

SPECTROSCOPIC EMISSIONS FROM THE RECOMBINATION OF N_2O^+ , $\text{N}_2\text{OH}^+/\text{HN}_2\text{O}^+$, CO_2^+ , CO_2H^+ , $\text{HCO}^+/\text{COH}^+$, H_2O^+ , NO_2^+ , HNO^+ , AND LIF MEASUREMENTS OF THE H ATOM YIELD FROM H_3^+ .

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Using the flowing-afterglow technique in conjunction with emission spectroscopy, we have obtained quantitative yields for several radiating states that arise from the dissociative recombination of N_2O^+ , $\text{N}_2\text{OH}^+/\text{HN}_2\text{O}^+$, CO_2^+ , CO_2H^+ , and $\text{HCO}^+/\text{COH}^+$. An application of laser-induced fluorescence (LIF) to the determination of the H-atom yield of H_3^+ recombination gave results in good agreement with those of merged-beam and ion-storage ring measurements.

1 Introduction

The goals of our work are to provide recombination coefficients for model calculations of planetary and cometary ionospheres and other space plasmas, to determine branching ratios for product atoms or radicals, and to study optical emissions that arise from recombining ions. In this paper, we present recent results on spectroscopic emissions from several recombining ions, and the H atom yield from the recombination of H_3^+ . Several investigators have obtained yields of ground-state, excited, and metastable products (see e.g. the review by Adams¹); however, very few data are available on absolute yields of radiating species. The formation of products in radiating states is of potential interest for the interpretation of planetary spectra and gives some insight into the mechanisms of recombination.

Recent experimental and theoretical work on dissociative recombination has led to two new findings: (a) It has become clear that the "standard curve crossing mechanism" does not provide the only route to recombination² and (b) that polyatomic ions tend to fragment into more different products than a single-bond-breaking model would predict. It has been suggested that recombination of polyatomic species proceeds through intermediate long-lived states³ (reaction complexes) in which a partial energy randomization occurs before dissociation. Unfortunately, theoretical models assuming completely randomized complexes, e.g. the statistical phase-space calculations by Galloway and Herbst⁴ have not been entirely successful in predicting branching fraction. Our spectroscopic data complement product information obtained in ion-storage rings (ISR)⁵ and thus lead to a more complete picture of the process.

2 Experimental methods

The flowing-afterglow system⁶ that was used for this work has the configuration shown in Fig. 1. A plasma in the pure carrier gas (helium) is generated in a microwave discharge. Argon gas (at a pressure of typically 15% of the helium pressure) is added further downstream to convert metastable helium atoms to argon ions by Penning ionization. At this point, the plasma contains mainly atomic Ar^+ ions at densities near $4 \times 10^{10} \text{ cm}^{-3}$. The slow dielectronic recombination of Ar^+ ions produces a small concentration of argon metastables (~ 10 to 15% of the electron density). In addition, a small concentration of He^+ ($\sim 1\%$ of the electron density) of atomic helium ions arises from collisions between helium metastables. The reagent gases that initiate formation of the desired molecular ions are added through several movable and fixed reagent inlets. The region downstream from the reagent inlet is the recombination zone where most observations are carried out.

The principal diagnostic tools are:

a) A quadrupole mass filter is used to analyze the ion composition of the plasma. Its primary purpose is to make sure that the plasma contains predominantly the ion species whose recombination is to be studied.

b) A movable Langmuir probe (diameter = $25\mu\text{m}$, length = 3–4 mm) serves to measure electron densities at different points in the plasma. We use Langmuir probes exclusively in the electron-collecting mode since a series of tests⁷ showed that ion-collecting probes can produce misleading results.

c) Emission spectroscopy of the plasma is carried out in narrow, disc-shaped sections along the entire length of the flow tube by means of a movable monochromator that views the plasma through a long quartz window. The system is sufficiently sensitive to detect weakly-emitting species and minor channels arising from electron-ion recombination with a spectral resolution of $6\text{ \AA}$ in the wavelength range from 180 to 800 nm. The spectral response is measured using standard procedures.

d) The identification of non-emitting products of dissociative recombination relies on laser-induced fluorescence (LIF) using an excimer-pumped tunable dye laser. The laser beam enters through a port at the downstream end of the tube and is deflected by a diagonal mirror to an exit port at the upstream end. The LIF signal is observed by a filtered phototube that moves along the flow tube and measures the concentration of recombination products at different points.

