Optical Spectroscopy of Recombining Ions in Flowing Afterglow Plasmas

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1.   INTRODUCTION

Spectroscopy has been an important tool in studies of dissociative recombination (DR) for many years. The early work by Biondi[1] and co-workers established the dissociative nature of the process by demonstrating the Doppler broadening of spectral lines due to the momentum that is imparted on the separating recombination fragments. In more recent work, spectroscopic methods have been used to identify products of DR of diatomic and polyatomic ions and to quantitatively measure yields for specified states of radiating recombination products. The formation of products in radiating states is of potential interest for the interpretation of planetary spectra and perhaps those observed from interstellar clouds, and of course, experimenters hope that their identification of product states will lead to new insights into the mechanisms of recombination.

Both stationary or flowing afterglow plasmas are excellent media for studying emissions from recombining molecular ions. A good introduction and references to the relevant methods can be found in the review article by Adams[2] who carried out a survey of emission spectra from several recombining ions. Quantitative spectroscopy is considerably more difficult and hence data on quantitative yields of radiating species are still quite sparse. As was pointed out by Herbst[3] in this meeting, absolute yields are

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needed for the interpretation of spectra from interstellar clouds. Such measurements are being carried in our group at the University of Pittsburgh and they are the principal subject of this contribution to the symposium.

It is acknowledged that, compared to spectroscopic afterglow methods, ion-storage rings (ISR)[4] are a more powerful tool for measuring <u>complete</u> product yields into all channels, but at this time it is not possible to carry out optical spectroscopy in ion storage rings due to the low concentration of ions and electrons. Thus, we view afterglow methods and the ISR techniques as complementary rather than as competing with each other.

In the following, we will use the term "spectroscopic yield " to denote the fraction of recombination events that results in formation of a specified electronic state. This yield is not necessarily identical to the nascent recombination yield of this product state since the state may also be populated by a radiative transition from a higher state that is formed in recombination. The nascent yield may be obtained by measuring and subtracting the cascading contribution, if there is any, from higher states. The procedure usually requires comparing photon count rates that are observed at widely different wavelength, which in turn requires a precise knowledge of the wavelength-dependence of the photometric sensitivity of the optical detection system. The finer points will be discussed later.

2.   STATIONARY AND FLOWING AFTERGLOWS

In a stationary (or static) afterglow system[5], a plasma is generated by exposing a suitable gas mixture, generally a rare gas with small admixtures of other gases, to a pulsed microwave or other electrical discharge, or to an intense flux of ultraviolet radiation, or perhaps a high-energy electron beam. The microwave discharge is used most often. Upon termination of the discharge, the electron density decay is measured by using Langmuir probes, by measuring the frequency shift of a resonant microwave cavity mode, or by measuring the real part of the plasma conductivity using a radio-frequency method. Other diagnostic tools typically include a mass spectrometer that records the evolution of the relative ion concentrations as a function of afterglow time.

The spectroscopic measurements most often employ monochromators, sometimes interference filters, and, for line-shape measurements, Fabry-Perot interferometers. Photon counting techniques are used almost exclusively. The analysis of the plasma decay in stationary afterglows is

simple when only a single-ion species is present and when ambipolar diffusion is very slow. In general, numerical solutions are required. Since the intensity of emissions that result from short-lived radiating recombination products is proportional to the square of the electron density n_e, a simple but very useful test of the consistency of experimental observations consists of comparing the rates of decay of the electron density, the square root of the emission intensity, and the mass selected ion currents that are detected by the mass spectrometer (where available).

The stationary afterglow method has some strength but also some weaknesses. One problem is that the molecular additives that are required to make the desired ions are exposed to an intensive discharge, which may result in dissociation, electronic and vibrational excitation, and formation of new chemical species. Vibrational excitation of the neutral gases can persist into the afterglow, produce heating of the electron gas and persistent vibrational excitation of the ions under study[6]. In pure rare gases, of course, such problems do not arise.

The flowing afterglow, to be described in detail later, has the virtue of allowing far better control over the ion-chemistry than is possible in the stationary afterglow. Here, the molecular gases are added downstream from the discharge region and they are never directly exposed to the discharge that typically operates in pure helium. Energetic particles, mainly metastable helium atoms, are safely converted to argon ions before molecular gases are added.

