the  $A^2\Sigma^+ (\nu' = 0) \leftarrow X^2\Pi (\nu'' = 0-3)$  transitions. For the (0,0) and (0,2) bands the wavelengths used,  $\sim 225$  and 247 nm, were from the second and first anti-Stokes transitions of doubled

Rhodamine 6G dye laser output, and for the (0,1) and (0,3) bands the wavelength regions were 234 and 259 nm from the corresponding transitions of doubled Rhodamine B dye output. The tuning range of the stimulated Raman output was restricted by the laser power available, such that not all rotational transitions within all bands could be recorded, and the effect of this is discussed below.

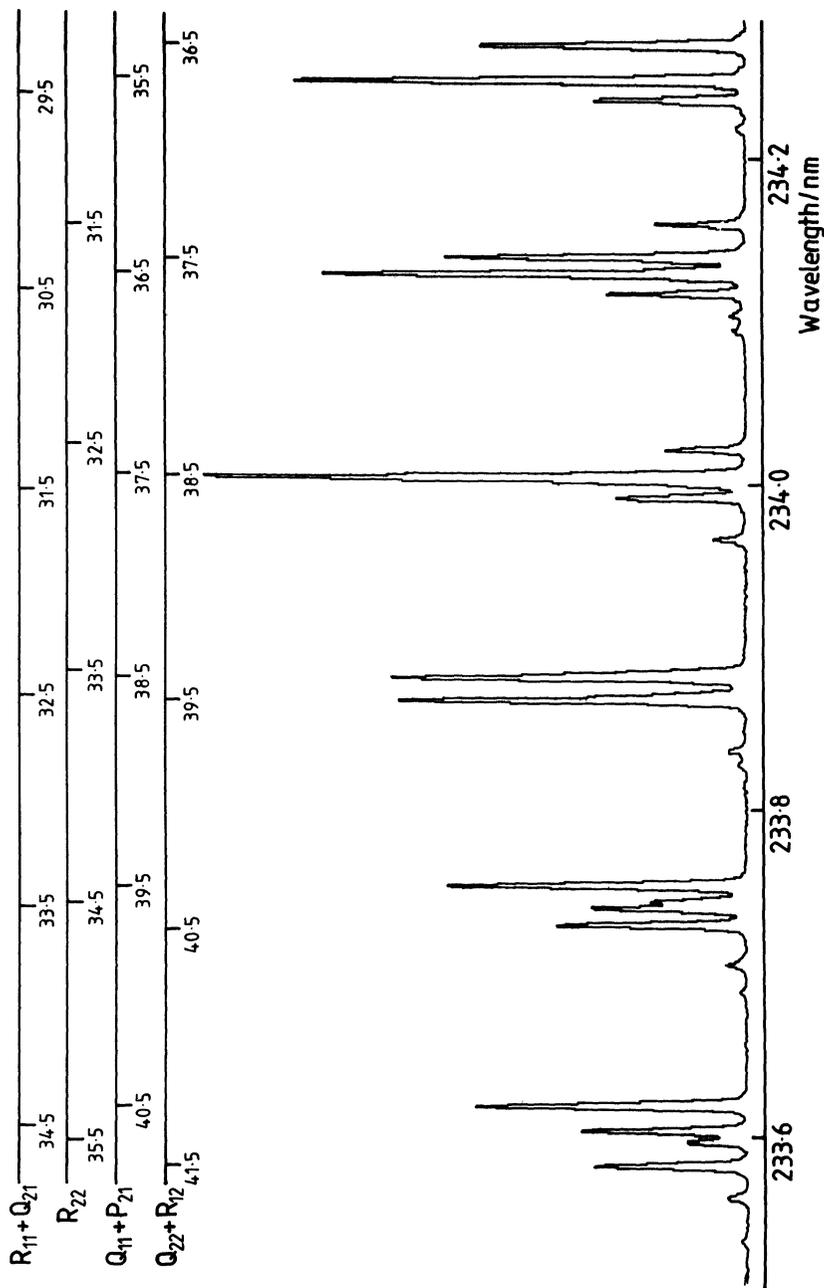
The 335 nm beam (>90% horizontally polarised, diameter 10 mm, energy 20 mJ/pulse) and the anti-Stokes probe beam (80% vertically polarised, diameter ~3 mm, energy <10  $\mu$ J/pulse) crossed in a horizontal plane at an angle of 60° inside a stainless steel hexagonal reaction vessel fitted with Brewster angle windows. Fluorescence was detected perpendicular to the horizontal plane with a solar blind photomultiplier (EMI GEMCON G-26E314LF) observing the (0,0) emission near 225 nm through an interference filter. The fluorescence signal was amplified, digitised (Biomation 8100) and averaged for a preset number of shots (normally 20) at each wavelength. The signal was measured to be linear with both photolysis and probe laser energies, showing that saturation was not occurring in either step. Probe laser energies were monitored with a uv photodiode and used to normalise the fluorescence signals.

