

Available online at www.sciencedirect.com



Chemical Physics Letters 368 (2003) 568-573



www.elsevier.com/locate/cplett

# Photodissociation dynamics of ClN<sub>3</sub> at 203 nm: the NCl $(a^{1}\Delta/X^{3}\Sigma^{-})$ product branching ratio

N. Hansen<sup>a</sup>, A.M. Wodtke<sup>a,\*</sup>, A.V. Komissarov<sup>b</sup>, M.C. Heaven<sup>b</sup>

<sup>a</sup> Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106, USA <sup>b</sup> Department of Chemistry, Emory University, Atlanta, GA 30322, USA

Received 13 August 2002; in final form 14 November 2002

#### Abstract

Velocity map imaging was applied to study the photodissociation dynamics of ClN<sub>3</sub> near 203 nm under collision free conditions. Images of state-selected N<sub>2</sub>(X<sup>1</sup> $\Sigma_g^+$ ,  $\nu = 0, J = 68$ ) characterize the internal energy of the photofragments and reveal the energetics of reactions (\*) and (\*\*):

$$\operatorname{ClN}_3 \to \operatorname{N}_2(\operatorname{X}^1\Sigma_g^+) + \operatorname{NCl}(a^1\Delta) \quad \Delta E = +0.21 \pm 0.07 \text{ eV}$$
<sup>(\*)</sup>

$$\operatorname{ClN}_3 \to \operatorname{N}_2(\operatorname{X}^1\Sigma^+_{\sigma}) + \operatorname{NCl}(\operatorname{X}^3\Sigma^-) \quad \Delta E = -0.93 \pm 0.08 \text{ eV}$$
(\*\*)

These experiments provide the most accurate thermodynamics for these reactions presently available and are in good agreement with other recent experimental results. Photofragment angular distributions indicate that  $\tilde{B}^1A' \leftarrow \tilde{X}^1A'$  excitation is the most important pathway to photoproducts. Branching measurements between the dominant spin-allowed channel (1) and the spin-forbidden channel (2) showed  $a^1\Delta/X^3\Sigma^- = 0.78/0.22$ . © 2002 Elsevier Science B.V. All rights reserved.

#### 1. Introduction

Recent interest in photochemical production of  $NCl(a^1\Delta)$  derives from demonstrations that this metastable can be used as an effective energy carrier in chemical iodine lasers [1–3]. Furthermore, photolysis of  $ClN_3$  has been used as a convenient source of  $NCl(a^1\Delta)$  for kinetic measurements [4–8] that are required for further development of this chemical laser system. One of the key sets of nee-

ded measurements are NCl( $a^{1}\Delta$ ) removal rate constants. If the rate constants are measured under pseudo-first order conditions, photolysis of ClN<sub>3</sub> can be used without knowledge of the absolute initial concentration, [NCl(a)]<sub>0</sub>. However, for rate constants that can only be measured under second-order conditions such as the important self-annihilation reaction, knowledge of [NCl(a)]<sub>0</sub> is essential. In this case, [NCl(a)]<sub>0</sub> may be measured or deduced from the fraction of ClN<sub>3</sub> removed by photolysis as long as the quantum yield for formation of NCl( $a^{1}\Delta$ ) is known.

Unfortunately the present understanding of the primary photochemical dynamics of chlorine azide

Corresponding author. Fax: 1-805-893-4120.

E-mail address: wodtke@chem.ucsb.edu (A.M. Wodtke).

<sup>0009-2614/02/\$ -</sup> see front matter @ 2002 Elsevier Science B.V. All rights reserved. PII: S0009-2614(02)01886-9

is incomplete. The photolysis of ClN<sub>3</sub> by near UV radiation has been examined by Coombe and coworkers [4,9–12], Henshaw et al. [5], and Komissarov et al. [6,7]. In these studies photodissociation was accomplished using pulsed excimer lasers operating at 248 and 193 nm. At these wavelengths, excitation within both the  $\tilde{A}^1A'' \leftarrow \tilde{X}^1A'$  and  $\tilde{B}^1A' \leftarrow \tilde{X}^1A'$  systems is possible, yet the relative importance of these absorption systems is not known. At both wavelengths the dominant dissociation channel is believed to be the spin-allowed channel (1)

$$\operatorname{ClN}_3 + hv \to \operatorname{NCl}(a^1\Delta) + \operatorname{N}_2(\operatorname{X}^1\Sigma_g^+)$$
 (1)