Whenever possible, we seek to determine absolute branching fractions of product channels. The calibration of photon count rates from emission and LIF measurements makes use of well-characterized reactions. For instance, the emission detector is calibrated using N_2^+ (B-X) emission from the $\text{He}^* (2^3\text{S}) + \text{N}_2$ reaction⁸, the He^* flux being determined from Langmuir probe measurements of the Penning-ion yield. The LIF signal is calibrated using reactions of $\text{Ar}^* ({}^3\text{P}_{2,0})$ ⁹ as a source of the radical of interest while the Ar^* concentration is determined either by Penning ionization analysis, or by measurement of the N_2 (C-B) emission intensity from the reaction $\text{Ar}^* + \text{N}_2$.

To distinguish emissions from recombining ions from those of extraneous sources, an electron scavenging gas (SF_6) was added.

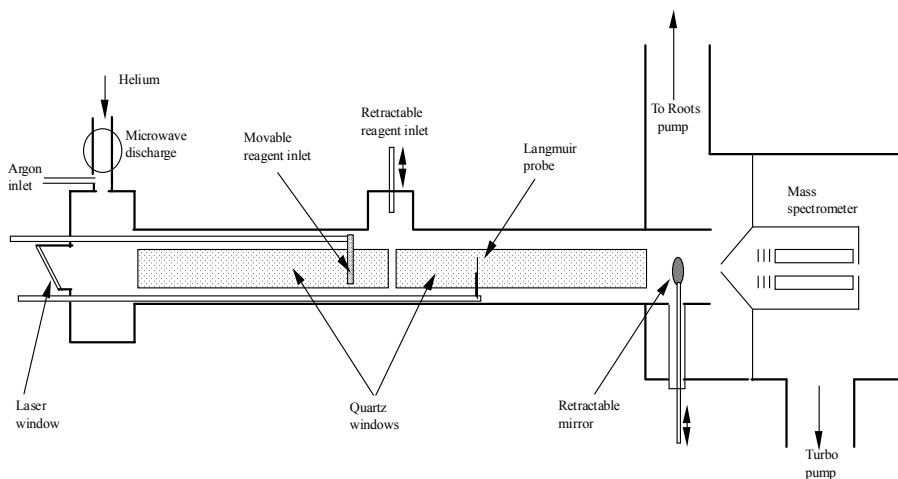


Fig. 1 Schematic diagram of the flowing afterglow apparatus

The methods of analyzing flow-tube data are very well known and will not be described here. We have developed computer models that allow accurate modeling of diffusion, gas mixing, ion-molecule reactions, recombination, and product formation. Some details of these methods have been presented in a recent publication⁶.

3 Emission spectra produced by dissociative recombination

3.1 H_3^+

We had expected to observe emissions from H_3^+ plasmas, since other work seemed to suggest that such emissions should be present (see discussion and references in Gougousi et al.¹⁰). However, no spectral emissions that could be ascribed to dissociative recombination of H_3^+ were found in the wavelength range from 550 to 750 nm. This confirms the negative findings of Adams¹¹.

3.2 N_2O^+

In the case of several other ions, significant spectral emissions were observed but the absolute yields of the radiating states were quite small. For instance, the yield for $N_2O^+ + e \rightarrow NO(B^2\Pi_i) + N(^4S)$ (0.6 %)

is only 0.6 percent. The spectrum (Fig. 2) also shows emissions of the N_2 ($C^3\Pi - B^3\Pi$) bands. In addition, the $NO(A^2\Sigma^+ - X^2\Pi)$ bands were observed.

