Measurement of the absolute yield of CO(a \textsuperscript{3}Π) + O products in the dissociative recombination of CO\textsuperscript{2+} ions with electrons

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A flowing-afterglow technique is described for measuring the absolute yield of a radiative product state from ion–electron recombination. The technique is applied to CO\textsuperscript{2+} + e\textsuperscript{−} dissociative recombination. The measured yield of CO(a \textsuperscript{3}Π) + O(\textsuperscript{3}P) is 0.29 ± 0.10. This includes cascade from higher triplet states of CO. The vibrational distribution in CO(a \textsuperscript{3}Π, v = 0–3) is approximately Boltzmann, with an effective temperature of 4200 ± 300 K. The measured rate constant for quenching of CO(a) by CO\textsubscript{2} is (1.0 ± 0.2) × 10\textsuperscript{−11} cm\textsuperscript{3} s\textsuperscript{−1}, somewhat lower than previous measurements.

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I. INTRODUCTION

Gas-phase recombination of cations and electrons is important in many energy-rich systems such as planetary ionospheres, laser plasmas and in plasma-induced vapor deposition on surfaces.\textsuperscript{1−5} For molecular ions, the measured neutralization rate coefficients are extremely large, often of the order of 10\textsuperscript{−7} or 10\textsuperscript{−6} cm\textsuperscript{3} molecule\textsuperscript{−1} s\textsuperscript{−1}. Much less is known about the products of this process, but dissociation of the energy-rich neutral intermediate is expected.\textsuperscript{6−8} Initial data have recently been obtained, using laser-induced fluorescence,\textsuperscript{9,10} emission spectroscopy,\textsuperscript{11,12} and kinetic energy analysis\textsuperscript{13,14} to identify the resulting fragments and, in suitable cases, to measure their absolute yields.

Light emission from electronically excited fragments is of particular interest because it can, in principle, be applied to remote sensing of the parent ion in practical environments. The dissociative recombination of CO\textsubscript{2} ions

\[
\text{CO}_2^+ + e^- \rightarrow \text{CO} + \text{O}(\text{3}P, \text{1}D, \text{1}S)
\]  

(1)

can give rise to a range of excited states of CO, including a \textsuperscript{3}Π, v < 12, a \textsuperscript{+} \textsuperscript{3}Σ\textsuperscript{+}, v < 11, d \textsuperscript{3}Σ\textsuperscript{−}, v < 6, e \textsuperscript{3}Σ\textsuperscript{−}, v < 3, A \textsuperscript{1}Π, v < 2, and I \textsuperscript{1}Σ\textsuperscript{−}, v < 2, these limits applying to recombination of the \textsuperscript{2}Π\textsubscript{3/2} ground state of CO\textsubscript{2} with formation of O(\textsuperscript{3}P). Figure 1 shows potential-energy curves for relevant electronic states of CO. Emission from CO\textsubscript{2}\textsuperscript{+} dissociative recombination has been observed from both singlet and triplet states of CO. From a study of CO(A \textsuperscript{3}Π − X \textsuperscript{1}Σ\textsuperscript{+}) uv emission, Gutchev and Zipf\textsuperscript{15} deduced a branching fraction of 0.05 for CO(A \textsuperscript{3}Π) formation. Wauchop and Broida\textsuperscript{16} studied CO(a \textsuperscript{3}Π − X \textsuperscript{1}Σ\textsuperscript{+}) emission from discharged He + CO\textsubscript{2} in a flowing afterglow. Taking account of the long radiative lifetime,\textsuperscript{19,20} 7.5 ms, of CO(a \textsuperscript{3}Π), they deduced a branching fraction of 0.55 for CO(a \textsuperscript{3}Π) formation. They also reported emission from a few vibrational levels of the a' \textsuperscript{3}Σ\textsuperscript{+}, d \textsuperscript{3}Σ\textsuperscript{−}, and e \textsuperscript{3}Σ\textsuperscript{−} states but the extremely small branching fractions which they derived for these states, 0.008 for d \textsuperscript{3}Σ\textsuperscript{−} and 4 × 10\textsuperscript{−4} for a' \textsuperscript{3}Σ\textsuperscript{+}, are probably not reliable, being based on an incomplete spectrum.\textsuperscript{17}

