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Electron-temperature dependence of the recombination of HCO^+ ions with electrons

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A microwave-afterglow mass-spectrometer apparatus employing microwave heating of the electrons has been used to determine the dependence on electron temperature T_e of the recombination coefficient of electrons with HCO^+ ions. By comparison of the observed electron-density decays to the computed behavior of a recombination- and ambipolar-diffusion-controlled afterglow, it is found that the electron-temperature dependence of the recombination coefficients follows a power law of the form $\alpha(HCO^+)\ (cm^3/s)=(2.4\pm0.4)\times10^{-7}[T_e\,(K)/300]^{-0.69\pm0.07}$ over the range 293 $K<T_e<5500$ K. The magnitude of the recombination coefficient is similar to that observed and calculated for simple diatomic ions, while the temperature dependence is somewhat stronger than the $T_e^{-0.5}$ dependence predicted by a simplified theory for diatomic ions.

I. INTRODUCTION

The rate coefficient for recombination of electrons with HCO^+ ions is of interest primarily because of their presence in interstellar gas clouds,[1,2] in flames,[3] and possibly in the ionospheres of the outer planets, where dissociative recombination plays an important role in determining the plasma characteristics. The first experimental determination of the recombination coefficient at temperatures of 205 and 300 K was carried out by Leu *et al.*,[4] who used a static microwave-afterglow apparatus with mass-spectrometric identification of the plasma ions. Subsequently, Adams *et al.*[5] used a flowing-afterglow Langmuir-probe apparatus to measure these coefficients at 95 and 300 K. The present study extends these measurements to electron temperatures from 293 to 5000 K.

In Secs. II–V we briefly describe the experimental method and apparatus, discuss methods of data analysis, compare the results to previous data, and discuss the potential implications of our findings.

II. EXPERIMENTAL METHOD AND APPARATUS

The microwave-afterglow mass-spectrometer apparatus has been described in detail in earlier publications.[6–8] The apparatus was essentially unchanged in the present studies, except for placing a liquid-nitrogen cooled, cold finger in a sidearm of the microwave cavity. The cold trap was used to reduce troublesome water-vapor impurities.

The weakly ionized plasma (electron densities of 10^9-10^{10} cm^{-3}) was generated by pulsed, microwave energy (microwave pulses of 40 μs duration, repeated ten times per second) applied to gas mixtures composed predominantly of neon (typically 12 torr) with small additions of hydrogen and carbon monoxide (both at pressures of 0.16 torr). The steps leading to production of the desired HCO^+ ions are thought to involve Penning ionization by metastable neon atoms of CO and H_2, followed by the ion-molecule reactions

$$CO^+ + H_2 \rightarrow HCO^+ + H\ , \tag{1}$$

$$H_2{}^+ + CO \rightarrow HCO^+ + H\ , \tag{2}$$

and

$$H_2{}^+ + H_2 \rightarrow H_3{}^+ + H\ , \tag{3}$$

followed by

$$H_3{}^+ + CO \rightarrow HCO^+ + H_2\ . \tag{4}$$

The rate coefficients for these reactions are large [$>10^{-9}$ cm^3/s (Refs. 9–12)]. At the H_2 and CO concentrations used in the experiment, the reactions go to completion in a short time compared to the time scales characteristic for electron-ion recombination, i.e., HCO^+ dominates the ion composition during the afterglow phase of interest, as confirmed by mass-spectrometric sampling of the afterglow ions.

In addition to HCO^+ ions, we observed a small but non-negligible concentration of H_3O^+ ions, a product of the secondary, undesired reaction

$$HCO^+ + H_2O \rightarrow H_3O^+ + CO\ . \tag{5}$$

The water-vapor impurity apparently was produced by chemical reactions in the microwave discharge. As described later, the non-negligible effect of this impurity ion on the plasma recombination has been taken into account in the data analysis.

