LASER INDUCED FLUORESCENCE OF $N_2^+(X, v'')$ RESULTING FROM THE THERMAL ENERGY DISSOCIATIVE CHARGE TRANSFER REACTION $He^+ + N_2O \longrightarrow N_2^+ + O + He^{(*)}$

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The vibrational (and rotational) energy distribution of $N_2^+(X)$ ions produced in the He^+/N_2O charge transfer reaction at thermal energy has been measured by laser induced fluorescence using an Ion Cyclotron Resonance cell to store the ions. Vibrational levels up to $v''=5$ have been observed.

The relaxation processes experienced by the $N_2^+(X)$ ions before laser detection are discussed.

KEY WORDS: Charge transfer reaction, N_2O^+ , N_2^+ , laser induced fluorescence.

I- INTRODUCTION

Laser Induced Fluorescence is a very powerful method to investigate the internal energy of reaction products and get

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information on the reaction dynamics. However, most of the experiments concern neutral reactants and only a few results are available for ions. There are indeed some specific experimental difficulties for ions due to smaller achievable concentrations and very efficient deactivation by charge exchange and collision. Therefore to observe the nascent internal states of ion molecule reaction products one has to find experimental conditions where reaction is much faster than relaxation. Two types of such experiments have been reported in the literature : flowing afterglow¹⁻³ and more recently a single collision molecular beam device³⁻⁶. The standard flowing afterglow experiments take advantage of the fact that the relaxation rate with He as a carrier gas is very low and, for fast ion molecule reactions, the reactant gas concentration can be kept small enough to minimize deactivation by symmetrical charge transfer. Relaxation is further reduced in the beam experiment where the ions undergo a supersonic expansion into the interaction region where they cross a pulsed supersonic jet of reactant gas. This allows the investigation of reactions such as :

whose rate is much smaller than the relaxation rate of the ion product. The above mentioned reaction has also been investigated by LIF in an Ion Cyclotron Resonance cell^{7,8}, but only the relaxed $\text{CO}^+(X, v''=0)$ could be observed because, in the pressure conditions imposed by the detection sensitivity, relaxation was much faster than reaction. Further improvement in the detection sensitivity, although insufficient to study slow reactions, made possible the observation of nascent products of fast ion molecule reactions.

In the present paper we will report on the dissociative charge transfer reaction of He^+ with N_2O . This reaction occurs at collision rate since the experimental rate constant ($2.3 \cdot 10^{-9} \text{ molecule}^{-1} \text{cm}^3 \text{s}^{-1}$)⁹ is very close to the locked dipole value ($2.1 \cdot 10^{-9} \text{ molecule}^{-1} \text{cm}^3 \text{s}^{-1}$). It is most probably an energy resonant process which means that the recombination energy of He^+ (24.56 eV) is used to ionize N_2O and produce highly excited dissociative state(s) of N_2O^+ ¹⁰. The most abundant product ion is N_2^+ (54 %) followed by NO^+ (21 %), N^+ (13 %), O^+ (12%) and N_2O^+ (< 1%)¹¹.

Although production of electronically excited N_2^+ is energetically possible more than 95% of the N_2^+ are in their ground electronic state¹⁰. So the overall rate constant of the channel(s) leading to ground state N_2^+ :

is large ($\sim 1.17 \cdot 10^{-9} \text{ molecule}^{-1}\text{cm}^3\text{s}^{-1}$) and we could observe vibrational states from $v'' = 1$ to 5. The relaxation processes experienced by the $\text{N}_2^+(\text{X})$ product ions are slow enough compared to the production rate to make their observation possible and they do not perturb much the nascent vibrational distribution as discussed in part IV. In contrast translation and rotation are certainly almost completely relaxed at the time of observation.

II-EXPERIMENTAL

A block diagram of the experiment is shown on fig 1. As the experimental set up has already been described in detail⁷ we will only give a brief outline of the main modifications and of the experimental conditions used in the present investigation.

A mixture of the reactant gases ($\text{He}, \text{N}_2\text{O}$) is introduced into an ICR cell and ionized by a 100 eV electron beam (typical intensity

Figure 1 Bloc diagram of the experimental setup.