A brief note of warning to flowing-afterglow users: While helium metastables are indeed removed by Penning ionization with argon, the resulting atomic argon ions recombine with electrons by three-body recombination and form metastable argon atoms (with concentrations of 10 to 20 % of the ion density) and those can lead to unexpected reactions. Also, there is some evidence that radiatively trapped ultraviolet photons from the discharge enter the reaction region. This seems to happen in spite of the usual precaution of putting a right-angle bend into the discharge inlet such that there is no line-of-sight path to the reaction region.

Modeling of the ion-kinetic processes in flowing afterglow plasmas is almost always required. In the work in Pittsburgh, we use computer models that include the relevant kinetic processes, ambipolar diffusion in gas flowing with the proper parabolic dependence of flow velocity on the radial coordinate, and an approximate treatment of the gas mixing downstream from the gas injection port.

2.1   Stationary-afterglow data on molecular dimer ions

We mention this subject here, in part, to draw attention to the problem of accounting for the anomalously large recombination coefficients of cluster and dimer ions. It is striking that weakly-bound molecular dimer ions, such as $N_2^+N_2$ and CO^+CO recombine much faster than the monomers. At one time D. Bates[7] postulated that such ions undergo what he called "super dissociative recombination" and he ascribed the high recombination rate to the availability of dissociation channels into excited states of the molecular fragments. Bates proposed that the super-dissociative mechanism is also responsible for the high recombination rates of the weakly-bound rare-gas dimer ions (except for He_2^+) which were the first ions studied by Biondi[1]

Partly in response to Bates' suggestion, Cao and Johnsen[8] carried out measurements on $N_2^+N_2$ recombination in a high-pressure (several hundred Torr) stationary afterglow system that was well-suited for this work because the high pressure promotes rapid conversion of the monomer to dimers ions. In addition, $COCO^+$ ions were studied (unpublished). The recombination rates indeed were found to be very large ($\sim$2.5 x 10^{-6} cm^3/s) and both exhibited strong emissions of molecular bands. In the case of N_4^+, the second positive band system of N_2 ($C^3\Pi_u - B^3\Pi_g$) was observed while three band systems were found to arise from recombination of $COCO^+$, the third positive band ($b^3\Sigma -a^3\Pi$), the Angström band ($B^1\Sigma-A^1\Pi$), and the Herman band ($e^3\Sigma-a^3\Pi$) . The origin of the emissions was clearly recombination, as evidenced by their disappearance on adding an electron scavenger (SF_6) and the observed scaling of intensities with n_e^2.

The observation of the molecular bands supports Bates conjecture, but since absolute yields were not determined it has not been shown that the observed dissociation channels are dominant and responsible for the large recombination coefficient. The same statement applies to the recombination of rare-gas dimer ions; we still do not know if the spectroscopically observed states are indeed dominant. It would be interesting to perform measurements on dimer ions in an ion storage ring experiment to see if (a) similar high rate coefficients are found and (b) if other product channels exist.

## 3. ABSOLUTE SPECTROSCOPY IN FLOWING AFTERGLOWS

We now turn our attention to measurements of absolute yields. The flowing-afterglow system[9] that we used has the configuration shown in Fig. 1. Metastable helium atoms, produced in a microwave discharge in helium, are converted by Penning ionization to Ar^+ ions by downstream addition of argon (density ~ 15% of that of helium). Ion and electron densities at this point are ~ 4×10^{10} cm^{-3}. The reagent gases that initiate formation of the desired molecular ions are added through movable and fixed reagent inlets.

The diagnostic tools include a quadrupole mass filter that analyzes the ion composition of the plasma at a point downstream from the reagent inlet, and a movable Langmuir probe (diameter = 25μm, length = 3-4 mm) that measures electron densities. The Langmuir probes are used in the electron-collecting mode since a series of tests[10] showed that ion-collecting probes produce misleading results.