III. DATA ANALYSIS

The analysis of the plasma decay in terms of recombination of ions with electrons and ambipolar diffusion of charged particles to the cavity walls has involved two different methods to extract recombination coefficients from the observed electron-density decay data.

The first method, which has been traditionally applied to obtain recombination coefficients by the afterglow method, relies on several simplifying, and, in part, unjustified assumptions. The electron temperature obtained by microwave heating of the plasma electrons is assumed to be spatially uniform and is calculated from Margenau's theory[13] by neglecting energy loss of electrons in inelastic collisions with the minority molecular gases in the afterglow plasma.

It has been realized only recently[14,15] that inelastic collision of electrons with molecular gases can be surprisingly effective in reducing the electron temperatures attained by microwave heating. Also, the assumption of spatial uniformity of the electron temperature has been found not to be valid in most resonant-cavity heating-mode studies, as has been discussed in detail by Dulaney *et al.*[16]

The second, more realistic method of analysis, developed by Dulaney *et al.*, has been applied to the present data; however, as will be seen, under the experimental conditions used here the results do not differ greatly from those obtained from the simpler analysis. Therefore, while we include the results of the more rigorous analysis, we refer the reader for details of the analysis to the work of Dulaney *et al.*[16]

If one assumes that the electron temperature is spatially uniform, the analysis of the electron density decay is relatively simple: one solves the continuity equation for the electron density numerically and obtains recombination coefficients by fitting the model predictions to the data. The electron-density continuity equation is given by

$$\partial n_e(r,t)/\partial t = -\alpha_{\text{eff}} n_e^2 + D_a \nabla^2 n_e \ , \tag{6}$$

where

$$\alpha_{\text{eff}} = \sum_i f_i \alpha_i \tag{7}$$

is the effective recombination coefficient and

$$D_a = \sum_i f_i D_{ai} \tag{8}$$

is the ambipolar diffusion coefficient appropriate to a mixture of ion species i with recombination coefficients α_i, ambipolar diffusion coefficients D_{ai}, and fractional concentrations f_i. In the case of interest here, the ion species are (1) HCO^+, the dominant species, and (2) the impurity ion species H_3O^+ mentioned earlier. The numerical solution of this equation is greatly simplified if the concentration of the impurity ion species is small and remains essentially constant during the afterglow, as is the case in these measurements (see Sec. IV), and if the ambipolar diffusion coefficients of the two ion species are not too different. Equation (6) may then be written in the form

$$\partial n_e/\partial t = -\alpha_1 n_e^2 - (\alpha_2 - \alpha_1) C n_e + D_a \nabla^2 n_e \ , \tag{9}$$

where $C = n(H_3O^+)$ denotes the time-independent concentration of the impurity ion species. The term "linear" in the electron density describes an attachmentlike loss of electrons, a case that has been numerically treated by Frommhold and Biondi.[17]

The preceding analysis remains valid if the electron temperature is elevated above that of the neutrals and ions by microwave heating of electrons, provided that the electron temperature is spatially uniform. The ambipolar diffusion constant then depends on electron temperature as

$$D_a = D_+(1 + T_e/T_+) \ , \tag{10}$$

where the subscripts e and $+$ refer to electrons and positive ions, respectively.

The electron temperature is calculated from the formula given by Margenau,[13]

$$T_e = T_n + [Me^2/6k(2\pi f)^2 m^2] \langle E_{\text{MWH}}^2 \rangle \ . \tag{11}$$

Here, M and m denote the masses of the neutral gas atoms and electrons, respectively, k is Boltzmann's constant, f the microwave frequency, e the electronic charge, and $\langle E_{\text{MWH}}^2 \rangle$ is the electron-density weighted, spatial average of the squared amplitude of the microwave heating field. The amplitude of the microwave field was obtained from a measurement of the microwave power entering the cavity, measured values of the quality factor Q of the cavity, and the TE_{111}-mode field distribution.