3×10^{-7} A). The electron source is located in a separate section pumped differentially and the electron beam enters the cell parallel to the magnetic field through a small diaphragm (diameter ~ 1 mm). The ions formed in the cell are constrained by the magnetic field (~ 1 Tesla) into a cylindrical volume of about 1 mm diameter around the axis of the electron beam. No trapping potential was applied on the plates perpendicular to the beam since, in the pressure range used here, trapping along the beam is not very efficient.

The laser beam crosses the electron beam at right angles in the middle of the ICR cell. The fluorescence photons are collected through a lens system, focussed on the entrance slit of a broadband monochromator (Jobin Yvon H10 UV, 8nm bandwidth) and detected, after wavelength selection, by a fast photomultiplier (XTC 2254B) operated in a single photon counting mode. Replacement of the interference filters used previously⁷ by a monochromator reduces considerably the background signal due to light emissions from the electron source and various excited species produced by electron impact on the gas mixture. The photomultiplier output signal is sent to a 16 channels time to digital converter (time resolution 10 ns, full scale 5.12 μ s). Signal averaging and treatment are performed by a microcomputer.

Two different lasers have been used : a pulsed nitrogen laser (Molelectron UV24) pumping a tunable dye (Sopra) and a Nd-Yag pumped dye laser (Datachrom 5000 from Quantel). The spectra were obtained either in the linear absorption regime or in the saturation limit. With the Datachrom 5000 we could get 6-10 mJ/pulse depending on the dye but the spectra were recorded with 2 mJ/pulse. With the nitrogen pumped dye laser the maximum intensity was 150 μ J/pulse and the spectra were recorded at 50 μ J/pulse. In both cases the laser pulse width was 10 ns. The spectral width was 0.5 cm^{-1} with the Datachrom and $0.5\text{-}2.5 \text{ cm}^{-1}$ with the Sopra dye. The repetition rate was 50Hz (N_2 laser) or 30 Hz (Nd - YAG laser). The wavelength was calibrated with a monochromator (Jobin et Yvon HRS 100) and the beam intensity was recorded during the experiments using a pyroelectric detector.

Production of the ions, laser excitation and light detection are performed in a pulsed mode. An experimental cycle consists of two sequences A and B as shown on fig. 2a. The electron beam is turned

Figure 2 (a) Timing diagram of the experiment (b) fluorescence decay of $\text{N}_2^+(\text{B}, v'=0)$ (lifetime 60 ns). The time interval over which the fluorescence decay is integrated during the spectra is delimited by arrows.

on at the beginning of each sequence for 100 μs . The laser is triggered every two sequences with a variable time delay Δt_L after the end of the electron pulse. The photon counting starts just after the laser pulse in sequence A and after an identical delay from the end of the electron beam in sequence B. The photons are counted during 5ms in each sequence and, in order to get good counting statistics, each cycle is repeated typically over 4000 laser pulses. The counts may be integrated over any time interval from 10 ns to 5 μs . Subtraction of signals A and B (laser-on, laser-off) eliminates all emissions except LIF.

Figure 3 LIF excitation spectra for (a) the $N_2^+(B, v'=0) \leftarrow (X, v''=1)$ and (b) the $N_2^+(B, v'=0) \leftarrow (X, v''=2)$ transitions, recorded at 60 μJ laser intensities (with the N_2 pumped dye laser).

Fig. 2b shows a typical decay curve of $\text{N}_2^+(\text{B}, v'=0)$. The lifetime deduced from this curve is 60 ns, in good agreement with the literature values^{12,13}. This determines the time interval Δt_c over which the photon counts have to be integrated to get a good signal to noise ratio. We used $\Delta t_c = 360$ ns, i.e. 6 radiative lifetimes, starting 15 ns after the laser pulse in order to avoid detection of scatter light.

The detection limit of the experiment is estimated to be around 10^4 ions per cm^3 and per quantum state with the highest available laser pulse intensity (2 mJ). It is however very difficult to evaluate the fraction of the emitted photons detected by the photomultiplier and even more the density of ions probed by the laser. This density is limited by space charge effects, it decreases very rapidly as soon as the electron beam is turned off and then much more slowly.