Emission spectroscopy of the plasma is carried out by a movable (along the direction of the flow) monochromator/phototube system (McPherson 0.3 m monochromator, Hamamatsu R943-02 phototube) that views the plasma through a long quartz window. The system covers the spectral range from 200 to 900 nm. An in-situ absolute calibration of the optical systems was performed by measuring the intensity of the $N_2(C^3\Pi_u\text{-}B^3\Pi_g)(0,0)$ band at 337 nm, excited by the reaction

$$Ar^* + N_2 \rightarrow Ar + N_2(C^3\Pi_u) \quad \text{(yield } 0.80\pm0.20))^{11,12}$$
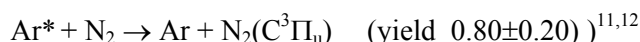
The flux of Ar* was determined by converting the Ar* atoms to NO^+ ions in the reaction

$$Ar^* + NO \rightarrow Ar + NO^+ + e \quad \text{(yield } 0.35\pm0.10)^{13,14}$$
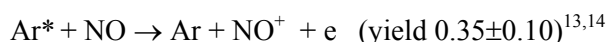
and using the Langmuir probe to measure the electron density increase due to this reaction. The spectral response of the system at other wavelengths was measured using a calibrated tungsten lamp in the red, a deuterium lamp in the uv-to visible range, and joining the two response curves in the overlapping spectral range.

To distinguish emissions from recombining ions from those of extraneous sources, an electron scavenging gas (SF_6) was added.
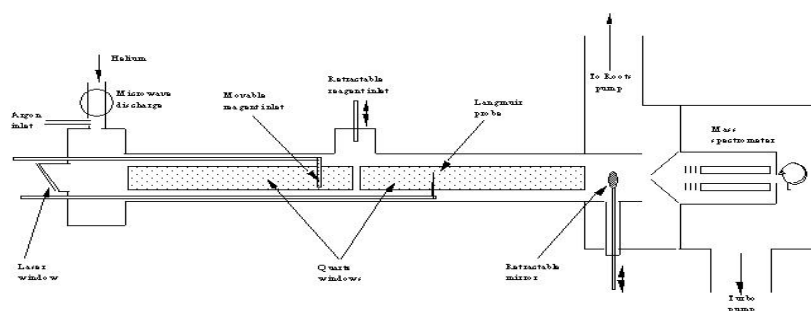
Figure 1. Schematic diagram of the flowing-afterglow tube

The methods of analyzing flow-tube data are very well known and will not be described here. We use 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 publication [9].

3.1   Emission spectra and yields from DR of N_2O^+, HCO_2^+, N_2OH^+, HCO^+/COH^+, and CO_2^+

In this section, we will give a few examples of recent and ongoing flowing-afterglow measurements of spectroscopic yields from the recombination of several ions. Due to space limitations, we cannot reproduce figures of all spectral scans. Some may be found in a recent book chapter[15].

Many recombining ion species were found to produce measurable spectral emissions but the absolute yields of the radiating states were often found to be quite small.

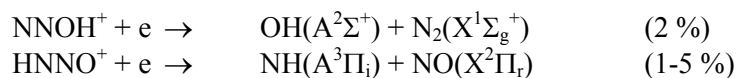For instance, the yield for $NO(B^2\Pi_i)$ from the recombination

$$N_2O^+ + e \rightarrow \quad NO(B^2\Pi_i) + N(^4S),$$

as determined from the intensity of the NO $(B^2\Pi-X\ ^2\Pi)$ band, is only 0.6 percent. The spectra show additional weak emissions of the N_2 $(C^3\Pi - B^3\Pi)$ bands and the $NO(A^2\Sigma^+- X^2\Pi)$ bands.

Similarly, the yield of the recombination branch

$$HCO_2^+ + e \rightarrow \quad OH(A^2\Sigma^+) + CO(X^1\Sigma^+) ,$$

as determined from the intensity of the observed $OH(A^2\Sigma^+-X^2\Pi_i)$ (v=0 and v=1) band system, also is quite small (1.5%).

One interesting result of this work, which still awaits a complete analysis, is the finding that both $NH(A^3\Pi_i-X^3\Sigma)$ and $OH(A^2\Sigma^+-X^2\Pi_i)$ spectra are emitted in recombining plasmas containing N_2OH^+ ions. This suggests that the emissions arise from recombination of the two isomeric species $HNNO^+$ and $NNOH^+$

$$NNOH^+ + e \rightarrow \quad OH(A^2\Sigma^+) + N_2(X^1\Sigma_g^+) \quad\quad\quad (2\ \%)$$
$$HNNO^+ + e \rightarrow \quad NH(A^3\Pi_i) + NO(X^2\Pi_r) \quad\quad\quad (1\text{-}5\ \%)$$