The ambipolar diffusion constant D_a required for the data analysis was determined in a separate experiment at a temperature of 293 K and a reduced gas pressure [$p(\text{Ne}) = 1.8$ torr]. Under these conditions, the plasma decay is dominated by diffusion rather than by recombination. The electron density decayed exponentially, with a decay frequency $\nu_d = 137/\text{s}$. Since $\nu_d = D_a/\Lambda^2$ (Λ, the fundamental diffusion length of the cavity, is 1.25 cm in the present case), a value of $D_a p(\text{Ne}) = 385\ \text{cm}^2\,\text{torr/s}$, quite close to values observed for similar mass ions in neon, is obtained.

In analyzing the recombination and diffusion data, we made use of the recombination coefficient for H_3O^+ measured by Leu *et al.*[18] at a gas temperature of 540 K and assumed that it varies with temperature as $T_e^{-0.5}$, thus

$$\alpha(H_3O^+)\ (\text{cm}^3/\text{s}) = 1.3 \times 10^{-6} [T_e\,(\text{K})/300]^{-0.5} \ . \tag{12}$$

After the experimental studies had been completed, it was shown that in the case of microwave heating in a cavity, spatial uniformity of the electron temperature cannot be assumed[16] and that the calculation of the electron temperature attained by microwave heating of plasma electrons is complicated by inelastic collisions of electrons with minority molecular constituents,[14,15] such as the hydrogen and carbon-monoxide gases used here. A complete account of the more rigorous methods of data analysis has been given by Dulaney *et al.*[16]

In the case of interest here, the effect of inelastic collision between electrons and molecular constituents was found to be fairly small because of the small concentration of hydrogen and carbon monoxide used. The assumption of a spatially uniform electron temperature, however, was found to be unjustified. An analysis of the heat transfer within the electron gas showed that the electron temperature could vary with position in the cavity by a factor of 3 and more, being a maximum at the center of the cavity and considerably lower near the walls. We have applied the method of data analysis described by Dulaney *et al.*[16] to the present data and compare the results to the approximate results in Sec. IV. In applying this model we have used the values of the inelastic energy loss frequencies of electrons with H_2 and CO obtained by Frost and Phelps,[19] by Hake and Phelps,[20] and the collision frequencies of electrons with neon atoms obtained by Baille *et al.*[21] It will be seen that the approximate treatment, although oversimplified, leads to fairly accurate results in this case.

IV. RESULTS

Examples of measured electron- and ion-density decays under recombination controlled conditions are shown in Fig. 1. As may be seen, the HCO^+ ion wall current tracks the electron-density decay curve quite well during most of the afterglow period. Additionally, the impurity ion H_3O^+, produced by reaction (5), is seen to be present at a nearly constant concentration, justifying the assumption made in the analysis earlier. The electron temperatures T_e' given in the figure refer to the "Margenau" temperatures calculated from Eq. (11), assuming a uniform temperature in the plasma and neglecting the effect of molecular constituents on the electron temperature scale.

In Fig. 2, measured values of the reciprocal, microwave-averaged electron density are compared with the results of numerical solutions of the electron-density continuity equation. As in Fig. 1, the electron temperatures T_e' are the Margenau temperatures. The solid curves represent the best fits to the data from which the recombination coefficients were obtained.

The resulting values of $\alpha(HCO^+)$ for different electron temperatures are shown in Fig. 3. The solid line in that figure represents the results of a reanalysis of the experi-