Different conclusions were reached in a recent emission study by Tsuji et al.\textsuperscript{21} of the reactions of CO\textsubscript{2} in a He afterglow. They report relative intensities of emission from all the above-mentioned states. The a' and d states were the strongest emitters and they conclude that the yield of A \textsuperscript{1}Π is smaller than 0.0033. Only about 1% of CO(a) emitted within their observation region. However, they estimated the relative formation rate of this state and concluded that it is populated principally by a' → a and d → a cascade emission. The implication of their conclusions is that, of these five excited states, only two, the d and a', states are populated initially to an appreciable extent.

In the present study, we have measured the absolute branching fraction for CO(a \textsuperscript{3}Π) formation in the CO\textsubscript{2} + e\textsuperscript{−} reaction and have obtained a value which is comparable to, but smaller than, that of Wauchop and Broida. This value is the sum of direct formation of the CO(a) state and contributions from cascade from the higher triplet states.

The experimental procedure was similar to that adopted in our recent LIF study\textsuperscript{10} of the absolute OH yield from the dissociative recombination of H\textsubscript{2}O\textsuperscript{+} ions. We determined the absolute intensity of CO(a \textsuperscript{3}Π) emission produced by the recombination of a known concentration (or flux) of CO\textsubscript{2} ions by means of a calibration technique utilizing reactions with a known branching fraction into emitting states. Two sequences were examined.

Firstly, the well-characterized Penning ionization reaction of He\textsuperscript{+}(2 \textsuperscript{3}S) metastable atoms with N\textsubscript{2}

\[
\text{He}^+ + \text{N}_2 \rightarrow \text{N}_2^+(B \textsuperscript{2}Σ\textsuperscript{+}) + \text{He} + e^- \quad (2a)
\]

\[
\rightarrow \text{N}_2^+(X \textsuperscript{2}Σ\textsuperscript{+}, \textsuperscript{2}Π_a) + \text{He} + e^- \quad (2b)
\]
was used, which has a branching fraction\(^{22}\) for channel \((2a)\) of \(0.41 \pm 0.04\). The procedure was to monitor the electron density using a Langmuir probe, and the \(N_2\) density measured.

In the second calibration method, two reactions of \(Ar^+(3P_2)\) metastable atoms were monitored

\[
Ar^+ + NO \rightarrow Ar + NO^+ + e^- 
\]

for which the branching fraction\(^{23,24}\) is \(0.35 \pm 0.10\); and

\[
Ar^+ + N_2 \rightarrow Ar + N_2 (C^3Π_u)
\]

for which the branching fraction\(^{25,26}\) is \(0.80 \pm 0.20\). Electron-density measurements for reaction \((3)\) yielded the flux of \(Ar^+\) metastables. The \(N_2 (C–B)\) emission signal then provided the absolute calibration of the photon detection system.

Although the \(He^+ + N_2\) approach appears to be more direct, the data analysis was somewhat more involved than for the second sequence and the calibration somewhat less precise. We therefore preferred the latter route. However, results obtained using the \(He^+ + N_2\) calibration reaction proved to be consistent, within the experimental error limits, with those obtained from the preferred sequence.

II. EXPERIMENT

The flowing afterglow system has been described fully elsewhere.\(^{10}\) For this experiment, two separate discharge regions, upstream of the entrance to the 3 cm radius, stainless-steel flow tube, were used. Pure \(He\) was passed through a microwave discharge. The resulting mix of \(He^+\) metastables and \(He^+\) ions was converted, by \(Ar\) addition, to an \(Ar^+/e^-\) plasma. \(CO_2\) was added downstream through a movable injector to convert \(Ar^+\) rapidly to \(CO_2^+\) ions. For the \(He^+ + N_2\) experiments, an analogous technique was employed, except that no \(Ar\) was added.