The excitation spectra have been recorded at constant pressures ($P_{\text{He}} = 40$ mtorr, $P_{\text{N}_2\text{O}} = 4$ mtorr) and constant delay time between the electron and laser pulses ($\Delta t_L = 10 \mu\text{s}$) in order to determine the vibrational and rotational populations of $\text{N}_2^+(\text{X})$. Two dyes were used: coumarine 440 for the (0,1) transition and coumarine 460 for the other transitions.

The contribution of N_2^+ ions formed by electron impact on N_2O to the LIF signal was small for the vibrational states probed. This was checked by introducing pure N_2O into the cell and is confirmed by the linear dependence of the LIF signal on the He pressure.

III- RESULTS

We will first give the results concerning the vibrational population distribution, then we will analyse the rotational distribution in the $v'' = 1$ and 2 levels and briefly discuss the relaxation processes occurring before LIF detection of the N_2^+ ions. A detailed analysis of the vibrational relaxation and of the reaction dynamics will be given later¹⁴.

Vibrational populations

The $\text{N}_2^+(\text{X}, v'', N'')$ ions were probed by laser excitation on $\Delta v = 1$ and $\Delta v = 2$ sequences of the first negative system of N_2^+ for laser excitation ($\text{B}^2 \Sigma_u^+ - \text{X}^2 \Sigma_g^+$).

Subsequent emission from $N_2^+(B, v', N')$ takes place down to many vibrational levels of $N_2^+(X)$ but only photons emitted on a particular vibronic transition were detected. In order to get a good signal to noise ratio one has to choose for each vibrational state the vibronic transitions in absorption and emission with the largest possible Franck Condon Factors. The transitions used in this investigation and the corresponding FCF are summarised in table I. The LIF spectra were obtained in the linear regime (with the nitrogen pumped dye laser) for the (0,1) and (0,2) transitions and near the saturation limit (with the Nd-YAG pumped dye laser) for the (0,2), (1,3), (2,4), (3,5) transitions. We were not able to probe $N_2^+(X, v''=0)$ as the (0,0) transition at 391.4 nm was not accessible to our apparatus.

Fig.3 gives as an example the spectra obtained when scanning over the (0,1) and (0,2) transitions. The rotational structure is well resolved but not the fine structure components of each rotational line. The intensity alternation due to nuclear spin¹⁵ is clearly visible. These spectra were recorded in the linear absorption regime. The dependence of the LIF signal recorded on the maximum of the P branch bandhead as a function of laser intensity is shown on fig.4a. Fig.4b gives the dependence of the LIF signal with laser intensity when working near the saturation limit. Even at high intensities there is still a small variation of the fluorescence signal mainly because saturation is not complete over all the beam profile.

Table I Wavelength and Franck-Condon Factors for the transitions used in absorption and emission.

Excitation			Detection		
(v', v'')	λ_{abs} (nm)	FCF ^a	(v', v'')	λ_{em} (nm)	FCF ^a
(0,1)	427.8	0.2619	(0,0)	391.4	0.6481
(0,2)	470.9	0.705	(0,0)	391.4	0.6481
(1,3)	465.2	465.2	(1,2)	423.6	0.2889
(2,4)	460	0.1699	(2,3)	419.9	0.2250
(3,5)	455.4	0.1720	(3,4)	416.7	0.1467

^a From A. Loftus and P.H. Krupenie¹².

Figure 4 Dependence of the LIF signal with the laser intensity obtained (a) with the N_2 pumped dye laser and (b) with the Nd-YAG pumped dye.

To derive the relative vibrational populations from the fluorescence spectra integration was performed over all rotational transitions between $N''=0$ and $N''=20$, for the P and R branches. As rotational states with $N''>20$ are only weakly populated, neglecting them is not a major error source. The relative populations $n(v_1)/n(v_2)$ are deduced from the integrated LIF signals $I_{\text{LIF}}(v_1)/I_{\text{LIF}}(v_2)$. In the linear regime the relative population are corrected for the laser fluence F , the Franck-Condon factors $q_{v',v''}$ for absorption and emission (the electronic transition moment is assumed to be constant¹⁶), the overall detection efficiency η for the emitted photons, and the frequency dependence of the Einstein coefficients (in ν^3 for the spontaneous emission coefficient A and in λ^2 for the absorption coefficient B , the dye laser being scanned in constant wavelength increments³).