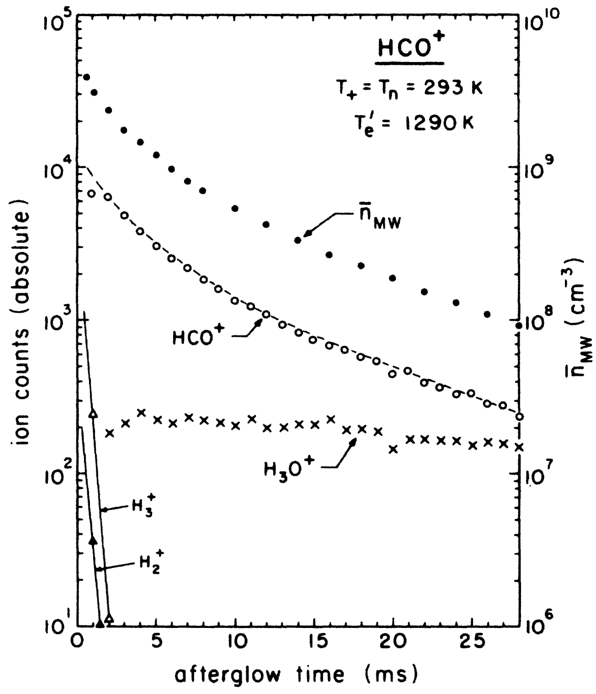

FIG. 1. Observed decay of the microwave-averaged electron density and the time-dependent ion composition. The average electron temperature was 1290 K; neutral and ion temperatures were 293 K. The dashed line represents the electron density decay, renormalized to show the tracking of ion and electron decays.

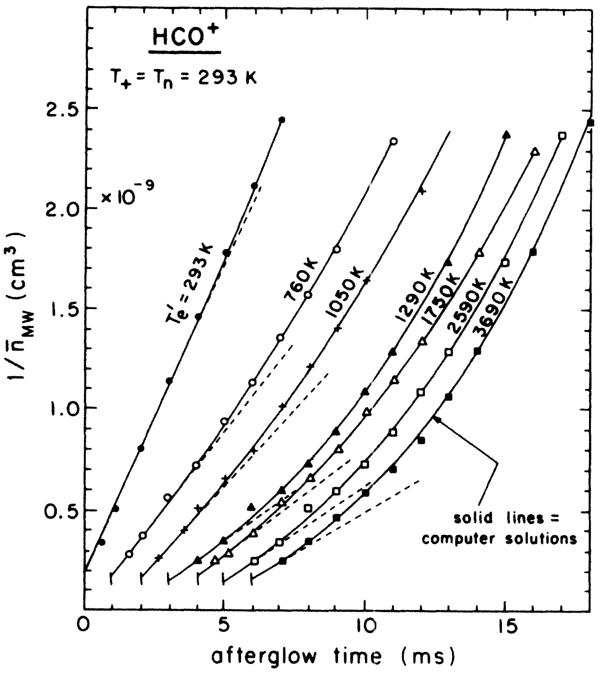

FIG. 2. Reciprocal of the microwave-averaged electron density is plotted vs afterglow time for different average electron temperatures. Time origins of the data sets have been displaced for clarity. The neon buffer gas pressure was 12 torr, the pressures of H_2 and CO were 0.16 mtorr for each gas. Lines drawn through the data points represent the best-fitting computer solutions, assuming spatially uniform electron temperatures.

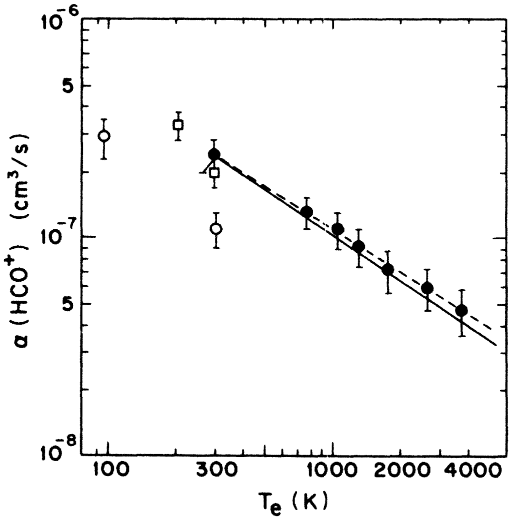

FIG. 3. Variation of $\alpha(HCO^+)$ with average electron temperature. Solid points: Present results, as obtained from the approximate analysis. Solid line: present results, reanalyzed using the more rigorous analysis. Open circles: flowing-afterglow data observed by Adams *et al.* (Ref. 5). Squares: microwave-afterglow data of Leu *et al.* (Ref. 4).

