Electron-temperature dependence of dissociative recombination of electrons with $CO^+ \cdot (CO)_n$-series ions

Marlin Whitaker, Manfred A. Biondi, and Rainer Johnsen

Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

(Received 29 September 1980)

A microwave-afterglow mass-spectrometer apparatus has been used to determine the dependence on electron temperature T_e of the recombination coefficients α_n of the dimer and trimer ions of the series $CO^+ \cdot (CO)_n$. We find $\alpha_1 = (1.3 \pm 0.3) \times 10^{-6} [T_e(K)/300]^{-0.34}$ and $\alpha_2 = (1.9 \pm 0.4) \times 10^{-6} [T_e(K)/300]^{-0.33}$ cm³/sec. These dependences on T_e are quite different from those obtained previously for polar-cluster ions of the hydronium and ammonium series but are similar to that for simple diatomic ions.

I. INTRODUCTION

The capture of electrons by ions of the carbon monoxide series, $CO^+ \cdot (CO)_n$, where $n = 0, 1, 2, \ldots$, is of interest for several reasons. These ions may be important in ionized media where CO or CO_2 are among the neutral constituents, as in some laser plasmas or in the ionospheres of certain planetary atmospheres. Thus, determinations of the electron-ion recombination coefficients for the appropriate ions provide needed inputs to model calculations of the behavior of these plasmas. More fundamentally, previous studies[1-3] have shown that recombination coefficients for ions to which strongly polar molecules are clustered exhibit a very different variation with electron temperature than that observed for dissociative recombination of unclustered molecular ions.[4] The present study extends the cluster-ion work by examining recombination of ions clustered with weakly polar molecules, i.e., the dimer and trimer ions, $CO^+ \cdot CO$ and $CO^+ \cdot (CO)_2$, where the recombination reaction is most probably

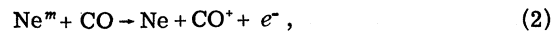$$CO^+ \cdot (CO)_n + e^- \rightleftharpoons CO^* \cdot (CO)_n \rightarrow C^* + O^* + n(CO); \tag{1}$$
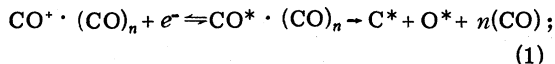
the asterisks indicate that the products may be electronically excited.

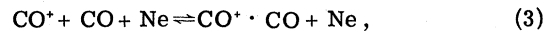## II. METHOD OF MEASUREMENT AND DATA ANALYSIS

The microwave-afterglow mass-spectometer apparatus is the same as that used previously in a study of the polar-cluster ions[3] and has been described in some detail.[5] A microwave discharge lasting typically 0.1 msec and repeated at a 10-Hz rate is generated in 5–20 Torr of neon containing an admixture of a few tenths percent of carbon monoxide. The "microwave-averaged" electron density $\bar{n}_{\mu w}$ during the afterglow is obtained from measurements of the resonant-frequency shift of the high-Q TM_{010} cavity mode,[1] while steady elec-

tron heating is achieved by application of microwave power via a low-Q ($\sim$10) TE_{111} cavity mode. The time histories of the various afterglow ions are determined by sampling the ions which diffuse to the cavity wall and effuse through a small orifice into a differentially pumped quadrupole mass filter.

The principal steps in the formation of the ions of interest are thought to be (a) electron-impact excitation of neon to a metastable state Ne^m, (b) Penning ionization of CO molecules via

$$Ne^m + CO \rightarrow Ne + CO^+ + e^-, \tag{2}$$

and (c) clustering and breakup reactions,

$$CO^+ + CO + Ne \rightleftharpoons CO^+ \cdot CO + Ne, \tag{3}$$

and

$$CO^+ \cdot CO + CO + Ne \rightleftharpoons CO^+ \cdot (CO)_2 + Ne. \tag{4}$$

The relative abundance of ions in the afterglow is controlled by varying the gas temperature from $\sim$250 to 300 K and the partial pressure of CO from $\sim$20 to 100 mTorr, thereby affecting the equilibria of reactions (3) and (4). (Under the conditions of the present measurements the CO^+ ion was never a significant ion throughout the afterglow, so that its recombination coefficient was not determined.)