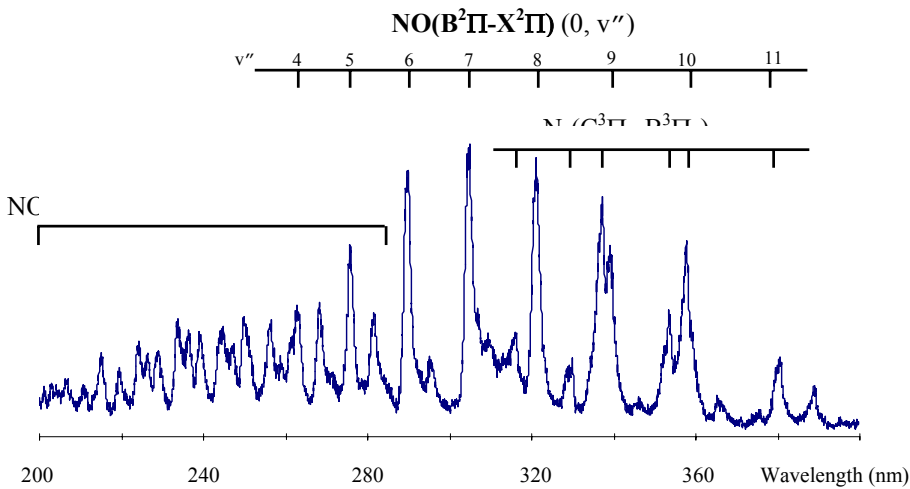
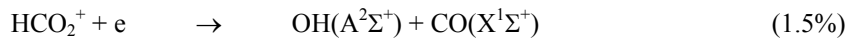


Fig. 2 Emission spectrum arising from recombination of N_2O^+ ions

3.3 HCO_2^+

The recombination of HCO_2^+



leads to formation of OH (A) in $v=0$ and $v=1$, but again the yield is quite small. An example of a recorded spectrum is shown in Fig. 3

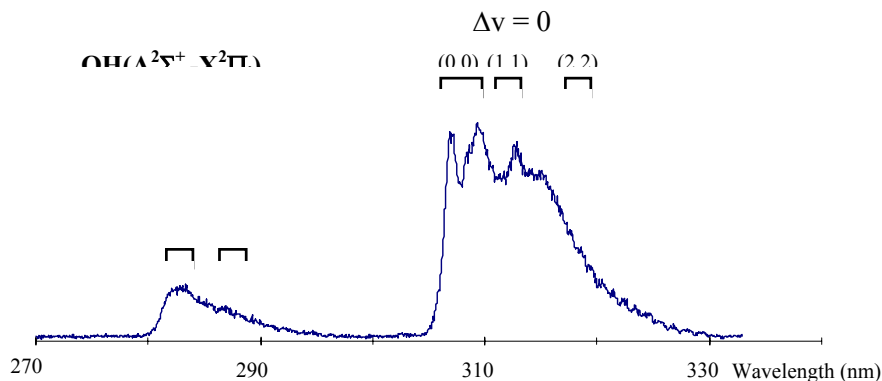
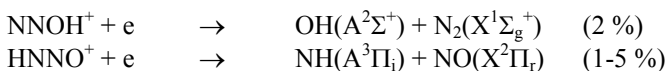


Fig. 3 Emission spectrum arising from recombination of HCO_2^+ ions

3.4 N_2OH^+

One of the more interesting findings of this work was the observation that both NH and OH spectra (Fig.4) are emitted in recombining plasmas containing N_2OH^+ ions. They appear to arise from recombination of the two isomeric species HNNO^+ and NNOH^+ :



The yields of both radiating states are again quite small.