For the studies of the \(Ar^+ + N_2\) and NO reactions, pure \(Ar\) was passed through a dc discharge. The reagent was added, as before, through the movable injector. In order to maximize the \(Ar^+\) density, \(He\) gas was added downstream of the discharge. In all experiments, the total gas pressure was between 0.8 and 1.1 Torr and the mean flow velocity was approximately 2500 cm/s. The mole fraction of \(Ar\) was about 0.15 in the \(CO_2^+ + e^-\) system and about 0.6 in the \(Ar^+ + N_2\) NO studies. \(He^+, Ar^+,\) and \(Ar^+\) concentrations were in the range: \(1 \times 10^9\) to \(5 \times 10^{10}\) cm\(^{-3}\). The concentrations of the stable reagents were \(10^{12}\) to \(5 \times 10^{14}\) cm\(^{-3}\).

The electron density along the flow tube was measured by a movable Langmuir probe. In general, this was positioned on the tube axis; however, it could be rotated to measure the density off-axis. The operation of the Langmuir probe has been described previously;\(^{27}\) it yields absolute local concentrations of electrons.

Emission was collected in a direction perpendicular to the tube axis through a quartz window, which extends most of the length of the flow tube. An assembly consisting of a baffled collimator (which included a collimating lens), 0.2 m monochromator (Acton VM-502) and uv-sensitive photomultiplier (EMI 9789Q) was moved along a rail to collect emission as a function of position along the tube \((z\) direction). The field of view of the detection system was approximately a rectangle, 0.4 cm width (along the \(z\) direction) and 1 cm high at the center of the flow tube. The monochromator slit width was 150 \(μm\) for all experiments: this corresponds to a spectral resolution of 0.6 nm. The photomultiplier was used in a pulse-counting mode and the output signal was processed by a lab computer. The spectral response of the detection system was measured between 200 and 400 nm using a calibrated \(D_2\) lamp.

The principal measurements are of the electron density and the emission signal as a function of \(z\). It was considered critical to understand the observed behavior in terms of the chemical reactions involved and diffusion (radial and axial) of all species. As described previously,\(^{10}\) the continuity equation, including diffusion, was solved numerically over a grid with a step size of 1 mm in both the radial and axial directions. The chemistry was initiated by “addition” of \(CO_2\) reagent at a single \(z\) value. To represent the loop injector, the addition was limited to a ring-shaped region of suitable radius and thickness. The reagent spread radially by diffusion only: no “jetting” was incorporated into the simulation. For typical flow conditions, the simulations showed that appreciable radial mixing (with concentration on axis equal to about one-half of the reagent concentration for complete mixing) was achieved 2–3 cm downstream of the loop. The interference to the carrier gas flow caused by the injector loop was also ignored. The following chemical processes were included:

\[
Ar^+ + CO_2 \rightarrow CO_2^+ + Ar,
\]

\[
k_1 = (6.0 \pm 1.5) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad \text{(Refs. 28, 29)}.
\]
CO\(_2^+\) + e\(^-\) → CO(a) + O, \(k_{2a}\)

→ other products, \(k_{2b}\),

\[ (\text{Refs. 30, 31}) \]

CO(a) → CO(X) + h\(\nu\), \(k_3 = 133 \pm 18 \text{ s}^{-1}\)

\[ (\text{Refs. 19, 20}) \]

CO(a) + CO\(_2\) → products, \(k_4\).