Under the conditions obtaining in the present study, that is, the ions present in significant concentrations decay together during the afterglow, it has been shown[3] that the electron continuity equation can be written as

$$\frac{\partial n_e(r, t)}{\partial t} \simeq -\alpha_{\text{eff}} n_e^2 + D_a \nabla^2 n_e, \tag{5}$$

where α_{eff}, the effective recombination coefficient, is given by $\alpha_{\text{eff}} = \Sigma \alpha_j f_j$, in which the f_j are the fractional concentrations (essentially time independent) of each afterglow ion and D_a is the ambipolar diffusion coefficient appropriate to a mixture of positive ions,[6] whose separate D_a values are

estimated from the Langevin (polarization) mobilities[7] of ions moving in neon. Usually only two ionic species are present in significant concentrations during the afterglow (e.g., the dimer and trimer ions); therefore α_{eff} may be written as

$$\alpha_{eff} = f_1\alpha_1 + (1-f_1)\alpha_2 , \qquad (6)$$

with α_1 the dimer- and α_2 the trimer-ion recombination coefficients.

A computer solution[8,9] of Eq. (5) with appropriate values of α_{eff} and D_a yields the predicted spatial and temporal variation of the electron density, from which predicted values of $\bar{n}_{\mu w}$ (t) can be obtained. Since the measurements of the microwave cavity's resonant-frequency shift during the afterglow directly yield $\bar{n}_{\mu w}$ (t), the value of α_{eff} may be determined from these measurements by obtaining a best fit to the data of computer-generated solutions of Eq. (5), using the known values of D_a and treating α_{eff} as a parameter.

III. RESULTS

A number of attempts were made to achieve conditions in which CO[+] ions were the principal afterglow ions, however, without success. Consequently, we were unable to determine the recombination coefficient for the CO[+] monomer ion.

The recombination coefficient for the dimer ion, CO[+]·CO, was inferred from those data runs in which the dimer was the only ion of significance,

FIG. 2. $1/\bar{n}_{\mu w}$ vs time "recombination decay" plots for various electron temperatures under the same conditions as Fig. 1. The solid lines represent best-fit computer solutions of Eq. (5) to the data. The zero times for the different T_e runs are displaced for clarity.

representing greater than 90% of the total ion count. Referring to Fig. 1, it will be seen that in this example of our measurements the electron density decay tracks the CO[+]·CO wall current decay (the dashed lines are renormalized $\bar{n}_{\mu w}$ values) and that the CO[+] concentration is $\leq 5\%$ of the dimer ion concentration during the ~12 msec of the after-
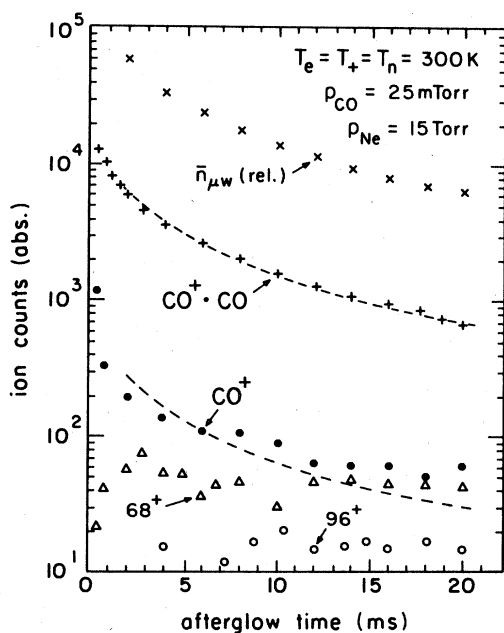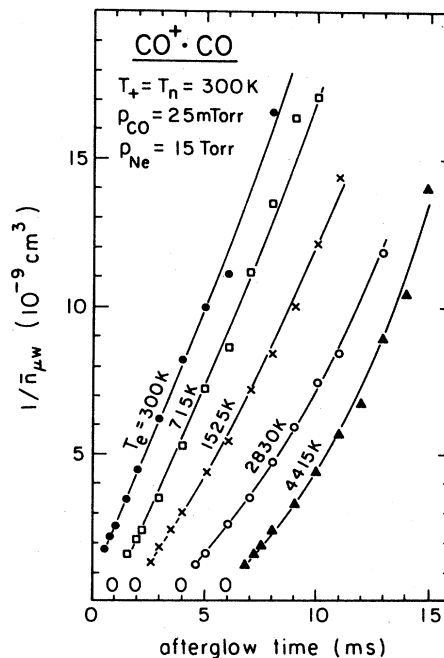