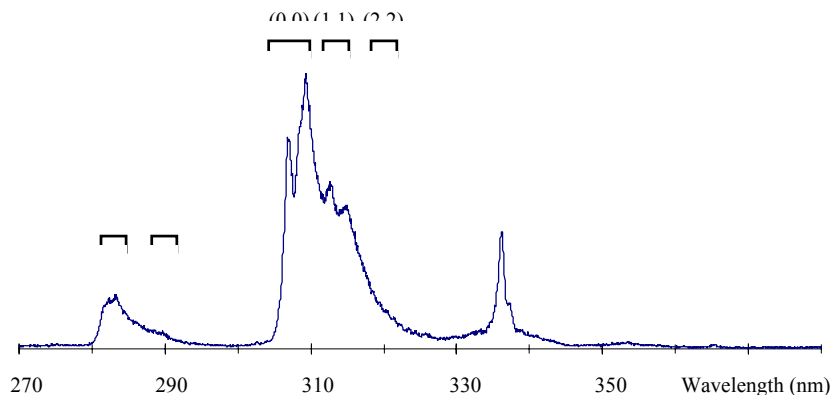


Fig. 4 Emission spectrum arising from recombination of $\text{N}_2\text{OH}^+/\text{HN}_2\text{O}^+$ ions

3.5 CO_2^+

It had been known from the work by Wauchop and Broida,¹² and Taieb and Broida¹³ that several emissions features arise from DR of CO_2^+ . Our results¹⁴ show substantial emissions (see Fig. 5) from the long-lived $\text{a}^3\Pi_r$ state which is populated in part directly by the recombination channel



but also by cascading from higher states. This yield is only about one half of that obtained in the earlier work(55 %) ^{12, 13}.

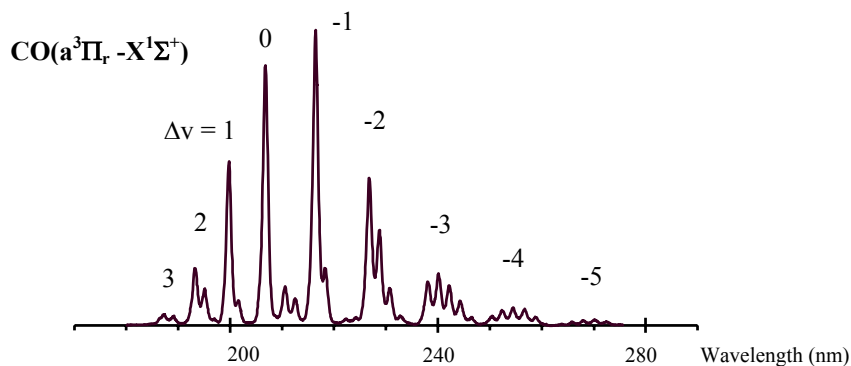
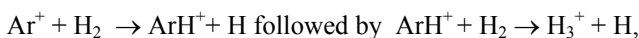


Fig. 5 UV-emission spectrum arising from recombination of CO_2^+ ions.

We have obtained spectroscopic evidence that the $\text{CO}(a^3\Pi_r)$ state is, in part, populated by radiative transitions from higher states ($a^3\Sigma^+$, $d^3\Delta_i$, $e^3\Sigma^-$) but we have not yet been able to determine the magnitude of the cascading contribution.

3.6 HCO^+ , COH^+

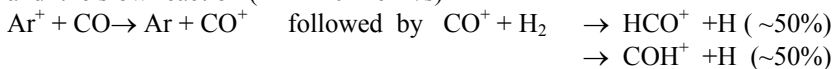
In a further experiment, we studied the emission spectra that arise from the dissociative recombination of HCO^+ and from its isomer COH^+ . We employed a reaction scheme that starts from