Quenching of the long-lived CO(a) state by Ar and He is very slow\(^{32}\) and could be neglected. However, quenching by CO\(_2\), process (8), is significant. Previous measurements\(^{32}\) have given a range of values of \(k_4\) from 1.2 to 4.1 \(\times 10^{-11} \text{ cm}^3 \text{s}^{-1}\), with a “recommended” value of 1.7 \(\times 10^{-11}\). The values of \(k_1\), \(k_2\), and \(k_4\) were varied in the simulations to obtain the best fits to the observed \(z\) dependence of the electron densities and of the CO(a-X) emission intensity. The simulations also required input of diffusion coefficients for the relevant species. Published values\(^{33-35}\) of diffusion coefficients (in He and Ar buffer gas) for Ar\(^+\), CO\(_2\), and CO\(_2^+\) were used. An experimental value for CO(a) in He is also available.\(^{35}\) For CO(a) in Ar, the diffusion coefficient was estimated by analogy with \(N_2(A \rightarrow \Sigma^+_1)\) in Ar and Cl(2\(P\)) in Ar (Refs. 36, 37); the effective diffusion coefficient of CO(a) was varied in the simulations. The simulations were carried out with \(k_{2a} = k_{2b}\). Comparison of the results with the measured emission intensity yielded the branching fraction for CO(a) formation.

High-purity He (99.997%) and Ar (99.998%) were purified further by passage through cold traps in the gas handling system. CO\(_2\) (99.8%) and N\(_2\) (99.998%) were used without purification. NO was purified by passing it through a soda lime trap, as described previously.\(^{10}\)

III. RESULTS

A. CO(a-X) emission from recombination of CO\(_2^+\)

When CO\(_2\) was added to a stream of Ar\(^+\) ions and electrons, CO(a-X) emission was observed in the region of the reagent inlet and extending more than 10 cm downstream. A typical spectrum measured 4 cm downstream of the inlet is shown in Fig. 2. All features could be assigned to transitions from CO(a,\(v=0-4\)); the absence of emission from electronically excited CO\(_2^+\) and CO\(_2^+\) indicated\(^{38}\) that essentially no He\(^+\) ions or He* metastables remain in the flow at the point where the CO\(_2\) is added. To verify that the emission does indeed arise from dissociative recombination, traces of SF\(_6\), an efficient electron-scavenger,\(^{39}\) were added with the CO\(_2\). In the concentration range [SF\(_6\)] = 1-3 \(\times 10^{12} \text{ cm}^{-3}\), the CO(a-X) intensity 1 cm downstream of the injection point was reduced by approximately 90%. Part of this small remaining signal is due to reaction of Ar(3\(P\)) metastables in the flow, at approximately 10% of the Ar\(^+\) concentration.\(^{40}\)

\[ \text{Ar}^8(3\mathcal{P}) + \text{CO}_2 \rightarrow \text{Ar} + \text{CO}(a 3\mathcal{P}) + \text{O}, \]

which has a branching fraction\(^{41}\) of 0.16\(+0.08\). The influence of this small contribution to the CO(a 3\(\Pi\)) signal is discussed in Sec. IV.

Spectra were obtained over a range of CO\(_2\) concentrations 2 \(\times 10^{13}\) to 3.4 \(\times 10^{14} \text{ cm}^{-3}\). No significant change in the relative intensities of the bands was seen, indicating negligible vibrational relaxation of CO(a,\(v=0\)) by CO\(_2\) under our conditions. The vibrational distribution, \(N_{v=0}\), in the CO(a) state was determined by analyzing the spectrum in standard fashion

\[ I_{v,v'v''} \propto N_{v=0} \cdot q_{v,v'} \cdot q_{v'',v''} \cdot \text{Re}_{v,v',v'',v''}^2, \]

where \(I_{v,v''}\) is the integrated (over wavelength) \(v,v''\) band intensity in counts/s/nm, corrected for the spectral response of the detection system, \(q_{v,v'}\) is the Franck–Condon factor,\(^{42}\) \(v_{v',v''}\) is the transition frequency and Re is the electronic transition moment. All bands in the observed spectrum, excepting those which were very weak, were included in the analysis. Comparison of different bands arising from a given CO(a,\(v=0\)) level indicated a weak dependence of the electronic transition moment on the \(r\) centroid of the transition; this effect was included in the analysis. The resulting vibrational distribution for levels \(v'=0\) to 3 is 0.49 \(+0.01:0.25\pm0.01:0.17\pm0.01:0.10\pm0.01\). The population clearly decreases monotonically with increasing vibrational quantum number and can be described by a vibrational temperature of 4200\(+300\) K. Weaker emission was observed from higher vibrational levels of CO(a), as described in Sec. IV C. In the remaining experiments described in this section, the monochromator was set to the peak of the \((0,1)\) CO(a-X) band at approximately 216 nm.