Production of NCl( $X^{3}\Sigma^{-}$ ) is possible via spin-forbidden channel (2)

$$\operatorname{ClN}_3 + h\nu \to \operatorname{NCl}(X^3\Sigma^-) + \operatorname{N}_2(X^1\Sigma_g^+)$$
 (2)

as well as the spin-allowed channel (3)

$$\operatorname{ClN}_3 + h\nu \to \operatorname{NCl}(X^3\Sigma^-) + \operatorname{N}_2(A^3\Sigma_u^+)$$
 (3)

 $N_2(A^3\Sigma_u^+)$  presumably from channel (3) has been detected [9,10], along with NCl(b<sup>1</sup> $\Sigma^+$ ) which can be produced by a second spin-allowed channel [9,13].

$$\operatorname{ClN}_3 + h\nu \to \operatorname{NCl}(b^1\Sigma^+) + \operatorname{N}_2(X^1\Sigma_g^+)$$
 (4)

Up to now, a quantitative knowledge of the relative importance of these four channels is not in hand. Coombe et al. [10] reported that formation of  $NCl(b^{1}\Sigma^{+})$  and  $N_{2}(A^{3}\Sigma_{u}^{+})$  amount to only about 1% of the 193 nm photolysis products. Komissarov et al. [7] examined the prompt and delayed production of NCl( $X^{3}\Sigma^{-}$ ) using absorption spectroscopy after ClN<sub>3</sub> photolysis at 248 nm. Assuming that the delayed signal came from collisional relaxation of NCl( $a^{1}\Delta$ ), they were able to estimate that 80% of the primary NCl was formed in the a state and, apart from the 1% of NCl( $b^1\Sigma^+$ ), the remaining NCl was produced in the electronic ground state. Similar measurements for 193 nm photolysis indicated production of approximately 70% NCl( $a^{1}\Delta$ ) with 30% NCl( $X^{3}\Sigma^{-}$ ) [6].

Measurements of photofragment quantum yields are not equivalent to knowledge of the quantum yield for a specific reaction, since photofragments may be produced by more than one reaction. Furthermore, measurements of quantum yields of highly reactive photoproducts may be less accurate unless measured under collision free conditions. Velocity map imaging [14,15] solves both of these problems. First, it is a collision free molecular beam technique. Second, the measurement of specific velocities of state-selected photofragments may be used together with the principles of conservation of linear momentum and energy, to clearly identify the electronic state of the undetected counter-fragment, allowing unambiguous identification of the reaction from which the photofragment is being produced.

In this work, we report velocity map imaging data for single photon dissociation of ClN<sub>3</sub> at  $\lambda \approx 203$  nm, providing the first look at the photodissociation of ClN<sub>3</sub> under collision free conditions. Velocity map images obtained using resonance enhanced multiphoton ionization (RE-MPI) of selected states of recoiling  $N_2(X^1\Sigma_g^+)$  were resolved and unambiguously assigned to dissociation channels (1) and (2). The relative importance of these two channels at 203 nm was obtained and shows that ground state  $NCl(X^{3}\Sigma^{-})$  is produced mainly by the spin-forbidden channel (2). Analysis of the kinetic energy release data yielded an accurate determination for the exoergicity of  $ClN_3 \rightarrow NCl(a^1\Delta) + N_2(X^1\Sigma_g^+).$  The angular distribution of the photofragments observed at this wavelength is consistent with initial excitation of the  $\mathbf{B}^{1}\mathbf{A}' \leftarrow \mathbf{X}^{1}\mathbf{A}'$  absorption system.

## 2. Experiment

The technique of velocity map imaging has been described fully elsewhere [14]. Chlorine azide (ClN<sub>3</sub>) was formed by passing a mixture of 5% Cl<sub>2</sub> in He over the surface of moist sodium azide (NaN<sub>3</sub>). A standard drying agent was used to remove water from the ClN<sub>3</sub>/Cl<sub>2</sub>/He mixture at the exit of the generator. The mixture was then expanded through a pulsed nozzle (General Valve) with a backing pressure of  $\approx 0.5$  bar.

Laser light at  $\lambda \approx 203$  nm was generated by upconverting the output from a Nd:YAG/dye laser combination (Continuum) operating on a rhodamine 610/640 mixture. The output from the dye laser was frequency doubled in a KDP crystal and then the fundamental and second harmonic was summed in a BBO crystal. About 1 mJ/pulse of this light was focused with a 10 cm focal length lens onto the molecular beam. One photon of the 203 nm light was used to dissociate the ClN<sub>3</sub> and three more photons were used to carry out 2+1 REMPI of the N<sub>2</sub> photoproducts [16].