The intensity of the NH band decayed far more rapidly with axial position than that of OH. This observation supports the assumptions that the bands arise from two distinct ions species, while ruling out the alternative explanation that recombination involves a major rearrangement of the molecule. The yields of both radiating states are again quite small, 2% for $OH(A^2\Sigma^+)$ and 1-5 % for $NH(A^3\Pi_i)$.
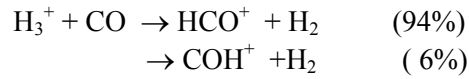
Recombination of HCO^+ and its isomeric form COH^+ are interesting processes for astrophysical applications. In a still ongoing experiment, we study the emission spectra that arise from the dissociative recombination of HCO^+/ COH^+ by producing a mixture of those ions using the a reaction scheme that starts from
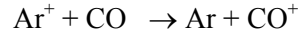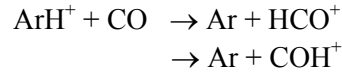
$$Ar^+ + H_2 \quad \rightarrow ArH^+ + H$$

and

$$ArH^+ + H_2 \rightarrow H_3^+ + H.$$
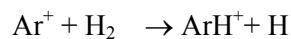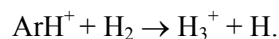
By adding CO and H_2 the subsequent reactions[16]

$$H_3^+ + CO \rightarrow HCO^+ + H_2 \qquad (94\%)$$
$$\rightarrow COH^+ + H_2 \qquad (\ 6\%)$$

and the reactions

$$ArH^+ + CO \rightarrow Ar + HCO^+$$
$$\rightarrow Ar + COH^+$$

$$Ar^+ + CO \rightarrow Ar + CO^+$$

and

$$CO^+ + H_2 \rightarrow HCO^+ + H \qquad (\sim 50\%)$$
$$\rightarrow COH^+ + H \qquad (\sim 50\%)$$
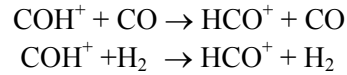
produce both isomers[17]. Kinetic modeling, based on currently available branching fractions, shows that the fractional concentration of the more energetic COH^+ isomer should remain small (several %) under our conditions. Conversion of COH^+ to HCO^+ occurs by the reactions[18]

$$COH^+ + CO \rightarrow HCO^+ + CO$$

and

$$COH^+ + H_2 \rightarrow HCO^+ + H_2$$

The intensity of the wavelength-integrated uv-spectra show that recombination of HCO^+/ COH^+ results in $CO(a^3\Pi_r)$ with an effective yield (including cascading from higher states) of (26+ 10) % for a mixture of the two isomeric forms. Since HCO^+ is far more abundant, the $CO(a^3\Pi_r)$ product must predominantly arise from HCO^+. However, several intense visible emissions (e-a, d-a, a'-a) from higher-lying states of CO are observed also. It is energetically possible to populate the e and d states in recombination of COH^+ but not in recombination of HCO^+.
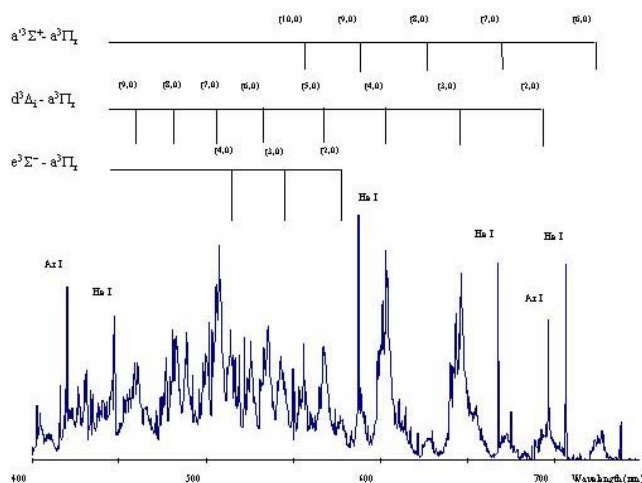
Figure 2. Spectral scan from 400 to 700 nm of (e-a, d-a, a'-a) band emissions from recombination of a mixture of HCO^+/COH^+ ions. The atomic helium and argon lines are due to scattered light from the discharge and upstream region of the plasma.