By moving the optical detection assembly along the track, the variation of CO(a-X) emission intensity along the flow tube, for a fixed position of the CO\(_2\) injection point, was recorded. Representative data are shown in Fig. 3 for three
CO₂ concentrations. The CO₂ is added at the point marked 4 cm. The emission extends far downstream of this point, particularly at low CO₂ concentrations. A small amount of CO₂ diffuses upstream of the injector; the dip in the signal at z = 4 cm is due to blocking of the light path by the injector loop. As [CO₂] increases, the downstream intensity is reduced, due to quenching of CO(a) by CO₂. The combination of the large radiative lifetime of CO(a) and the electronic quenching means that only about 10% of the CO(a) emits in the observed region of the flow tube.

In order to derive a reliable CO(a) yield, extensive simulations were carried out. Representative fits are included as the solid lines in Fig. 3. These use the values given above for k₁, k₂, and k₃. k₄ was set to 0.8 × 10⁻¹¹ cm³ s⁻¹ and the diffusion coefficient of CO(a) (in the He/Ar mix) to our best estimate, D(CO(a)) = 450 cm² s⁻¹. For the simulations, the ordinate is the integrated number of CO(a) molecules in a 1 cm disk-shaped slice of the flow tube. The simulations were normalized to the experimental curves at a single point, the maximum in the profile for [CO₂] = 5 × 10¹³ cm⁻³. It is seen that the simulations match the dependence of the maximum intensity on [CO₂] and the general shape of the z dependence fairly well, although the simulated curves decay at large z slightly faster than the experimental data. Figure 4 shows the effect of varying D(CO(a)) and k₄ in the simulations. As expected, increase in either parameter increases the decay rate at large z. Over the range of CO₂ concentrations used, quenching is a more important loss process than diffusion and thus the z profile depends more strongly on k₄ than on the diffusion coefficient. Figure 4 shows clearly that a value of k₄ of (0.8 to 1.0) × 10⁻¹¹ cm³ s⁻¹ yields a much better fit to the data than higher values such as 1.7 × 10⁻¹¹ cm³ s⁻¹. From these and other simulations over the whole range of CO₂ concentrations, we deduce a best estimate of k₄ of (1.0±0.2) × 10⁻¹¹ cm³ s⁻¹. Although the variation of k₄ and the diffusion coefficient alters the z profile quite significantly, the effect on the maximum intensity is much smaller, as shown in Fig. 4.

B. N₂(C–B) emission from the reaction of Ar⁺ with N₂

This reaction has been well studied⁴³,⁴⁴ and the spectrum is very well characterized.⁵² We measured spectra between 280 and 410 nm, including band sequences with Δυ = +2 to −3, involving N₂(C ³Π_u) levels with v' = 0–3. The spectral intensities were analyzed, using the known absolute transition probabilities,⁴⁵ to obtain the vibrational distribution in the N₂(C) state: it was found to agree with previous measurements⁴³ for the Ar⁺(3P₂)+N₂ reaction. In the remaining experiments, the monochromator was set to the peak of the (0,0) band at about 337 nm.

For a fixed N₂ injector position, the variation of intensity along the flow tube was measured and is shown in Fig. 5 for N₂ concentrations in the range 1.7 × 10¹³ to 1.3 × 10¹⁴ cm⁻³. The profile differs from that for CO(a−X) because the N₂(C) state has a very short radiative lifetime,⁴⁵ about 40 ns. The profile thus should parallel that of Ar⁺ concentration and a linear dependence of ln(intensity) versus z is expected. The slight deviation from linearity in Fig. 5, particularly at the highest N₂ concentration, is not fully understood; when the injector was positioned a few centimetres further downstream, improved linearity of the plots was found.