Velocity map images were accumulated while the laser frequency was scanned repetitively over the Doppler profile of a single rotational transition. The images were taken with the laser vertically polarized, such that the electric vector was parallel to the image plane. Background subtraction of ions produced by the ion decomposition channel [17] was required and image reconstruction was accomplished with the Basis-Set-Expansion-Method [18].

The velocity space was calibrated by recording  $D^+$  images produced by three-photon dissociation of  $D_2$  [19]

$$\mathbf{D}_2 + 3hv \to \mathbf{D} \ (n=1) + \mathbf{D} \ (n=2) \tag{5}$$

The electronically excited atomic fragment, D (n = 2), subsequently absorbs an additional photon and is ionized, producing the D<sup>+</sup> ions with kinetic energies of about 1.87 eV. The high velocity D<sup>+</sup> ions were needed to calibrate the system for the detection of the fast moving fragments that were expected from one-photon dissociation of ClN<sub>3</sub>.

#### 3. Results

Fig. 1 shows the velocity map image of the  $N_2^+$  produced by laser excitation at  $\lambda = 203.205$  nm, which probes the N<sub>2</sub> ( $\nu = 0, J = 68$ ) photoproduct. This image was recorded using a high acceleration voltage (repeller: 7000 V and extractor: 4900 V) to ensure that fragments produced with the highest possible velocities would land on the active area of the detector.

The center-of-mass frame kinetic energy distribution derived from the inverse Abel transformation is shown in Fig. 2. Two peaks separated by about the NCl singlet-triplet splitting are assigned to channels (1) and (2). The high kinetic energy peak corresponds to formation of ground electronic state NCl in coincidence with the detected





Fig. 1. Inverse Abel transform of the velocity map image of the N<sub>2</sub> product recoiling from ClN<sub>3</sub> photolysis. The excitation wavelength used,  $\lambda = 203.205$  nm, dissociates ClN<sub>3</sub> and probes the N<sub>2</sub>(X<sup>1</sup>\Sigma<sup>+</sup><sub>g</sub>,  $\nu = 0, J = 68$ ) dissociation products. The velocities marked with arrows reflect a center-of-mass frame energy difference of 1.14 eV. When this is compared to the singlet–triplet splitting in NCl (1.15 eV), compelling evidence is found for assignment of the inner ring to reaction (\*) and the outer ring to reaction (\*\*).

N<sub>2</sub> (v = 0, J = 68) molecules. At ~4.75 eV and lower, one sees an abrupt rise in intensity, corresponding to the onset of formation of NCl(a<sup>1</sup> $\Delta$ ) in coincidence with the N<sub>2</sub> (v = 0, J = 68). Exploiting the thermodynamic cycle shown in Fig. 3, we have used this threshold to extract the energetics of reaction (\*), assuming that NCl(a<sup>1</sup> $\Delta$ , v = 0, J = 0) can be formed at threshold. To accomplish this one must use the rotational and centrifugal distortion constants [20] for N<sub>2</sub> to find the rotational energy of N<sub>2</sub> (J = 68):  $E_{rot}(N_2) = 1.14$  eV. The derived results (+0.21 ± 0.08 eV) represents a rigorous upper limit to the exoergicity of reaction (\*).

Also indicated in Fig. 2 is the singlet-triplet splitting in NCl,  $\Delta E(a - X)$ . From this one can see that there is an additional threshold (albeit less abrupt) for formation of ground electronic state NCl observed in the data. Using the literature value for  $\Delta E(a - X) = 1.15$  eV [21], we arrive at the following thermodynamic results:



Fig. 2. Observed center-of-mass frame kinetic energy distribution for reactions (\*) and (\*\*):  $CIN_3 + h\nu \rightarrow NCl(a^1\Delta, X^3\Sigma^-) + N_2(X^1\Sigma_g^+)$ . The bimodal distribution is assigned to the elementary chemical processes as shown in the figure. The abrupt threshold at 4.75 eV can be used to derive the energetics of reaction (\*),  $\Delta E_{reac.(1)} = +0.21$  eV. Also shown is the singlet-triplet energy splitting in NCl,  $\Delta E(a - X)$ .