Methyl nitrite was prepared by reaction of octyl nitrite and excess methanol,<sup>18</sup> purified by distillation and freeze thaw cycling, and stored in darkened glass bulbs to prevent photochemical decomposition. Purity was established by infrared absorption and mass spectrometry. The gas was flowed through the reaction vessel at a pressure of 40 mTorr (measured by a capacitance manometer) to ensure that photolysis products did not contaminate the sample. Despite this, LIF from thermalised NO ( $v'' = 0$ ) was always present, but did not significantly affect the measured population of that vibrational level. The pressure was such that during the time of coincidence of the laser pulses (10 ns), less than 1% of the molecules would undergo a gas kinetic collision, ensuring that the measured distributions were nascent.

## RESULTS AND DISCUSSION

### (a) Analyses of spectra

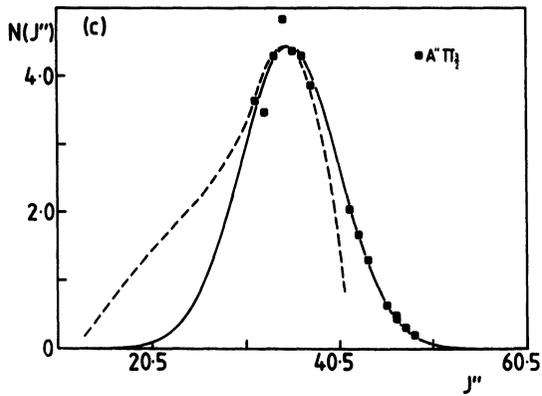
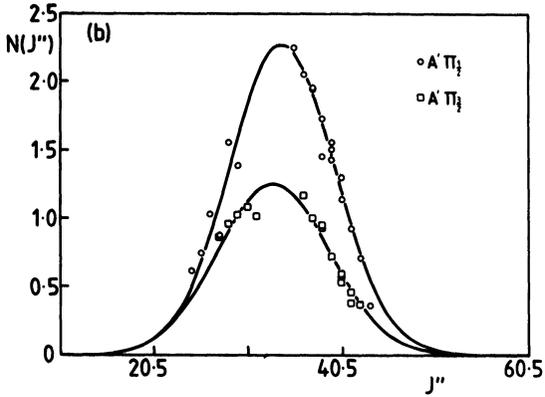
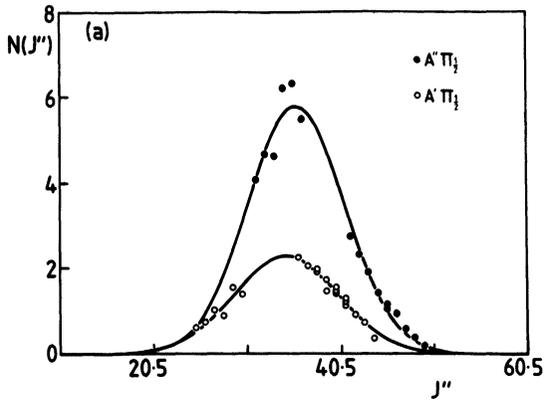
Figure 1 shows part of the observed excitation spectrum of the NO photofragment produced in  $v'' = 1$ . The width of individual isolated