FIG. 1. Comparative decays of volume electron density $\bar{n}_{\mu w}$ and ion wall currents during the afterglow. The dashed lines represent renormalized values of $\bar{n}_{\mu w}$.
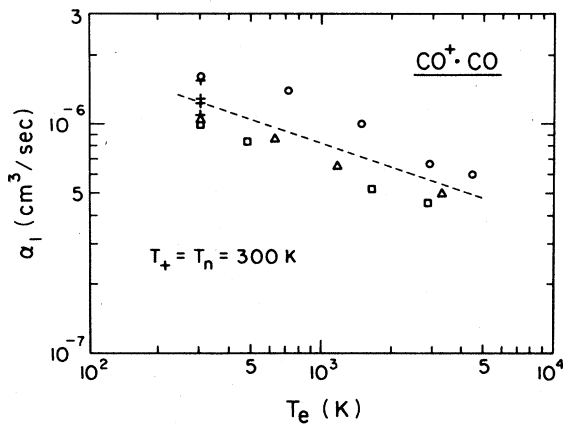

FIG. 3. Variation with electron temperature of the dimer-ion recombination coefficient with $T_+ = T_n = 300$ K. Each type of symbol indicates a run taken with a given gas filling on a given day. The dashed line represents a $T_e^{-0.34}$ power-law dependence for α_1.
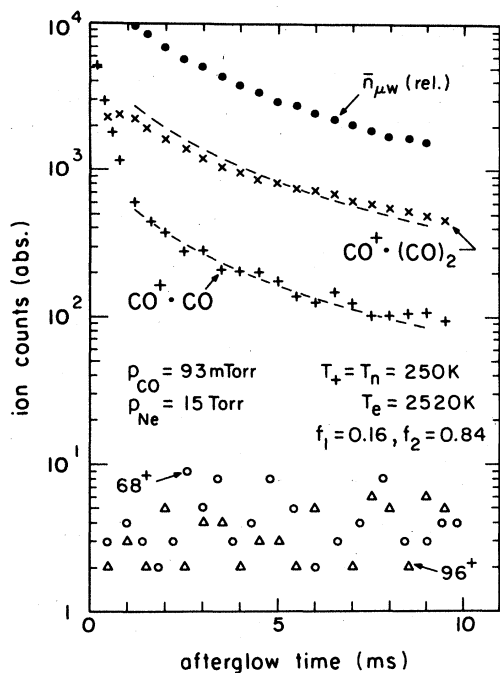
FIG. 4. Comparative decays of $\bar{n}_{\mu w}$ and ion wall currents in an afterglow in which trimer and dimer ions are the principal positive ions.
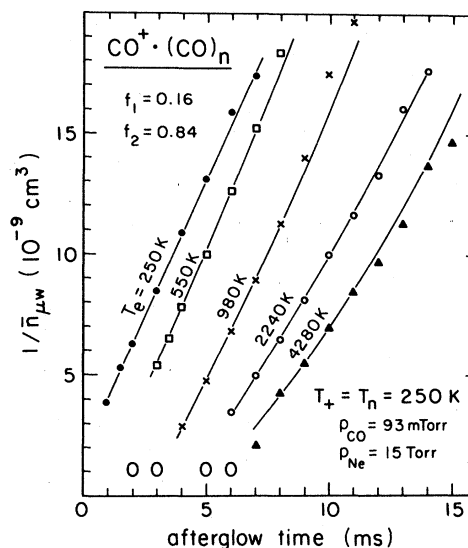