Fig. 3. Energy diagram showing species involved in this experiment. Photolysis of ClN<sub>3</sub> at  $\lambda = 203.205$  nm yields NCl(a<sup>1</sup> $\Delta$ ) or NCl(X<sup>3</sup> $\Sigma^{-}$ ) and N<sub>2</sub>(X<sup>1</sup> $\Sigma^{+}$ ) through exothermic reactions. The total amount of excess energy released was ~5.89 and 7.03 eV, respectively. The results derived from this work are shown in bold face.

$$\operatorname{ClN}_3 \to \operatorname{N}_2(\operatorname{X}^1\Sigma_g^+) + \operatorname{NCl}(\operatorname{a}^1\Delta)$$
  
 $\Delta E = +0.21 \pm 0.08 \text{ eV}$  (6)

$$ClN_3 \rightarrow N_2(X^1\Sigma_g^+) + NCl(X^3\Sigma^-)$$
$$\Delta E = -0.93 \pm 0.08 \text{ eV}$$
(7)

Also from Fig. 2, we see that the most probable internal energy in the NCl counter-fragment is 0.51 and 0.42 eV for channels (1) and (2), respectively. It is interesting to note that the exoergic channel tends to produce NCl with less ro-vibrational excitation. This suggests that there are significant differences between the singlet and triplet potential surfaces governing the dynamics of each reaction.

Angular distributions of the N<sub>2</sub> (X<sup>1</sup> $\Sigma_g^+$ ) fragments were analyzed assuming the center-of-mass angular distributions,  $f\theta$ ), exhibit the usual form [22]

$$f(\theta) \propto 1 + \beta_2 P_2(\cos \theta),$$
 (8)

were  $P_2(\cos \theta)$  is the second-order Legendre polynomial. Fig. 4 shows the observed angular distribution of N<sub>2</sub> photofragments from reaction (\*), integrating over velocity at each recoil angle. The solid smooth line shows the fit to Eq. (6). This



Fig. 4. Observed angular distribution of N<sub>2</sub> photofragments obtained in a one-photon dissociation of ClN<sub>3</sub> at  $\lambda = 203.205$  nm into N<sub>2</sub>(X<sup>1</sup> $\Sigma_g^+$ ) + NCl(a<sup>1</sup> $\Delta$ ). The solid smooth line shows the fit to Eq. (6) yielding an anisotropy parameter  $\beta_2 = 1.95(6)$  indicating a parallel transition.

fitting procedure (which was also performed for data at higher recoil velocities important for the triplet channel) allows us to derive the anisotropy parameters for both singlet and triplet products. We find that within experimental error both channels exhibit the same anisotropy parameter ( $\beta_2 = 1.95 \pm 0.06$ ). This result suggests that both singlet and triplet channels result after initial excitation in the  $\tilde{B}^1A' \leftarrow \tilde{X}^1A'$  parallel absorption system. Presumably, production of triplet products requires a curve crossing between the  $\tilde{B}^1A'$  surface and a nearby triplet surface.

Having assigned the two rings in the N<sub>2</sub> velocity map to the production of NCl(a<sup>1</sup> $\Delta$ ) and NCl(X<sup>3</sup> $\Sigma^{-}$ ) we integrated the velocity map image to obtain the branching ratio between the a and X-states of NCl appearing in coincidence with N<sub>2</sub> ( $\nu = 0, J = 68$ ). We obtained a ratio of 0.78/ 0.22 in favor of NCl(a<sup>1</sup> $\Delta$ ). While this value is strictly speaking only applicable to the specific channel observed in this work where N<sub>2</sub> is formed in  $\nu = 0$  and J = 68, we do not expect that the singlet triplet branching will be strongly dependent on N<sub>2</sub> rotational state. Furthermore, these results are similar to previous cell experiments which are integrated over all N<sub>2</sub> internal states [6,7].

# 4. Discussion

From a study of the dissociative photo-ionization of ClN<sub>3</sub>, Hansen et al. [17] obtained upper limits to the exoergicities of reactions (\*) and (\*\*). In that work two-photon ionization of ClN<sub>3</sub> gave rise to ionic fragments and the exoergicity of the ion decomposition channel (forming  $NCl^+ + N_2$ ) could be obtained from velocity map images. Using previously determined values for the ionization energies of ClN<sub>3</sub> and NCl, the following results were obtained :  $\Delta E_1 < 0.3$  and  $\Delta E_2 < -0.85$  eV, which are in excellent agreement with the present work. Both experiments yield upper limits for the thermochemistry. However, now that two independent means arrive at similar results, we conclude that these 'upper limits' represent the best experimental values of the energetics of reaction (\*) and (\*\*) and we recommend these be used in the future. These results may be compared to recent high-level ab initio calculation. Using a MRSDCI-CASSCF(12e/10o)/D95+d level calculation, Morokuma [23] obtained a value for  $\Delta E_1$  of +0.52 eV, close to the value (+0.21) reported here.