$$\frac{n(v_1)}{n(v_2)} = \frac{I_{LIF}(v_1)}{I_{LIF}(v_2)} \frac{F_1}{F_2} \frac{q_{v'1,v_1}}{q_{v'2,v_2}} \frac{q_{v'1,v''1}}{q_{v'2,v''2}} \frac{\eta(v_1^{em})}{\eta(v_2^{em})} \left[\frac{v_1^{em}}{v_2^{em}} \right]^3 \left[\frac{\lambda_1^{abs}}{\lambda_2^{abs}} \right]^2$$

In the saturation regime the formula simplifies to

$$\frac{n(v_1)}{n(v_2)} = \frac{I_{LIF}(v_1)}{I_{LIF}(v_2)} \frac{q_{v'1,v''1}}{q_{v'2,v''2}} \frac{\eta(v_1^{em})}{\eta(v_2^{em})} \left[\frac{v_1^{em}}{v_2^{em}} \right]^3$$

As shown on fig.5 the relative populations are inverted, in qualitative agreement with the observations of Sekiya et al.¹ for the $v''=0-3$ levels. The significance of the much higher population found in the flowing afterglow experiment for the $v''=3$ level is not clear since the corresponding uncertainty was high due to the low FCF of the $\Delta v=0$ transition used ($q_{33}=0.001628$).

We did not observe any signal from vibrational levels higher than $v''=5$. However the overall detection sensitivity being much smaller for these levels they may be populated but not detected under our experimental conditions.

The high vibrational excitation observed suggests that highly excited states of N_2O^+ are involved in the charge transfer process with important changes in the N_2 bond strength and internuclear distance¹⁴.

Figure 5 Relative vibrational population of the $N_2^+(X,v'')$ ions produced from the He^+/N_2O charge transfer.

Rotational populations

Because of signal to noise ratio limitations only the rotational distributions within the $v''=1$ and $v''=2$ states have been analysed.

In the linear regime the LIF intensity of a rotational line in a given vibronic transition is proportional to the population in the initial rotational state $n(v'', N'')$ (normalised to its multiplicity), to the rotational line strength in absorption $S(N', N'')$, and to the detection efficiency for the emitted photons $\eta(h\nu_{em})$.

$$I_{\text{LIF}}(v', N' \leftarrow v'', N'') = \text{Cste } n(v'', N'') S(N', N'') \eta(h\nu_{em})$$

To analyse the rotational populations we compared the experimental spectra to simulated spectra. Simulation was performed using the line positions from Dick et al.¹⁷ and the rotational line strength factors

$$S^P(N'') = 6 N'' \text{ and } S^R(N'') = 6 (N''+1) \text{ for odd } N'' \text{ levels}$$

$$S^P(N'') = 12 N'' \text{ and } S^R(N'') = 12 (N''+1) \text{ for even } N'' \text{ levels}$$

which include the effect of nuclear spin.

Figure 6 Observed rotational populations of $\text{N}_2^+(\text{X})$ for (a) the $v''=1$ and (b) the $v''=2$ vibrational levels.

The rotational populations evaluated from the **R** branch line intensities are shown on fig.6. The rotational distribution in $v''=1$ is nearly completely relaxed at the time of the interaction with the laser beam and fitting to a Boltzmann distribution gives a rotational temperature of 300K. In $v''=2$ higher rotational states are populated and the mean rotational energy is around 50 meV (compared to 25 meV in $v''=1$).

IV-RELAXATION OF ROTATIONAL AND VIBRATIONAL ENERGY

The N_2^+ ions, resulting from from He^+/N_2O charge transfer reaction undergo several collisions with He and N_2O before beeing probed by the laser pulse. The time interval Δt_f between formation and detection of the ions ranges from 0 to 110 μs . However as most of the N_2^+ are formed during the electron pulse and as the fraction of ions lost because of space charge effects and charge transfer to N_2O increases with Δt_f , the average time interval can be roughly estimated to 20-50 μs . This corresponds to an average of 15 to 45 collisions with He and ten times less with N_2O in our experimental conditions ($P_{He} = 40$ mtorrs, $P_{N_2O} = 4$ mtorr).