**Figure 1** LIF excitation spectrum of part of the (0,1) band of  $\text{NO}(A^2\Sigma^+ - X^2\Pi)$  produced following 355 nm photolysis of  $\text{CH}_3\text{ONO}$ . Assignments are calculated from the spectroscopic data of Refs. 19 and 20.

features,  $\sim 1 \text{ cm}^{-1}$ , is predominantly due to the laser bandwidth, and is larger than the linewidth expected from Doppler broadening due to translational energy release.<sup>6,12</sup> No marked variations in lineshapes were observed for the various transitions probed; peak heights were thus used for subsequent data analysis. Transitions were identified by refining the spectroscopic constants for NO using the ground state term values of Amiot *et al.*<sup>19</sup> and data on the upper state derived from these values together with the  $A-X$  line positions (for  $J < 30.5$ ) recorded by Engleman *et al.*<sup>20</sup> The resultant calculated line positions agreed well with the experimental values, as shown on Figure 1.

In order to extract populations from observed line intensities, allowance must be made for alignment of the photofragment's angular momentum  $J$  relative to the vector properties of the photodissociating beam.<sup>21</sup> This is usually described in terms of the alignment parameter  $A_0^{(2)} = 2 \langle P_2(\cos \theta) \rangle$ , where  $P_2$  is the second order Legendre polynomial in  $\cos \theta$ ,  $\theta$  being the angle between  $J$  and the space fixed axis of polarisation of the dissociating beam,  $\epsilon$ .  $A_0^{(2)}$  thus represents the quadrupole moment of the angular distribution of  $J$  vectors. For photodissociation it takes values between 0.8 and  $-1$ , with the positive and negative limits implying preferential alignment of  $J$  parallel and perpendicular to  $\epsilon$  respectively. Dynamical information is thus gained, as the molecules which are preferentially dissociated have  $\mu$ , their transition dipole moments (linked to the molecular framework) parallel to  $\epsilon$ . Unfortunately in the present study the NO fragment was only observed with a single arrangement of the relative polarisations of the laser beams, and thus  $A_0^{(2)}$  could not be measured directly. We assume a value of  $A_0^{(2)} = 0.5$ , as determined by Lahmani *et al.*<sup>4</sup> for the  $\nu'' = 1$ ,  $20.5 \leq J'' \leq 40.5$  levels of NO formed by 355 nm photolysis of  $\text{CH}_3\text{ONO}$ , for all the observations reported in this paper. This value, close to the positive limit for photodissociation, implies that NO fragments depart with  $J$  preferentially parallel to  $\mu$ . As the  $\text{CH}_3\text{ONO } ^1A'' \leftarrow ^1A'$  transition has  $\mu$  perpendicular to the CONO skeletal frame, the observed value is consistent with dissociation taking place predominantly in this plane.<sup>4,6,9</sup> However, Brühlmann *et al.*<sup>7</sup> have recently found that for photolysis of  $\text{CH}_3\text{ONO}$  at a variety of wavelengths (including 350.8 nm, at the peak corresponding to  $\nu = 2$  in the N=O stretch), the alignment parameter decreases with increasing  $\nu''$  in NO (for example at 350.8 nm  $A_0^{(2)} = 0.48$  for  $\nu'' = 1$ , decreasing to 0.28 for  $\nu'' = 3$ ). The consequences of this observation will be discussed below.



A value of  $A_0^{(2)} = 0.5$  means that in the high  $J$  limit (which is assumed to apply in the present observations of  $J \geq 20.5$ ) our experimental arrangement of laser beams' polarisations and directions will lead to fluorescence following excitation of a given  $\text{NO}(X)$  quantum level in a  $P$  or  $R$  branch transition being 1.57 times as intense as that following  $Q$  branch excitation.<sup>21</sup> Experimental intensities were corrected for this factor, and quantum state populations extracted using calculated values for the Hönl-London factors for the transitions.