Fig 2 shows a spectrum of the overlapping visible emissions from the higher-lying states of CO. Clearly, the spectrum contains much information but it is difficult to identify the origin of particular features. It helps to investigate how the spectrum changes with the axial position in the flow tube ('afterglow time'). Measurements show that emissions from the d state and from a'(v>4) levels decay much faster than those originating from the a' (v≤4) levels. This seems to indicate that the d state is populated by recombination of COH^+ while different vibrational levels of a' may be populated by recombination of HCO^+ and COH^+. A faster decay of COH^+ is to be expected since this isomer is destroyed (converted to HCO^+) in the reactions with H_2 and CO. The data available at the time of this writing are compatible with the assumption that both isomers recombine with the same rate, but more data need at different conditions have to be taken to reach a firm conclusion.

Our earlier published work on CO_2^+ recombination[19] indicated substantial emissions from the long-lived $a^3\Pi_r$ state. This confirmed the work by Wauchop and Broida,[20] and Taieb and Broida [21] . It was concluded that this state is populated directly by the recombination channel

$$CO_2^+ + e \qquad \rightarrow \qquad CO(a^3\Pi_r) + O(^3P)$$

and, in addition, by cascading from higher states ($a'^3\Sigma^+$, $d\,^3\Delta_i$, $e^3\Sigma^-$) but the magnitude of cascading contribution was not determined at that time. The spectroscopic yield (~29%) of $CO(a^3\Pi_r)$ was only about one half of that obtained in the earlier work(55 %) [20, 21]. After a more thorough calibration of the optical system and additional model calculations, we concluded that cascading contributes from 50 to 100 % to the long-lived CO(a). The combined yield for the states a', d, and e was found to be (22+7) %. Using the relative yields measured by Tsuji et al [22] , the absolute yields would be 13 % for a', 8% for d, and 1.7% for e. The uncertainty in the cascading contribution to CO(a) is still rather large. One problem is that our computer models do not accurately reproduce the z-dependence of the measured intensities in the visible range, especially in the vicinity of the reagent inlet. Recent modifications of the gas inlet and a reduction of light scattering in the flow tube have improved the situation and we hope to be able to arrive at a more accurate determination of the cascading contributions.

4.   NO EMISSIONS FROM DR OF H_3^+?

We had expected to observe emissions from H_3^+ recombination since some experimental work suggested that such emissions should be present (see also discussion and references in Gougousi et al.[23]). The very recent work by Glosik and coworkers in Prague [24] strongly suggests that the recombination of H_3^+ proceeds via a long-lived H_3 complex which can reasonably be expected to undergo radiative transitions, as had been suggested earlier by Gougousi et al. However, no spectral emissions that could be ascribed to dissociative recombination of H_3^+ were found by us in the wavelength range from 200 to 900. Adams[25] reported a similar negative finding. It seems ironic that the first observations of the H_3 spectrum by Herzberg and coworkers (see e.g. Dabrowski and Herzberg[26]) were ascribed to recombination. At this time, the most likely explanation of the origin of the spectra observed by Herzberg and coworkers may be that the process

responsible was dissociative recombination of H_5^+ ions rather than of H_3^+. In this context, the observation of line broadening in some H_3 rotational lines by Miderski and Gellene [27] is very interesting. The authors ascribed the broadening to the energy released in dissociative recombination of H_5^+ into H_2 and H_3^* . It would be interesting to repeat these experiments in a cooled flowing afterglow experiment and with higher-resolution interferometric techniques.

5.   CONCLUSIONS

The spectroscopy of recombining afterglow plasmas provides a rich and important tool for investigating dissociative recombination process. However, the interpretation of observed spectra is subtle and complicated, more so if one seeks to obtain absolute yields for particular states. In many cases, the yields for radiating states are small. That does not make them uninteresting since the observed spectral features may still be useful for diagnostic purposes in laboratory and space plasmas. One also quickly discovers that the recombining plasma may contain mixtures of isomeric form of the same ion and that those can give rise to different spectra. While this complicates the interpretation further, it also allows studies of the different recombination behavior of different isomeric forms, which are difficult to do by other methods.

The recombination mechanism of H_3^+ ions received much attention during this symposium but it remains an 'enigma'. The absence of measurable emissions may contain some hints but we do not know in which direction they point.

ACKNOWLEDGMENT

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