For the absolute calibration of the emission detection system, the total emission signal from N₂ was used. This involved integration in two distinct dimensions:

(i) Spectral integration over all bands from v' = 0–3,
which was performed using the derived vibrational distribution and the known Einstein emission coefficients.

(ii) Integration of the signal along the flow tube. This involved three steps. First, the signal was integrated over the observed region \((z = 3\ldots 13)\), correcting for the spurious dip which occurs at the injector. Second, by extrapolation, the integration was extended further downstream, assuming exponential decay of the intensity in this region. Third, a small correction was made to minimize the effect of drifts in conditions. Such experiments were carried out on three separate days.

The size of the corrections arising from the second and third steps ranged from about 60% of the measured integrated signal at the lowest \(N_2\) concentration to about 7% at the highest concentration. After the corrections had been applied, the integrated signals at the four concentrations in this particular experiment agreed within a 6% range, showing the validity of the analysis procedure.

C. \(\text{NO}^+\) production from the reaction of \(\text{Ar}^+\) with NO

When NO was added to a stream of \(\text{Ar}^+\) metastable atoms, a sharp increase in the electron density, as measured by the Langmuir probe, was observed (Fig. 6). The measurements were normally made with the probe positioned on the tube axis. However, close to the injector, where the mixing of the NO with the carrier gas was not complete, the maximum electron density at a given \(z\) was located with the probe rotated off axis. The data in Fig. 6 represent the maximum electron density measured at each axial position. The data in all experiments, spanning the range of NO concentrations \(1.7\ldots 3.5 \times 10^{14} \text{ cm}^{-3}\), showed a small increase in the electron density, \(n_e\), following the jump, with a slow decrease further downstream. As shown by this figure, the observed behavior was independent of NO concentration. Simulations were carried out, which included the loss of \(\text{NO}^+\) by dissociative recombination [rate constant\(=4.0 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}\) (Ref. 48)] and diffusion. The general profile of the experimental data was reproduced, except that the maximum in \(n_e\) was predicted to occur closer to the injector. It was concluded that the electron loss processes could be accounted for by adding 10% to the maximum in the electron density profiles in plots such as Fig. 6.

D. Absolute yield of \(\text{CO}(a)\) in the reaction of \(\text{CO}_2^+\) with electrons

Each of the above experiments was repeated until consistent and reproducible relative data were obtained for each experiment. Then, all three reactions were investigated, over a limited range of reagent conditions, in a single experiment to minimize the effect of drifts in conditions. Such experiments were carried out on three separate days.

The \(\text{Ar}^+ + \text{NO}, \text{N}_2\) data provided an absolute calibration of the emission detection system (at a wavelength of 337 nm) by comparing the \(\text{Ar}^+\) flux (deduced from the \(\text{NO}^+\) yield) and the integrated \(\text{N}_2(C-B)\) emission signal. Use of the spectral response of the detection system extended this absolute calibration to 216 nm, the wavelength at which the \(\text{CO}(a-X)\) data were collected. The \(\text{CO}(a)\) simulations essentially yielded the fraction of \(\text{Ar}^+\) flux appearing as \(\text{CO}(a-X)\) emission at the peak in the \(z\) profile (Fig. 3).
together with the absolute calibration, this provided a prediction of the signal (counts/s at 216 nm) which would be measured if the yield of CO\(_2\) from CO\(_2^+ + e^-\) was unity. Finally, comparison of this predicted signal with the actual measured signal yielded the fraction of CO\(_2^+\) dissociative recombination which produced CO\(_a\). The value obtained from the complete data set was 0.29 ± 0.10, where the stated uncertainty represents one standard deviation and includes the propagated errors from all sources.