The NCl(a<sup>1</sup> $\Delta$ )/NCl(X<sup>3</sup> $\Sigma^{-}$ ) branching ratio of 0.78/0.22 obtained from the velocity map image for 203 nm photolysis is close to the 0.70/0.30 ratio observed using 193 nm photolysis with detection of NCl(X<sup>3</sup> $\Sigma^{-}$ ) by transient absorption spectroscopy [6]. This agreement has several implications. First it strongly suggests that the NCl(X<sup>3</sup> $\Sigma^{-}$ ) produced by the UV photochemistry of ClN<sub>3</sub> comes nearly exclusively from the spin-forbidden channel (2). If the spin-allowed channel (3) were an important source of NCl(X<sup>3</sup> $\Sigma^{-}$ ), agreement between these very different experiments would be quite unlikely. This also lends strength to the prior measurements that reported the formation of N<sub>2</sub>(A<sup>3</sup> $\Sigma_{u}^{+}$ ) as a minor channel [10].

As mentioned earlier, 203 nm light excites the  $\mathbf{B}^{1}\mathbf{A}' - \mathbf{X}^{1}\mathbf{A}'$  transition and the observed fragments arise from the dissociation of  $ClN_3$  ( $\hat{B}^1A'$ ). Consequently, the singlet-triplet branching ratio depends on the probability of crossing from the excited singlet to the ground-state triplet surface. The agreement between the branching ratio obtained here and that obtained in the cell experiment [7] appears to substantiate our statements above that the singlet-triplet branching ratio is at least not strongly dependent on the N2 rotational state. This fits well with an exit-curve-crossing mechanism where there is not a large  $N-N\equiv N$ bond angle change upon curve crossing. Furthermore, our experiments show that about 70-80% of the available energy appears as translation. In light of the large translational energies observed here compared to the amount of rotational excitation, we expect that the velocity at the curve crossing will not be greatly affected by switching rotational channels.

Alternative dissociation pathways for  $ClN_3$  excited at wavelengths below 320 nm include

$$\operatorname{ClN}_3 + hv \to \operatorname{Cl}(^2\mathbf{P}) + \mathbf{N}_3$$
 (9)

and

$$\operatorname{ClN}_3 + hv \to \operatorname{Cl}({}^2\mathrm{P}) + \mathrm{N}({}^2\mathrm{D}) + \mathrm{N}_2.$$
(10)

Both Cl(<sup>2</sup>P) and N(<sup>2</sup>D) atoms have been detected in imaging experiments that will be described in a subsequent publication. The branching fraction for production of atomic products has not been characterized, but indirect evidence indicates that production of diatomic fragments dominates for 193 and 248 nm photolysis. For example, Ray and Coombe [1] demonstrated an NCl(a<sup>1</sup> $\Delta$ ) driven iodine laser using 193 nm photolysis of a mixture of ClN<sub>3</sub> and CH<sub>2</sub>I<sub>2</sub>. Analysis of the pumping kinetics shows that the quantum yield for generation of NCl(a<sup>1</sup> $\Delta$ ) had to be greater than 0.5 to reach lasing threshold. The results of this work are consistent with that of Ray and Coombe [1].

## 5. Conclusions

We observed 2+1 REMPI signal and ion velocity maps of state-selected  $N_2(X^1\Sigma_g^+)$ , resulting from the one-photon dissociation of ClN<sub>3</sub>. Two channels with a maximum 4.75 and 5.90 eV translational energy were observed and assigned to channels (1) and (2):

$$\operatorname{ClN}_3 + h\nu \to \operatorname{NCl}(a^1\Delta) + \operatorname{N}_2(\operatorname{X}^1\Sigma_g^+)$$
 (1)

$$ClN_3 + h\nu \rightarrow NCl(X^3\Sigma^-) + N_2(X^1\Sigma_g^+)$$
(2)

These results show that ClN<sub>3</sub> decomposes exothermically to form N<sub>2</sub> and NCl. We derived exoergicities of  $\Delta E < +0.21 \pm 0.08$  eV and  $< -0.93 \pm$ 0.09 eV for decomposition of ClN<sub>3</sub> into N<sub>2</sub> and NCl(a<sup>1</sup> $\Delta$ ) or NCl(X<sup>3</sup> $\Sigma^{-}$ ), respectively. These results compare well with quantum chemical calculations and results obtained earlier from another experiment in which the two-photon dissociative ionization of ClN<sub>3</sub> was observed [17].

