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MEASUREMENTS OF DISSOCIATIVE RECOMBINATION OF CO_2^+ IONS WITH ELECTRONS*

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Recently, models of the Martian ionosphere have been proposed in an effort to explain electron-density and neutral-atmosphere-density data obtained from the Mariner IV occultation experiment[1] and from earth-based spectral observations.[2] A feature of these models is the critical dependence of the predicted ionospheric electron density on the value of the dissociative recombination coefficient $\alpha(CO_2^+)$ between electrons and CO_2^+ ions, with some models[3] apparently demanding an unusually large coefficient, $\sim 10^{-6}$-10^{-5} cm^3/sec, in the temperature range 130-300°K.

In view of the urgent need for a quantitative determination of this coefficient, we have applied our microwave-afterglow differentially pumped quadrupole mass spectrometer apparatus,[4] shown schematically in Fig. 1, to the study. The gas mixture (typically $\sim 5 \times 10^{-4}$ Torr CO_2 and 10 Torr of neon) within a copper TM_{010} microwave cavity is ionized by power from a pulsed magnetron (pulse length ~0.5 msec). The electron density is determined by the standard cavity frequency shift technique,[5] in which a low-energy probing signal from the klystron is used to determine the resonant frequency of the cavity as a function of time during the afterglow.

Some of the ions diffusing to the cavity wall effuse through a small (0.015-in.-diam) orifice in the bottom of the cavity and into the differentially pumped quadrupole mass spectrometer. A channeltron ion multiplier at the output has sufficient gain to permit individual ion counts to be detected and stored in a multichannel analyzer (operated in a multiscaling mode and synchronized with the magnetron pulse). In this way the mass-identified ion currents diffusing to the wall are determined as a function of time in the afterglow. The gas-handling system is of the ultrahigh vacuum type, permitting long-term bakeout at high temperatures to reduce contaminants to negligible levels.

The apparatus is operated in a "single-pulse" mode, in which one frequency-shift point is determined in each pulse-afterglow cycle, the ionizing pulses are repeated at sufficiently long intervals (> 10 sec) to permit the plasma to decay completely, and the ion counts for

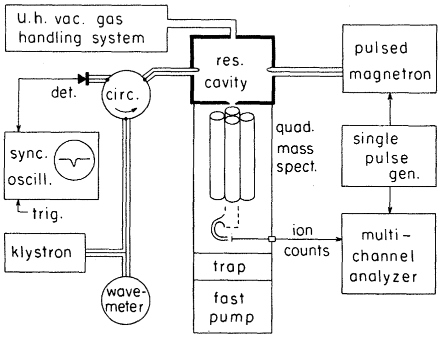

FIG. 1. Simplified block diagram of apparatus using microwaves to determine the electron density and a differentially pumped quadrupole mass spectrometer to measure ion wall currents.

each pulse-afterglow cycle are added together in the multichannel analyzer (~100 pulse afterglows are typically used). In this way, negative-ion accumulation effects are avoided, while data are readily obtained for the electron density and ion current versus time.

By adjusting the gas mixture and ionizing-pulse length we can obtain afterglow conditions in which electron-ion recombination is the dominant process, a single positive-ion species predominates,[6] and negative ions are negligible in concentration. Under these conditions the decay of electron density n_e is given by

$$\partial n_e/\partial t \simeq -\alpha n_e^2 + D_a \nabla^2 n_e, \qquad (1)$$

where we have used the quasineutrality of a plasma to set $n_+ \simeq n_e$, and D_a is the ambipolar diffusion coefficient of CO_2^+ ions and electrons in neon. Since the first term on the right of Eq. (1) is dominant, the electron density decay in the early afterglow is approximated by the "recombination solution," $1/n_e = 1/n_{e0} + \alpha t$. The effect of the diffusion term on the electron spatial distribution in the cavity and the loss rate is obtained by computer solution of Eq. (1) for cylindrical geometry.[7]