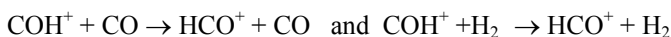
but we added CO along with H_2 so that the reactions



and the slow reaction ($k \sim 4 \times 10^{-11} \text{ cm}^3/\text{s}$)



produce a mixture of the two isomers. Kinetic modeling shows that the fractional concentration of the COH^+ isomer remains small (several %) under our conditions. Furthermore, as a result of the reactions¹⁵



the COH^+ isomer converts to HCO^+ , which makes modeling more difficult. The spectra, which are similar to those in Fig. 5 show that recombination results in $\text{CO}(a^3\Pi_r)$ with an effective yield (including cascading from higher states) of about 30% for a mixture of the two isomeric forms. Since HCO^+ is far more abundant, the spectrum must be predominantly due to this isomer. In addition, several intense emissions (e-a, d-a, a'-a) from higher-lying states of CO (see Fig. 6) were observed which can only arise from the more energetic COH^+ isomer.

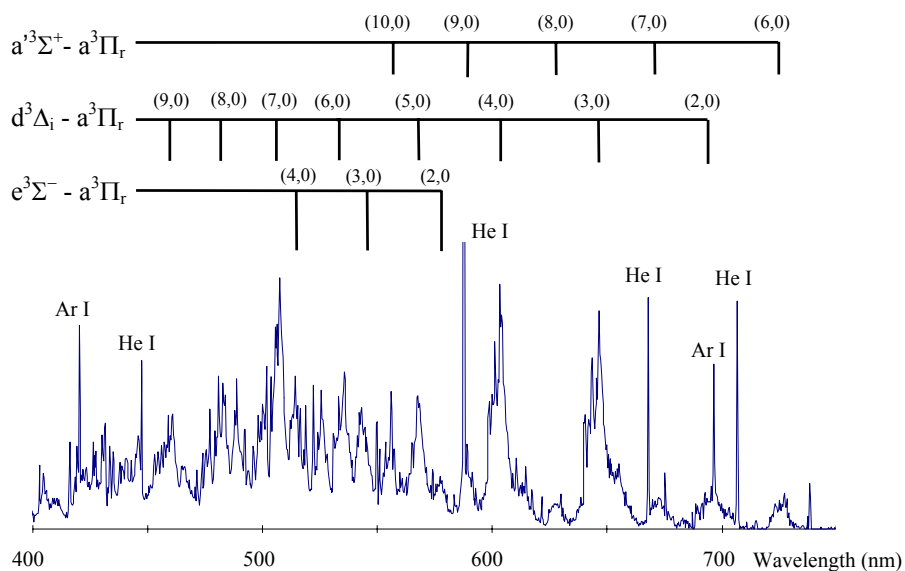


Fig. 6 Visible emission spectrum arising from recombination of COH^+ ions. The spectrum has not been corrected for the decreasing sensitivity of the photodetection system above 600nm.

3.7 H_2O^+ , NO_2^+ , HNO^+

In the course of this work we observed spectra produced by several other recombining ions but we did not obtain quantitative yields.

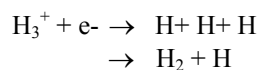
We confirmed the Sonnenfroh et al. observation that H_2O^+ recombination produces the $\text{OH}(\text{A}^2\Sigma^+ - \text{X}^2\Pi)$ bands. The observed vibrational distribution (70% for $v=0$, 30% for $v=1$) was substantially "colder" than that found by Sonnenfroh et al.¹⁶ at an elevated electron temperature of $\sim 1000\text{K}$ (53% for $v=0$, 47% for $v=1$).

The recombination of NO_2^+ ions was found to produce $\text{NO}(\text{A}^2\Sigma^+ - \text{X}^2\Pi)$ and weaker $\text{NO}(\text{B}^2\Pi - \text{X}^2\Pi)$ bands. We are not aware of any earlier results.