### (b) Rotational state distributions

The rotational levels of the  $^2\Pi$  ground state of  $\text{NO}$  can be divided into four groups, according to the combination of spin orbit and lambda doublet components. The spin orbit component  $\Omega$  takes the values  $\frac{1}{2}$  or  $\frac{3}{2}$ : for the lambda doublet component we follow the recent recommendations of Alexander *et al.*<sup>22</sup> and designate them as  $A'$  or  $A''$  according to whether, in the high  $J$  limit, the electronic wavefunction is symmetric or antisymmetric with respect to reflection in the plane of rotation of the diatomic molecule.  $A'$  and  $A''$  components have been designated as  $\Pi^+$  and  $\Pi^-$  in previous studies of  $\text{CH}_3\text{ONO}$  photolysis;<sup>4,6,7,15</sup> for the  $\text{NO}(X^2\Pi)$  state they correspond to the  $p\pi$  orbital of  $\text{NO}$  lying parallel or perpendicular to the plane of rotation respectively. Rotational distributions for each of these four groups were found to be well represented by Gaussian functions of  $J''$  for all vibrational levels measured, and are shown in Figure 2 for  $v'' = 1$ , the level for which the most complete set of results was available. For all groups, populations peak close to the same  $J''$  and show a propensity for  $A''$  over  $A'$  for both spin-orbit components (shown in Figure 2a for the  $\Pi_{1/2}$  level) and a propensity for  $\Pi_{3/2}$  over  $\Pi_{1/2}$  for both lambda doublets (shown in Figure 2b for the  $A'$  data). Figure 2c compares our result for the  $A''\Pi_{3/2}$  group with the only published data for  $v'' = 1$

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**Figure 2** Populations of the nascent  $\text{NO}(v'' = 1)$  fragment produced by 355 nm photolysis of  $\text{CH}_3\text{ONO}$ . Figure 2a compares populations for the two lambda doublets of the  $\Pi_{1/2}$  state,  $A''$  (filled circles) and  $A'$  (open circles); Figure 2b compares populations of the two spin orbit states for the  $A'$  lambda doublet,  $\Pi_{1/2}$  (open circles) and  $\Pi_{3/2}$  (open squares). Solid curves are Gaussian fits to the observed level populations. In Figure 2c the populations of the  $A''\Pi_{3/2}$  levels (filled squares and solid curve) are compared with populations for the same component reported by Lahmani *et al.* (Ref. 12, dashed line). Although the absolute values of  $N(J'')$  are arbitrary, the abscissae of Figures 2a, b and c are scaled to reflect the relative populations in all the sets of levels.

formed by 355 nm photolysis, that of Lahmani *et al.*,<sup>12</sup> which was measured by two photon excitation. The dashed line of Figure 2c shows the latter distribution for the  $A''\Pi_{3/2}$  group probed via the  $O_{12}$  branch, and which was indistinguishable from the  $A'\Pi_{1/2}$  group (probed by the  $O_{22} + P_{12}$  branch): no correction for fragment alignment appears to have been made in this early report, as later work from the same group shows clear lambda doublet propensity for the  $A''$  component.<sup>13</sup> Where the two sets of data in Figure 2c overlap the agreement is reasonable, but present results show more population in high  $J''$  levels and, at least in the cases shown in Figures 2a and 2b where the populations were observed over a wider range of  $J''$  than in Figure 2c, a more symmetric distribution. Brühlmann *et al.*<sup>6,7</sup> have measured Gaussian distributions with similar discrepancies at low and high  $J''$  with the data of Lahmani's group<sup>12,13</sup> and have suggested that lack of allowance for alignment effects or for rotational quenching in the latter experiments (which were carried out at pressures between 0.1–0.7 Torr) could be responsible.