FIG. 5. $1/\bar{n}_{\mu w}$ vs time curves for the same conditions as Fig. 4. The solid lines are best-fit computer solutions of Eq. (5) to the data. The zero times of successive runs are displaced for clarity.

glow used to determine α. Figure 2 shows examples of the measured electron-density decays for several electron temperatures displayed in the "recombination-decay" form of $1/\bar{n}_{\mu w}$ vs. t. The solid lines are computer solutions of Eq. (5) which provide the best fit to the data. The measured variation with electron temperature for α for the dimer ions is shown in Fig. 3. The different symbols (circles, triangles, squares) indicate separate sequences of runs taken some days apart and suggest that the T_e variation from one run to the next is more reproducible than is the absolute value of $\alpha[CO^+ \cdot CO]$ at a given value of T_e. The + symbols indicate the reproducibility of α values determined from several runs all at $T_e = 300$ K.

In those runs where the trimer ion, $CO^+ \cdot (CO)_2$, was dominant, it was necessary in many cases to correct for the presence of significant fractions of the dimer ion. An example of the tracking of the electron density decay with the decays of the trimer and dimer ions is given in Fig. 4. Electron density decays measured at various electron temperatures for the case where both trimer (at 84%) and dimer (at 16%) ions were present are shown in Fig. 5. The solid lines represent best-fits of the computer solutions of Eq. (5) to the data to obtain α_{eff} vs T_e. When the α_{eff} data were corrected via Eq. (6) for the dimer-ion contribution using the appropriate values of α_1, the inferred

variation of the trimer-ion recombination coefficient α_2 with T_e shown in Fig. 6 was obtained. Again the different symbols represent different runs.

If one fits the data of Figs. 3 and 6 to simple power-law variations of the form $\alpha \sim T_e^{-x}$, the results of the studies can be represented by the following expressions:

$$\alpha[CO^+ \cdot CO](cm^3/sec) = (1.3 \pm 0.3)$$
$$\times 10^{-6} [T_e(K)/300]^{-0.34} \quad (7)$$

and

$$\alpha[CO^+ \cdot (CO)_2](cm^3/sec) = (1.9 \pm 0.4)$$
$$\times 10^{-6}[T_e(K)/300]^{-0.33}, \quad (8)$$

where the stated uncertainties reflect our estimates of the systematic and random errors associated with the determinations. While the data of Fig. 3 show no systematic deviation from the expression given in Eq. (7), the data of Fig. 6 suggest that initially $\alpha[CO^+ . (CO)_2]$ may decrease more slowly with increasing T_e than the expression of Eq. (8) suggests and then, above 1000 K, more rapidly.

IV. DISCUSSION AND CONCLUSIONS

The present studies of recombination of electrons with the carbon monoxide family of cluster ions indicate a dependence of the recombination coefficient on electron temperature which is quite like that found for unclustered molecular ions. This
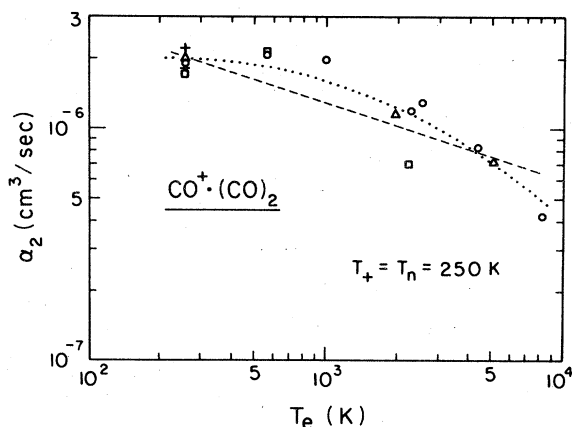
FIG. 6. Variation of the trimer-ion recombination co-efficient with T_e for $T_+ = T_n = 250$ K. While the dashed line represents a power-law variation of the form $\alpha_2 \sim T_e^{-0.33}$, the dotted line may better represent the actual variation.

