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The Cl to NCl branching ratio in 248-nm photolysis of chlorine azide

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Abstract

The primary reaction products from 248-nm chlorine azide photolysis are identified in a collision-free experiment. In contrast to all previous reports, the radical channel producing $Cl + N_3$ ($95 \pm 3\%$) is seen to dominate the photochemistry. The molecular channel producing $NCl + N_2$ ($5 \pm 3\%$) was also observed.

1. Introduction

This Letter reports the first direct measurement of the product branching ratio from photolysis of ClN_3. The photochemistry of this species [1] is of considerable interest because one of its photoproducts, $NCl(\tilde{a}\,^1\Delta)$, the isovalent analog of singlet-oxygen, is an important energy carrier in an all gas-phase iodine laser [2,3] (AGIL). While the molecular mechanism of the AGIL is not completely understood, the near-resonant energy transfer reaction

$$NCl(\tilde{a}^1\Delta) + I(^2P_{3/2}) \rightarrow NCl(\tilde{X}^3\Sigma) + I(^2P_{1/2}) \qquad (1)$$

and slow relaxation of $NCl(\tilde{a}^1\Delta)$ are important factors in its performance. The first reported observation of iodine lasing induced by $NCl(\tilde{a}^1\Delta)$ employed 193-nm photolytic production of $NCl(\tilde{a}^1\Delta)$ in mixtures of ClN_3 and CH_2I_2 [4]. In 1998, gain in a dc-discharge-driven chemical laser was reported [5]. The most recent prototype (AGIL-2) can produce more than 15 W of continuous radiation at 1.315 μm [6]. Such a light source has important potential applications in defense-related and medical research.

The importance of understanding the primary molecular processes relevant to the AGIL has led to a large number of laser-based kinetics studies, which utilize ClN_3 photolysis as a source of $NCl(\tilde{a}^1\Delta)$ [7–11]. Despite intensive effort, the fundamental photochemistry of ClN_3 is not yet understood. For example, only limited data is available concerning the relative importance and thermochemistry of the dissociation pathways, as listed below:

$$\begin{aligned} ClN_3(\tilde{X}^1A') + h\nu &\rightarrow Cl(^2P_J) + N_3(\tilde{X}^2\Pi, \text{cyclic}) && (2a)\\ &\rightarrow Cl(^2P_J) + N_2(\tilde{X}^1\Sigma_g^+) + N(^2D_J, {}^4S_{3/2}) && (2b)\\ &\rightarrow NCl(\tilde{X}^3\Sigma, \tilde{a}^1\Delta, \tilde{b}^1\Sigma) + N_2(\tilde{X}^1\Sigma_g^+) && (3a) \end{aligned}$$

The above kinetics studies and earlier photodissociation studies [1,12] of ClN_3 point to $NCl(\tilde{a}^1\Delta)$ (from reaction 3a) as the dominant photochemical product. However, none explicitly examine the $Cl + N_3$ channels, and all are vulnerable to problems related to the high reactivity of the primary products. For example, the photochemically-driven AGIL exhibited an induction time to reach the lasing threshold that could be modeled by a reaction mechanism where $NCl(\tilde{a}^1\Delta)$ is

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produced by chain reaction decomposition of ClN_3 [4]. Experiments employing 248-nm photolysis of ClN_3 also suggested that $NCl(\tilde{a}^1\Delta)$ is produced by secondary reactions [8]. On the other hand, a recent study presented kinetic data that appeared to reflect the prompt production of $NCl(\tilde{a}^1\Delta)$ as a primary product of ClN_3 photolysis [11]. Thus, there remains significant confusion regarding even the identity of the primary reaction products resulting from UV photolysis of ClN_3.

Only recently have collision-free studies of ClN_3 photochemistry been reported [13–15]. In these studies, both primary $Cl(^2P_J)$ [13] and $N_2(\tilde{X}^1\Sigma_g^+)$ [15] photoproducts were detected. The $NCl(\tilde{a}^1\Delta)/NCl$ $(\tilde{X}^3\Sigma)$ branching (reaction 3a) at 203-nm was also reported [15]. An unusual bimodal translational energy distribution of primary Cl-atom product [13] was consistent with photochemical production of a cyclic form of N_3 that had been predicted by theory [16]. Finally, a comprehensive and critical re-evaluation of the thermochemistry of all molecules containing a single Cl atom and three N atoms was put forth [13,14].

Here, we report results on the collision-free, 248-nm photolysis of ClN_3 using molecular beam photofragment translational spectroscopy [17,18]. This experiment, in addition to eliminating complications from secondary processes, enables one to observe all channels on an approximately equal footing. In contrast to all previous reports, we find clear evidence that Cl-atom production (2a) is by far the dominant ($95 \pm 3\%$) collision-free dissociation channel. Channel (2b) occurs only through secondary collision-free decomposition of highly energetic N_3. NCl production (3a) is an observed minor channel ($\sim 5 \pm 3\%$).