We also obtained the singlet-triplet NCl branching ratio (0. 78/0.22) in the UV photolysis of ClN<sub>3</sub> near 203 nm, that is, the relative importance of channels (1) and (2). These results also show that NCl( $X^3\Sigma^-$ ) is produced mainly by the spin-forbidden channel (2) and confirm that the formation of N<sub>2</sub>( $A^3\Sigma_u^+$ ) is a minor channel. Finally, angular distributions suggest that the  $\tilde{B}^1A' \leftarrow \tilde{X}^1A'$  absorption system is responsible for production of photoproducts at this wavelength.

# Acknowledgements

This work was supported by the AirForce Office of Scientific Research under Grant Numbers F49620-95-1-0234 (UCSB) and F49620-01-1-0070 (Emory). We thank H. Reisler (University of Southern California) for providing us with her software program for analysis of the imaging data. NH acknowledges the support of the Alexander von Humboldt Foundation under a Fyodor Lynen Stipend.

#### References

- [1] A.J. Ray, R.D. Coombe, J. Phys. Chem. 99 (1995) 7849.
- [2] T.L. Henshaw, G.C. Manke, T.J. Madden, M.R. Berman, G.D. Hager, Chem. Phys. Lett. 325 (2000) 537.
- [3] G.C. Manke, G.D. Hager, J. Mod. Opt. 49 (2002) 465.
- [4] A.J. Ray, R.D. Coombe, J. Phys. Chem. 98 (1994) 8940.
- [5] T.L. Henshaw, S.D. Herrera, G.W. Haggquist, L.A.V. Schlie, J. Phys. Chem. A 101 (1997) 4048.
- [6] A.V. Komissarov, G.C. Manke II, S.J. Davis, M.C. Heaven, Proc. SPIE 3931 (2000) 138.
- [7] A.V. Komissarov, G.C. Manke, S.J. Davis, M.C. Heaven, J. Phys. Chem. A 106 (2002) 8427.
- [8] A.J. Ray, R.D. Coombe, J. Phys. Chem. 97 (1993) 3475.
- [9] R.D. Coombe, D. Patel, A.T. Pritt, F.J. Wodarczyk, J. Chem. Phys. 75 (1981) 2177.
- [10] R.D. Coombe, S.J. David, T.L. Henshaw, D.J. May, Chem. Phys. Lett. 120 (1985) 433.
- [11] R.D. Coombe, M.H. Vanbenthem, J. Chem. Phys. 81 (1984) 2984.
- [12] R.H. Jensen, A. Mann, R.D. Coombe, J. Phys. Chem. A 104 (2000) 6573.
- [13] A.T. Pritt, D. Patel, R.D. Coombe, J. Chem. Phys. 75 (1981) 5720.
- [14] A. Eppink, D.H. Parker, Rev. Sci. Instrum. 68 (1997) 3477.
- [15] D.H. Parker, A. Eppink, J. Chem. Phys. 107 (1997) 2357.
- [16] K.R. Lykke, B.D. Kay, J. Chem. Phys. 95 (1991) 2252.
- [17] N. Hansen, A.M. Wodtke, A.V. Komissarov, K. Morokuma, M.C. Heaven, J. Chem. Phys. (submitted).
- [18] V. Dribinski, A. Ossadtchi, V.A. Mandelshtam, H. Reisler, Rev. Sci. Instrum. 73 (2002) 2634.
- [19] M.A. Buntine, D.P. Baldwin, D.W. Chandler, J. Chem. Phys. 96 (1992) 5843.
- [20] J. Bendtsen, F. Rasmussen, J. Raman Spectrosc. 31 (2000) 433.
- [21] R. Colin, W.E. Jones, Can.J. Phys. 45 (1967) 301.
- [22] R.N. Zare, Mol. Photochem. 4 (1972) 1.
- [23] K. Morokuma, private communication.