result is in sharp contrast to the virtually electron-temperature-independent recombination exhibited by the clustered ions of the ammonium[2] and hydronium[3] series. Thus, the dimer and trimer ions of the $CO^+ \cdot (CO)_n$ series exhibit some properties of both unclustered and polar-cluster molecular ions; i.e., they have large coefficients at $T_e \sim 300$ K (somewhat greater than 10^{-6} cm^3/sec), as do comparably clustered $NH_4^+ \cdot (NH_4)_n$ and $H_3O^+ \cdot (H_2O)_n$ series ions; however, the dependence of α on T_e approaches that predicted $(T_e^{-1/2})$ and observed $(\sim T_e^{-0.4}$ to $T_e^{-0.8})$ for the direct dissociative process for simple diatomic ions[4].

The substantially larger α values for the dimer and trimer ions compared to that expected[10] for the monomer ion CO^+ probably result from the increased likelihood of electron capture via an inelastic energy loss to the complex during the initial Coulomb collision. If the probability of such inelastic losses varies slowly with electron energy owing to the many closely spaced rotational and vibrational levels in the complex, then the Coulomb cross section's $1/\epsilon$ energy variation (ϵ is the electron energy) dominates the capture. If, in addition, the stabilization by dissociation of the core [refer to reaction (1)] is highly probable, one then expects a variation of α near $T_e^{-1/2}$. Although this argument makes plausible the $CO^+ \cdot (CO)_n$ data, it appears that a similar argument should apply to the hydronium and ammonium series ions. Thus, the observed lack of dependence of α on T_e in the latter cases[2,3] is difficult to understand.

Earlier studies[11-13] of electron-ion recombination in CO discharge afterglows did not employ mass identification of the recombining ions. Thus, the attribution of a measured recombination loss rate to a particular ionic species in such studies is, in our view, rather speculative.

Mentzoni and Donohue interpreted the lack of a pressure dependence over the range $0.2 \lesssim p(CO) \lesssim 2$ Torr in their recombination coefficient determinations[12] as evidence that CO^+ was the dominant afterglow ion, concluding that $\alpha [CO^+] \simeq 4 \times 10^{-7}$ cm^3/sec at $T_e = 775$ K. In their earlier work[11] they found a constant value, $\alpha \simeq 7 \times 10^{-7}$ cm^3/sec, even when the electron temperature was decaying to $T_e = 300$ K during the afterglow; however, in their second paper[12] they use this value for $T_e = 300$ K and, on the basis of these two T_e values, infer a $T_e^{-0.6}$ dependence for $\alpha[CO^+]$. While this T_e dependence is reasonable, the absolute value appears to be about a factor of 2, too high,[10] and may result from the presence of dimer or trimer ions along with the CO^+ monomer. Our mass analysis of ions in discharge afterglows in CO-Ne mixtures indicates the presence of a mixture of ions, e.g., CO^+, $CO^+ \cdot CO$, and $C_nO_m^+$, at CO pressures above 0.1 Torr.

As noted in Sec. III, we made substantial efforts to determine $\alpha(CO^+)$ but were unable to achieve conditions in the CO-Ne discharge afterglows where CO^+ was the dominant afterglow ion. For CO partial pressures below ~ 1 mTorr, both neon ions from the buffer gas and impurity ions as well as CO^+ ions were present, complicating analysis of the electron density decays, while for $p(CO) > 3$ mTorr, dimer or more complex ions were dominant.

Center[13] studied electron loss by recombination in high-pressure afterglows $(100 \lesssim p(CO) \lesssim 700$ Torr) where cluster ions were almost certainly present (as he noted). His values of "α" for the unknown ionic mixture are comparable to our values for the dimer or trimer ions at $T_e \sim 1000$ K but decrease much more rapidly with increasing T_e, differing from our results by a factor ~ 3 at $T_e \sim 5000$ K. In our view, this discrepancy points out the difficulty of making quantitative determinations of recombination coefficients for specified ions in molecular gases in the absence of ionic mass identification.

ACKNOWLEDGMENTS

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