2. Experimental

The molecular beam photodissociation instrument on which these experiments were performed has been described in detail previously [19,20]. ClN_3 was formed by passing a mixture of 5% Cl_2 in He over the surface of moist sodium azide (NaN_3). A standard drying agent (Drierite®) was used to remove water from the $ClN_3/Cl_2/He$ mixture at the exit of the generator. Under normal operating conditions, mass spectral analysis of the beam showed NCl^+, an ionizer-induced fragment of ClN_3^+ [14], and little or no Cl_2^+. Under conditions where Cl_2^+ signal could be detected, the NaN_3 sample was replaced. Using a backing pressure of approximately 0.5 bar, the mixture was formed into a pulsed molecular beam by expanding it through a piezoelectrically-actuated pulsed valve [21].

After passing through two collimating skimmers, the molecular beam intersected a 28-ns pulsed ultraviolet beam of unpolarized light produced by a Lambda-Physik® KrF laser (248 nm) operating at 100 Hz with 72 mJ pulse energy and focused to a ~ 10 mm^2 spot at the region of intersection. Photofragments scattered in the plane of the molecular and laser beams were detected as a function of laboratory scattering angle Θ with a rotatable, triply differentially pumped mass spectrometer; after passing through three collimating apertures, the photofragments were ionized by electron impact (~ 160 eV), mass-selected with a quadrupole mass filter, and detected with a Daly-style detector [22]. At various scattering angles, photofragment time-of-flight (TOF) distributions were taken for ions at selected mass-to-charge ratios (m/e's) using a multi-channel scaler interfaced to a PC. The velocity distribution of the parent ClN_3 molecular beam was characterized by TOF at $\Theta = 0°$ using a retractable slotted chopper wheel to modulate the molecular beam.

3. Results and analysis

Fig. 1 shows TOF distributions for $m/e = 35$ (Cl^+) and 49 (NCl^+) at several scattering angles, Θ. The data are represented by open circles. The solid lines are the results of forward-convolution simulations of the experiment using optimized center-of-mass translational energy ($P(E_T)$) distributions shown in Fig. 2 for the $Cl + N_3$ and $NCl + N_2$ channels. Other input data required for analysis include the molecular beam velocity distribution, the finite size of the intersection and ionization regions, the finite angular acceptance angle of the detector and the laser polarization [23]. The $P(E_T)$ distributions can also be used to generate TOF distributions of the momentum-matched counter-fragments (i.e. N_3 for Cl and N_2 for NCl), yielding distributions (not shown) that match components of the experimental TOF spectra at $m/e = 42$ (N_3^+) and 28 (N_2^+), although the latter is complicated by secondary dissociation of the N_3 primary product.

Successfully fitting the data allowed us to derive the center-of-mass frame flux of Cl and NCl reaction products after proper correction for the ionization efficiency of each species [24]. This procedure was simplified by the fact that electron impact induced fragmentation of NCl and Cl was insignificant. The relative total ionization efficiency was estimated by using a known empirical correlation between molecular polarizability and total electron ionization cross-section, which were calculated using the additivity rule proposed by Fitch and Sauter [25] as explained by Schmoltner [26]. Briefly, the electron impact cross section (in units of 10^{-16} cm^2) is estimated from the following additivity formula:

$$Q = 0.082 + \sum_i a_i n_i. \tag{4}$$

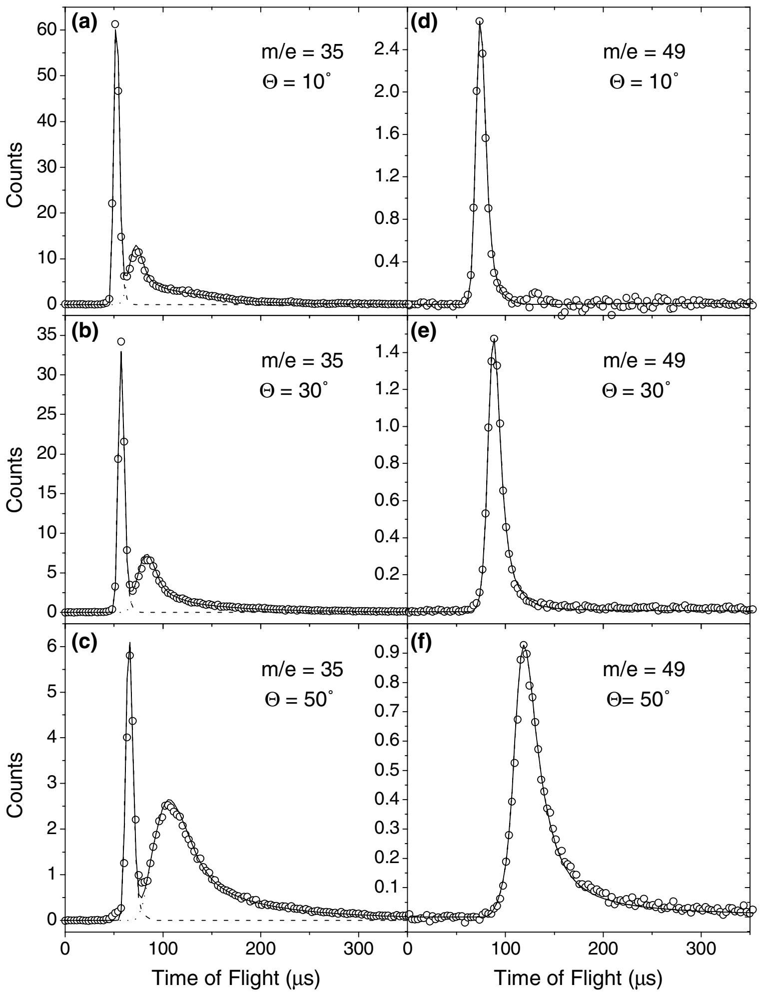

Fig. 1. TOF spectra for $m/e = 35$ (Cl^+) and 49 (NCl^+) at detection angles (Θ) of 10°, 30° and 50°. For all TOF spectra the open circles represent the data and the solid line represents the forward convolution fit to the data using the $P(E_T)$ distributions in Fig. 2. Note the appearance of a 'fast' (dashed) and a 'slow' (dotted) channel in the $m/e = 35$ TOF spectra.

This analysis resulted in a branching fraction:

$$\phi_{Cl} \equiv \frac{[Cl]}{[NCl] + [Cl]} = 0.95 \pm 0.03. \qquad (5)$$

This result stands in marked contrast to the 'conventional wisdom' that the $Cl + N_3$ channel is relatively minor. This assumption has been inferred from observations of the $NCl + N_2$ channel alone, not by any systematic comparison of the two channels. For example, measurements by Henshaw et al. [9] of the $NCl(a^1\Delta)$ concentration at early times via titration with Br_2 gave a quantum yield of 60% for $NCl(a^1\Delta) + N_2$ at 193 nm. Recent work by Komissarov et al. [11] which reported a rapid appearance of $NCl(\tilde{a}^1\Delta)$, also appeared to provide strong evidence for the dominance of the $NCl + Cl_2$ channel. However, analyses of these experiments are based on the assumption that the NCl is a primary product, not the result of rapid secondary reactions. Heaven and co-workers [27] have since obtained much improved kinetic results which strongly indicate that $NCl(\tilde{a}^1\Delta)$ is indeed formed by secondary reactions and the mechanism for its production under their conditions has been elucidated. Our result is quite unambiguous, since our experiment is conducted under collisionless conditions and the two channels were investigated using the same type of measurement.

It is not possible to identify the electronic states of NCl due to the fact that a large amount of the available energy appears as product rotation and/or vibration in the molecular channel. We note that the bimodal $P(E_T)$ distribution for the $Cl + N_3$ channel needed to fit the two peaks in the TOF spectra is quite similar to that obtained by Hansen et al. [13] in a recent photofragment velocity-map imaging experiment, in which the slower feature was interpreted as possible evidence for the photolytic production of cyclic-N_3. Thus, the experiments reported in this work confirm the existence of a bimodal translational energy distribution in the radical channel. This means that N_3 is formed in a low energy (linear azide radical) and a high energy (possibly cyclic-

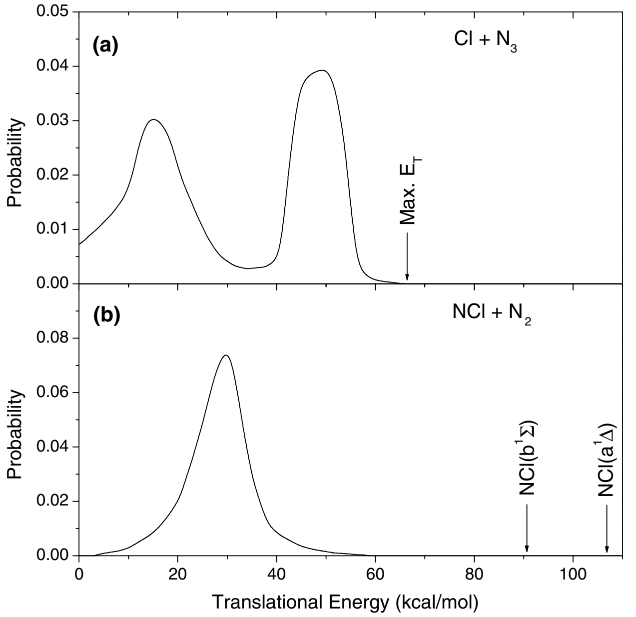

Fig. 2. Center-of-mass translational energy distributions, P(E_T), for the radical (a) and molecular (b) channels in ClN_3 photodissociation. The arrows indicate the maximum allowed translation energy release when products have no rotational or vibrational excitation. The distributions shown are able to produce the fit to all of the TOF data shown in Fig. 1.

N_3) form. The branching fraction for the radical channel found here suggests that the high energy form of N_3 formed in ClN_3 photolysis is produced with large quantum efficiency.

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