Data for the other vibrational levels showed similar Gaussian behaviour, with small upward shifts in the peak  $J''$  values with decreasing  $v''$ , e.g. for  $v'' = 2$  and 0,  $J''_{\max} = 30.5$  and 36.5 respectively, very similar to the trends observed in other studies.<sup>6,7,12,13</sup> For  $v'' = 0$  a contribution from thermal (300K) NO was always present, and was subtracted from the observed line intensities. This effect was only significant ( $>10\%$ ) at  $J'' \leq 26.5$ , and at this value the population from photolysis was less than 20% of its peak value at 36.5. For  $v'' = 3$  only a limited amount of data was available for each group of levels due to the tuning range of the laser. A Gaussian fit to these data was made constrained to a value of  $J''_{\max} = 28.5$ , the value reported for  $v'' = 3$  by Benoist d'Azy *et al.*<sup>13</sup>

### (c) Lambda doublet ratios

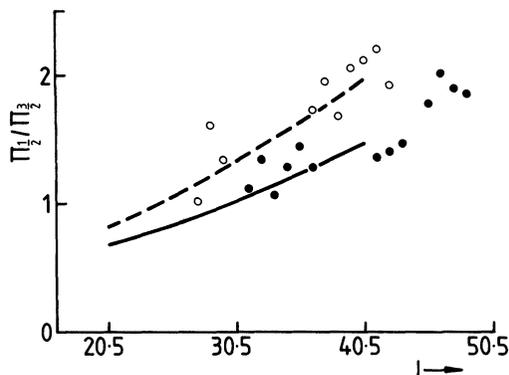
The propensity of  $A''$  over  $A'$  has been found in previous studies of the NO fragment from  $\text{CH}_3\text{ONO}$ <sup>4,6,7,15</sup> and other nitrites<sup>5,8</sup> and is straightforwardly explained<sup>4</sup> in terms of the symmetry of the upper state ( $A''$ ) and the essentially planar nature of the CONO framework in the dissociation process, so that the NO fragment departs with its  $p\pi$  orbital preferentially perpendicular to its plane of rotation. This explanation is true only for Hund's case (b) diatomic fragments, and

the degree of electronic alignment is expected to increase with  $J''$  as NO approaches this limit.<sup>4,23</sup> Our data confirm this trend, as can be seen from the fitted Gaussian curves in Figure 2a, but this figure also shows that the ratios  $A''/A'$  could be explicitly measured for a limited number of  $J''$  values. For both  $\Omega = 1/2$  and  $3/2$  these ratios at high  $J''$  were found to be considerably larger than those measured for 355 nm photolysis by Lahmani *et al.*,<sup>4</sup> and closer to the limit expected for complete electron alignment.<sup>23</sup> For example, at  $J'' = 36.5$ , the present results show  $A''/A' = 2.7$  for  $\Pi_{1/2}$ , 3.7 for  $\Pi_{3/2}$  compared to values of 2.0 and 2.7 respectively reported by Lahmani *et al.*,<sup>4</sup> and a complete alignment value of 5.8.<sup>23</sup> The reason for the differences in the two sets of experimental results is not clear. Part of the explanation could lie in the value of  $A_0^{(2)} = 0.5$  used in the present study to correct for polarisation effects. As the  $A''$  and  $A'$  levels are probed by the strong  $Q$  and  $P, R$  transitions respectively, the measured lambda doublet ratio will depend upon the alignment weighting factor used (1.57) and thus upon the value of  $A_0^{(2)}$ . This factor is not, for our experimental geometry, a strong function of  $A_0^{(2)}$ . Reducing the  $A_0^{(2)}$  value from 0.5 to 0.3 makes only a 15% reduction in the  $A''/A'$  ratios, a change insufficient to explain the discrepancies in the two sets of experiments and which would represent an extreme lowering of the alignment parameter from the values observed for  $\text{CH}_3\text{ONO}$  at a variety of wavelengths.<sup>4,6,7</sup>

Previously experimentally observed<sup>4,6</sup>  $A''/A'$  ratios decrease to values close to unity for  $J'' \sim 20.5$ . Our present data for  $v'' = 2$  and 3 encompass a range of low  $J''$  between 14.5 and 20.5 where these ratios could be measured, and the values, between 1.1 and 1.5, confirm this trend.