Rotational relaxation

As we will see below collisions with N_2O result in fast charge transfer reaction and do not contribute to rotational relaxation. So the distribution observed result most probably from relaxation induced by N_2^+/He collisions.

To our knowledge there is no data on the rotational relaxation rate of $N_2^+(X)$ but it should not be very different from that of $N_2^+(B)$ which is also a $^2\Sigma^+$ state and has a very similar geometry. Plain and Joly¹⁸ have measured in $N_2^+(B, v''=0)$ total quenching rate out of a given rotational state and they found $16-25.3 \cdot 10^{-11}$ molecule⁻¹cm³s⁻¹ for $N'=0-15$. This would give, in 40 mtorr of He, relaxation times ranging from 2.8 to 4.4 μs . In other words around ten rotational transitions may be expected between production and detection of the ions. This explains why rotation is almost completely thermalised in our experimental conditions and also indicates that the initial rotational excitation cannot be very high even if multiple quantum transitions have appreciable probabilities.

Vibrational relaxation of the $\text{N}_2^+(\text{X}, \text{v}')$ ions

The vibrational relaxation induced by collision with helium atoms is very slow and does not occur even at much higher pressures². In our experiments the relative populations stayed unchanged when helium pressure was varied between 20 and 40 mtorr.

The main relaxation mechanisms are induced by collision with N_2O molecules and we found that the decay rate of the $\text{N}_2^+(\text{X}, \text{v}')$ increases almost linearly when N_2O partial pressure is increased from 4 to 20 mtorr.

There are two possible decay channels for $\text{N}_2^+(\text{X}, \text{v}')$:

- charge transfer $\text{N}_2^+(\text{X}, \text{v}') + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{N}_2\text{O}^+$
- vibrational relaxation $\text{N}_2^+(\text{X}, \text{v}') + \text{N}_2\text{O} \rightarrow \text{N}_2^+(\text{X}, \text{v} < \text{v}') + \text{N}_2\text{O}$

Charge transfer of N_2^+ with N_2O is exothermic by 2.7 eV for ground state N_2^+ . The rate constants found in the literature^{19,20} range from $7 \cdot 10^{-10}$ ($\pm 30\%$) to $5 \cdot 10^{-10}$ ($\pm 30\%$) $\text{molecule}^{-1}\text{cm}^3\text{s}^{-1}$ at 300 K, and the calculated capture rate²¹ is $1.02 \cdot 10^{-9}$ $\text{molecule}^{-1}\text{cm}^3\text{s}^{-1}$. This means that charge transfer occurs at almost every collision. We did not find any published results on the vibrational relaxation of N_2^+ by N_2O but vibrational relaxation rates are usually much smaller than the collision rate. Systematic measurements of $\text{NO}^+(\text{v}=1)$ and $\text{O}_2^+(\text{v}=1 \text{ and } 2)$ vibrational quenching by neutral molecules have been made in flow drift tube experiments²². The vibrational quenching of O_2^+ by CO_2 for example requires an average of 8.7 collisions for $\text{O}_2^+(\text{v}=1)$ and 4.4 collisions for $\text{O}_2^+(\text{v}=2)$ and quenching of $\text{NO}^+(\text{v}=1)$ by N_2O requires 5 collisions. There seems to be no reason why vibrational quenching of N_2^+ should be faster so that charge transfer is most probably the dominant process. As charge transfer is already exothermic for $\text{N}_2^+(\text{v}'=0)$ its rate constant should not depend much on the vibrational state therefore the relative populations should not be perturbed by this relaxation process.

V-CONCLUSION

Using Laser Induced Fluorescence to probe the internal energy

of the $N_2^+(X,v''J'')$ product we have shown that the dissociative charge transfer reaction of He^+ with N_2O produces mainly N_2^+ ions in their ground electronic state with inverted vibrational populations. Vibrational levels up to $v''=5$ have been observed corresponding to at least 1.31 eV of internal energy. In contrast rotational populations are almost completely relaxed which indicates that the initial rotational excitation cannot be very high. This demonstrates the possibilities of the LIF technique coupled with an ICR cell in probing product ions even in low density conditions.

Additional information on the energy disposal is needed to discuss the reaction dynamics and try to identify the intermediate N_2O^+ state(s) involved. This problem will be discussed elsewhere¹⁴.

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