An example of the observed electron and ion decays at 300°K in CO_2-neon mixtures[8] is shown in Fig. 2. We plot the reciprocal of the "microwave average" electron density (defined by $\bar{n}_{\mu w} \equiv \int_{\text{vol}} n_e E^2 dV / \int_{\text{vol}} E^2 dV$, where E is the microwave field strength) in Fig. 2(a), while the ion wall currents and the electron density are plotted on a logarithmic scale in Fig. 2(b). It is found that CO_2^+ is the dominant ion throughout the afterglow, the O_2^+ ion current remaining at a low level. The O_2^+ is believed to originate from Penning ionization of CO or O produced by dissociation of CO_2 in the microwave discharge, rather than from the negligible O_2-molecule impurity. The O^+ and CO^+ ions quickly (~30 μs) are converted to O_2^+ on reaction with CO_2.

The initial decay (the first msec) of CO_2^+ wall current follows the electron decay, then becomes faster later in the afterglow. Such behavior is consistent with the fact that the recombination coefficient for O_2^+ ions, $\alpha(O_2^+) = 2.2 \times 10^{-7}$ cm^3/sec,[9] is substantially smaller than for CO_2^+ ions. As a result, as time progresses, the relative O_2^+:CO_2^+ concentration increases, n_e becomes noticeably greater than $n(CO_2^+)$, and the faster CO_2^+ decay is to be expected. One can assess the effect of the O_2^+ on the determination of $\alpha(CO_2^+)$; it is included in our evaluation. The computer fit of the solution to Eq. (1) to the data gives a value $\alpha(CO_2^+) = (3.8 \pm 0.5) \times 10^{-7}$ cm^3/sec at $T = 300$°K. The coefficient does not vary beyond these limits as $p(CO_2)$ is varied from 2×10^{-4} to 2×10^{-3} Torr and $p(Ne)$ from 4 to 10 Torr.

Preliminary studies at $T \simeq 210$°K yield linear curves of $1/\bar{n}_{\mu w}$ versus t comparable with that shown in Fig. 2(a). However, it has not been possible to observe the ion-current decays,

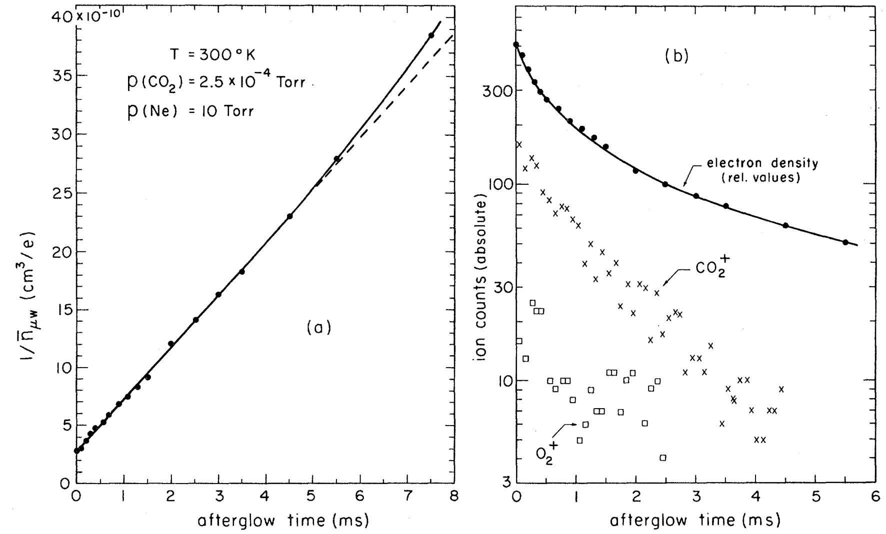

FIG. 2. (a) Recombination loss of electrons displayed by plotting $1/\bar{n}_{\mu w}$ versus time. (b) Semilogarithmic presentation of the decay of ion wall currents during the afterglow compared with the volume electron density decay.

since the signals cut off early in the afterglow. At low CO_2 pressures, a value $\sim 4\times10^{-7}$ cm^3/sec is noted at $\approx 210°K$.