#### (d) Spin-orbit ratios

As Figure 2b shows, the  $\Pi_{1/2}$  and  $\Pi_{3/2}$  levels of NO are not equally populated for  $v'' = 1$ , and the differences are most marked at high values of  $J''$ . Figure 3 shows the  $\Pi_{1/2}/\Pi_{3/2}$  ratio for individual value of  $J''$  where both components were measured, showing that the ratio increases with  $J''$  and is larger for the  $A'$  levels than for the  $A''$ . The Figure also shows good agreement with the two photon results of Lahmani *et al.*<sup>4</sup> The ratios were measured in the present study for lines whose polarisation properties are almost identical (e.g. ( $Q_{11} +$



**Figure 3** Ratios of the spin orbit populations in the  $\text{NO}(\nu'' = 1)$  product of the 355 nm photolysis of  $\text{CH}_3\text{ONO}$ . The filled circles show the ratios for the  $A''$  components, the open circles for the  $A'$  components. The solid and dashed lines show the ratios measured by Lahmani *et al.*<sup>14</sup> for the  $A''$  and  $A'$  components respectively, indicating excellent agreement for the range of  $J''$  for which these studies overlap.

$P_{21})/(Q_{22} + R_{12})$  for the  $A''$  levels) and thus they will be uninfluenced by either the assumed values of  $A_0^{(2)}$  or by the relative polarisation of the lasers.

Brühlmann *et al.*<sup>15</sup> have recently reported  $\Pi_{1/2}/\Pi_{3/2}$  ratios for NO formed from  $\text{CH}_3\text{ONO}$  photolyses at wavelengths corresponding to the peaks in the  $S_1$  absorption spectrum. When the quantum number of the product NO vibrational level formed ( $\nu''$ ) is equal to that for the  $\text{N}=\text{O}$  stretch initially excited in the  $\pi^* - n$  progression,  $\nu$ , then statistical values of the ratio are seen; when  $\nu > \nu''$  then the  $\Pi_{1/2}$  state predominates. The observations on  $\nu'' = 1$  after photodissociation at 355 nm (near the peak corresponding to  $\nu = 2$ ) agree with these results. Although the reasons for the  $\Pi_{1/2}$  propensity are not clear, the differences in behaviour between  $\nu = \nu''$  and  $\nu > \nu''$  appear to reflect the different dissociation dynamics when the initially excited vibrational level in the parent molecule decays adiabatically ( $\nu = \nu''$ ) or non adiabatically ( $\nu > \nu''$ ) into the NO product state.<sup>15,24</sup>

### (e) Vibrational populations

Populations for several  $A''\Pi_{3/2}$  rotational levels near the maxima of the  $\nu'' = 0, 1, 2$  and 3 levels were recorded sequentially, all by excitation to the  $\nu' = 0$  upper level. Relative  $\nu''$  populations were deduced by allowing for variations of the absorption cross sections for the  $(0 - \nu'')$

**Table I** Vibrational populations of the  $A''\Pi_{3/2}$  component of  $\text{NO}(v'')$  produced by 355 nm photolysis of  $\text{CH}_3\text{OHO}$ , compared with the data of Benoist d'Azy *et al.*<sup>13</sup> Errors quoted are explained in the text.

$v''$	Present results	Ref. 13
0	$0.38 \pm 0.06$	0.25
1	$0.52 \pm 0.08$	0.50
2	$0.09 \pm 0.015$	0.20
3	$0.009 \pm 0.0015$	0.05

transitions, and for the dye laser energy variations at the different wavelengths, and by integration over the previously determined Gaussian rotational distributions. The absorption cross sections depend on both the Franck-Condon factors and the variations of electronic transition moment with  $v''$ . For NO the latter effect is considerable (an increase of greater than 2 between the 0,0 and 0,3 bands) and experimental values of this variation<sup>25</sup> were used in the calculation of the vibrational populations.