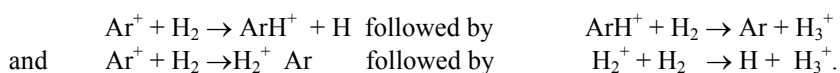
The only significant emissions from HNO^+ recombination appear to be $\text{NO}(\text{A}^2\Sigma^+ - \text{X}^2\Pi)$ bands.

4 H atom yield from H_3^+

As has been mentioned earlier, we failed to detect emissions from a recombining H_3^+ plasma. However, we did succeed in using laser-induced fluorescence (LIF) to determine the H-atom yield of the dissociative recombination of H_3^+ ions,



The H_3^+ plasma was prepared by the reactions:



H atoms produced by recombination were made detectable by LIF by converting them to OH radicals, using the reaction $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$.

Subsequently, the OH radicals were quantitatively measured¹ by LIF using the $\text{OH}(X^2\Pi \rightarrow A^2\Sigma^+)$ transition. The calibration of the LIF intensity relied on the known yields of H atoms from the recombination of N_2H^+ ($f_{\text{H}}=1$) and HCOS^+ ($f_{\text{H}}=0.1$)¹⁷ ions, which were produced by similar ion-molecule reaction schemes. All LIF observations were carried out in a spatially resolved manner (see Fig. 7), and the observed position-dependent LIF signal was compared to that obtained from computer modeling.

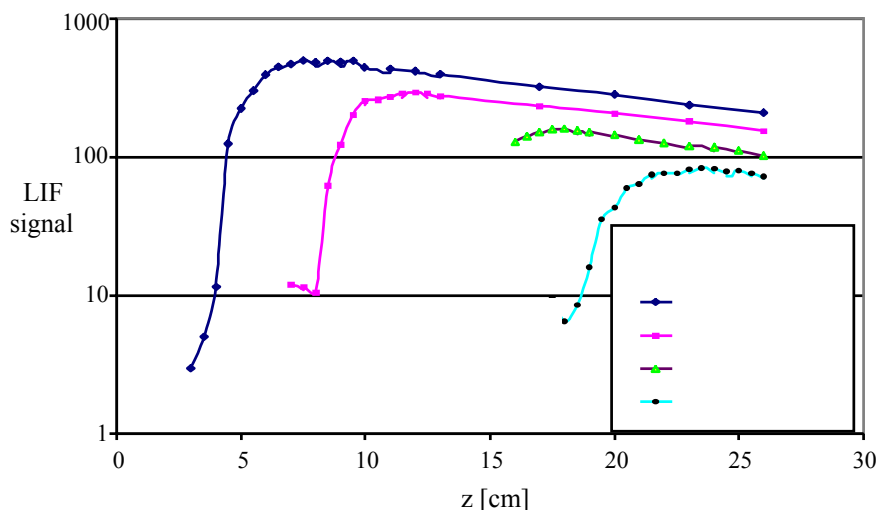


Fig. 7 Data on the H atom yield from H_3^+ recombination. The LIF signal reflects the concentration of OH radicals produced by conversion of H atoms to OH via the $\text{H} + \text{NO}_2$ reaction. The NO_2 was added at different positions in the flow tube (from $z=4.5$ cm to $z=19$ cm from the onset of the recombination region).

We encountered one technical problem in this work that made accurate computer modeling difficult: It is usually assumed that reagents added to a flowing afterglow are quickly carried downstream and that diffusion upstream can be ignored. The assumption turns out to be rather poor for a light gas like H_2 . As a consequence, the onset of the recombination zone is poorly defined, which leads to some uncertainty in the results.

The observations indicate that the recombination of H_3^+ ions on average produces 2.2 ± 0.3 H atoms, which implies a 63% probability of the channel producing 3 H atoms, and 37% probability for the $\text{H} + \text{H}_2$ channel. Considering the entirely different experimental method used here, the results are remarkably close to those obtained in merged beam experiments³ ($f_{\text{H}} \sim 2$) and those of storage-ring data⁵ ($f_{\text{H}} = 2.5$).

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