The CO_2^+ ions in the present study should be in the same ground electronic state ($\tilde{X}\,^2\Pi_g$) as those encountered in the photoionized Martian ionosphere, considering the energetics of their production from neon metastable atoms via the Penning reaction. Less can be said of the vibrational state of the ions, although available information on quenching of CO_2 vibration by noble gases[10] suggests that the ions may have been reduced to their ground vibration state within $\lesssim 10^{-4}$ sec. For these ions, the value of $\alpha(CO_2^+)$ at $T_e = T_+ = T_{gas} = 300°K$ is found to be $(3.8\pm0.5)\times10^{-7}$ cm^3/sec, while at $\sim 210°K$ it appears to be of the same order. Since it is doubtful that the room-temperature value is in error by more than the stated amount, and no remarkable increase in the coefficient seems to occur at 200°K, the present results suggest strongly the need for modification of the Martian ionospheric models to conform to values of $\alpha(CO_2^+)$ substantially less than 10^{-6} cm^3/sec.

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[3] J. W. Chamberlain and M. B. McElroy, Science 152, 21 (1966); M. B. McElroy, to be published. For a review of the models see D. M. Hunten, Kitt Peak National Observatory Contribution No. 242, 1967 (unpublished).

[4] C. S. Weller and M. A. Biondi, Bull. Am. Phys. Soc. 11, 495 (1966).

[5] M. A. Biondi, Rev. Sci. Instr. 22, 500 (1951).

[6] In these gas mixtures, ionization takes place when electron collisions produce neon metastable atoms ($V_x = 16.6$ eV), which then ionize the minority concentration ($1{:}10^4$) of CO_2 molecules ($V_i = 13.8$ eV) by the Penning reaction. As a result of the small CO_2 concentration, few ion-molecule conversion reactions occur in the afterglow.

[7] L. Frommhold and M. A. Biondi, Bull. Am. Phys. Soc. 12, 217 (1967), and L. Frommhold, M. A. Biondi, and J. Mehr, Phys. Rev. (to be published).

[8] The neon is research-grade gas from Air Products and is contained in a steel pressure tank holding 50 liter atm. A series refrigerated (77°K) zeolite trap is present in the high-pressure feed line to aid in further purification. The CO_2 is Airco assayed reagent grade in a 1-liter-atm Pyrex flask.

[9] W. H. Kasner and M. A. Biondi, Bull. Am. Phys. Soc. 12, 218 (1967).

[10] See, for example, T. L. Cottrell and M. A. Day, Molecular Relaxation Processes (Academic Press, Inc., New York, 1966).

RUTHERFORD SCATTERING OF PROTONS IN THE SURFACE LAYERS OF A TUNGSTEN SINGLE CRYSTAL

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Measurements of Rutherford scattering yields in single crystals have, during the last two years, been used to obtain information about the motion of fast charged particles through single crystals.[1] In the experiments, a very marked decrease in scattering yield is found whenever the particle beam is aligned within a certain critical angle ψ_c of a major crystal axis. The observed critical angles have been in good agreement with the theoretical estimate of Lindhard,[2] $\psi_c = (2Z_1Z_2e^2/dE)^{1/2}$. Z_1 and Z_2 are the atomic numbers of the particle and the crystal atoms, respectively; e is the electronic charge; E is the particle energy; and d is the repetition distance of the atoms in the crystal axis parallel to which the particles entered the crystal. ψ_c is typically of the order of 1°.

The minimum yields observed hitherto, have, with few exceptions, been higher than the theoretical estimate for a perfect crystal by a factor of 2-10 depending on the target material. The theoretical estimate is based on the assumption that only those particles in the exterior beam which hit the crystal surface within $\sim a$ [the screening distance in the Thomas-Fermi atomic potential, $a = 0.46(Z_1^{2/3}+Z_2^{2/3})^{-1/2}$