Table I shows the results, together with those of Benoist D'Azy *et al.*<sup>13</sup> for 355 nm photolysis. The agreement is good, considering the large experimental errors which can arise from LIF determinations involving marked changes in dye laser wavelengths. Errors quoted in Table I are estimates of the experimental uncertainties [ $2\sigma = 16\%$ ] obtained from measurements on different occasions. Within each set of measurements the statistical variations of the fits of the intensities to the previously determined rotational distributions were far smaller.  $Q_{22} + R_{12}$  branch lines were used in these experiments for  $v'' = 0$  and 1,  $P_{12}$  lines for  $v'' = 2$  and 3, and so for the latter two vibrational levels different corrections for alignment needed to be made from those for the former two, again using the value  $A_0^{(2)} = 0.5$ . A smaller value of  $A_0^{(2)}$  would tend to increase the  $v'' = 2$  and 3 populations relative to those of  $v'' = 0$  and 1, but, as in the lambda doublet experiments, the effect is likely to be less than 15%.

Benoist D'Azy *et al.*<sup>13</sup> used the same ( $0 - v''$ ) bands in their measurements, but their method of extraction of ground state populations appears to consider only Franck-Condon factors in allowing for the relative strengths of the vibrational transitions. Allowance for the increase in electronic transition moment with  $v''$  would decrease their

$\nu'' = 2$  and 3 populations by factors of 1.3 and 1.7 respectively, bringing them into closer agreement with the present values.

Hennig *et al.*<sup>24</sup> have recently shown that excitation of  $\text{CH}_3\text{ONO}$  in the  $\nu$ th level of the NO stretch should lead to predominant formation of NO in level  $\nu'' = (\nu - 1)$  by non-adiabatic predissociation. Good agreement between their theoretical predictions and the experimental results of Benoist D'Azy *et al.*<sup>13</sup> was found for photolyses at wavelengths corresponding to specific  $\nu$  levels, i.e. at the peaks of the  $\text{CH}_3\text{ONO}$  spectrum. At 355 nm excitation is predominantly to  $\nu = 2$  but with a contribution from  $\nu = 1$ : the present vibrational populations are seen to be in agreement with the predictions of this model.

## CONCLUSIONS

Two major points have emerged from the present study. First, general agreement has been found between the present results carried out with single photon LIF and those of previous studies on  $\text{CH}_3\text{ONO}$  in which two photon excitation was used,<sup>4,6,7,12,13,15</sup> giving confidence to the analyses of polarised fluorescence excited in these two different ways. The major differences are in the lambda doublet ratios at high  $J''$ , measured to be closer in the present study to the limiting values<sup>23</sup> than those measured by Lahmani's group.<sup>4</sup> Although the assumed value of  $A_0^{(2)}$  will affect these ratios, variations of  $A_0^{(2)}$  are not sufficient to explain these discrepancies, and a more complete investigation of the one photon excitation case with the standard variations of pump and probe relative polarisations would be needed to check this point.

Secondly, the results are in agreement with what is emerging as a common model for vector properties of the dissociation of alkyl nitrites in their first absorption bands.<sup>9</sup> Following absorption by a transition moment  $\mu$  perpendicular to the CONO planar framework, the NO fragment appears with its angular momentum vector predominantly parallel to  $\mu$ , i.e. an essentially planar fragmentation process, confirmed experimentally by rotational anisotropy factors  $A_0^{(2)}$ , lambda doublet ratios, and correlations between relative velocity and total angular momentum vectors.<sup>4,6-8,16,17</sup> The scalar properties of the dissociation process, namely the partitioning of energy in the degrees of freedom of the products, have in part been recently explained by theoretical calculations on an ab-initio potential energy surface.<sup>24</sup>

Vibrational energy distributions and their change with photolysis wavelength show details of the vibrational predissociation in the parent molecule: although it has been noted<sup>6</sup> that the Gaussian rotational distributions are of the form expected from the rotational reflection principle,<sup>26</sup> detailed predictions of the rotational energy release have so far not been attempted.

### Acknowledgement

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