mental data using the method of Dulaney *et al.*[16] The data points on the figure were obtained by the analysis which assumes a uniform electron temperature and neglects inelastic energy losses in collisions with molecules. This treatment yields a slightly weaker temperature dependence ($\sim T_e^{-0.64}$) than that inferred from the more rigorous analysis ($T_e^{-0.69}$), but the difference is within the uncertainties of the experimental values (about ±15%). Written in the form of a power law, the recombination coefficient may be represented by

$$\alpha(\mathrm{HCO})^+\ (\mathrm{cm}^3/\mathrm{s}) = (2.4\pm0.4) \times 10^{-7}[T_e\,(\mathrm{K})/300]^{-0.69\pm0.07}\ , \tag{13}$$

valid over the range 293 $K < T_e < 5500$ K.

V. DISCUSSION AND CONCLUSIONS

The present room-temperature value of $\alpha(\mathrm{HCO}^+)$ is close to, but 15% larger than, that obtained by Leu *et al.*[4] (2.0×10^{-7} cm^3/s). However, there is approximately a factor-of-2 disagreement with that obtained by Adams *et al.*[5] in a flowing-afterglow experiment (1.1×10^{-7} cm^3/s). The cause of this discrepancy is not clear. Sometimes, clustering of ions with molecules may result in more complex ions, for instance $\mathrm{HCO}^+\cdot\mathrm{CO}$, which generally have larger recombination coefficients. In the present measurements, the mass-spectrometric analysis of the ion composition did not show such ions under the condition used, although they were observable at reduced gas temperatures and higher concentrations of the molecular gases.

The dependence of $\alpha(\mathrm{HCO}^+)$ on gas temperature observed by Adams *et al.*[5] over the comparatively small range from 95 to 300 K follows approximately a $T_e^{-0.8}$ power law, slightly stronger than the $T_e^{-0.69}$ dependence established over the wider T_e range in the present experiment.

The values of $\alpha(\mathrm{HCO}^+)$ are similar to those typically found for simple, diatomic ions and nearly identical to that of the isoelectronic ion $\mathrm{N_2H}^+$ (Ref. 22). The presence of the third atom appears to be less effective in enhancing the resonant capture of the electron than one might expect on the basis of qualitative arguments. Kraemer and Hazi[23] have carried out electronic-structure calculations of the HCO molecule and reached the conclusion that there is a sparsity of HCO* resonance states available to low-energy electrons, and therefore dissociation into $\mathrm{H}(^2S)$ and $\mathrm{CO}(^1\Sigma^+)$ should occur with smaller probability than had been assumed. The dissociation channel of this recombination process is still open to question. Kraemer and Hazi also suggest that the experimental values for the HCO^+ recombination rate coefficient may refer to vibrationally excited ions, rather than to ions in their vibrational ground state, and thus may not be applicable to conditions in interstellar clouds. In afterglow experiments of the type used here, deexciting collisions of vibrationally excited ions with buffer gas atoms and especially with the minority $\mathrm{H_2}$ and CO molecules should result in ions with little internal energy, but the vibration state of the ions cannot be defined with certainty at the present time.

As far as applications to modeling of interstellar gas clouds are concerned, the importance of recombination of HCO^+ with electrons has been enhanced by the recent finding that recombination of the dominant ion species $\mathrm{H_3}^+$ is much slower than was indicated by earlier work.[22] Thus the equilibrium density of electrons in interstellar clouds may depend critically on their recombination with HCO^+, which is often the second most important interstellar ion species. Further experimental work to clarify the role of vibrational excitation and the nature of the products of the recombination would be desirable.

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