IV. DISCUSSION AND CONCLUSIONS

A. Collisional quenching of CO\(_a\) by CO\(_2\)

Collisional quenching of CO\(_a\) has been extensively studied.\(^{15}\) Many polyatomic species, especially those containing hydrogen, quench CO\(_a\) at close to the collision rate. It is accepted that CO\(_2\) is anomalously inefficient, but the rate constant is still uncertain. The present measurement, \((1.0 ± 0.2) \times 10^{-11} \text{cm}^3 \text{s}^{-1}\), is smaller than previous measurements, most of which lie in the range \((1.2 \text{ to } 2.0) \times 10^{-11} \text{cm}^3 \text{s}^{-1}\). It is known that CO\(_2^+ + e^-\) recombination contributed to CO\(_a\) production in several of the previous studies. Under those conditions, the present simulations reveal that, at high concentrations of CO\(_2\), the rate of decay of CO\(_a\) does not solely reflect the rate of quenching by CO\(_2\); rather, CO\(_a\) approaches a steady-state condition, at which the decay profile is determined by the rate of formation of CO\(_a\). If this was not taken into consideration in the analysis of the decay data, it would have led to an underestimation of the quenching rate constant. Unfortunately, this cannot explain the fact that most of the previous values are larger than the present result.

B. Formation of CO\(_a\) in CO\(_2^+ + e^-\) recombination

This study has confirmed the original findings of Wauchope and Broida\(^{17}\) that a substantial fraction of the recombination of CO\(_2^+\) with e\(^-\) passes through the CO\(_a\) \(^3\)II state. These authors give no details of the procedure used to extract the absolute yield and thus we prefer the value presented here. It is disconcerting that, as part of their analysis, Wauchope and Broida derived a quenching rate constant for CO\(_a\) + CO\(_2\) of \(4.1 \times 10^{-11} \text{cm}^3 \text{s}^{-1}\), considerably higher than most other measurements.

Measurements of absolute product yields are subject to several potential sources of error. Those arising from the experimental measurements, the calibration reactions and from the simulations are discussed here. The repeatability of the measurements was good, leading to a random error of less than 10%. The original determination\(^{23}\) of the NO\(^+\) yield from Ar\(^+\)-NO used Ar\(^+\)-N\(_2\)-N\(_2\)(C) as part of the calibration process. It can be deduced that the sizable uncertainty (30%) in the N\(_2\)(C) yield fortuitously does not enter into the yield of CO\(_a\) from CO\(_2^+ + e^-\). The agreement between the two measurements of the NO\(^+\) yield\(^{23,24}\) is very good, as discussed by Jones et al.\(^{24}\).

The simulations, which utilize rate constants \(k_1\) to \(k_4\), were also an integral part of our determination of the CO\(_a\) yield. The yield depends directly on the value of \(k_3\). \(k_2\) was fixed within a small range by the need to fit the z dependence of the electron density. Variation of \(k_1\) and \(k_2\) over their expected ranges of uncertainty had a minor effect on the final CO\(_a\) yield. Equivalent fits to the experimental CO\(_a\) \(~X\) profiles could be obtained by simultaneously changing \(k_4\) and the diffusion coefficient of CO\(_a\). Thus these quantities are not determined well, but the maximum CO\(_a\) concentration obtained in the simulations was affected only slightly by these changes. Based on this variation, the limited success in modeling the dependence of the peak CO\(_a\) \(~X\) emission intensity on CO\(_2\) concentration and the uncertainty in \(k_3\), we derive an 18% uncertainty in the CO\(_a\) yield arising from the simulations.

Measurements in our flow system have revealed the presence of a small concentration of Ar\(^+\) metastables, 10%–12% of that of the Ar\(^+\) ions. These react with CO\(_2\) to give CO\(_a\) with a branching fraction\(^{21}\) of \(~0.16\). Simulations carried out including this reaction led to an 8% contribution to the maximum CO\(_a\) concentration. The derived CO\(_a\) yield of 0.29 presented in the previous section has been corrected for this contribution.

C. Other processes in CO\(_2^+ + e^-\) recombination

At present, insufficient information is available to provide a complete picture of energy disposal in CO\(_2^+ + e^-\) recombination, even amongst the triplet states of CO. Intense CO emission from the \(\\left(a'\ 3\Sigma^+\right), \ (d\ 3\Delta), \text{ and } (e\ 3\Sigma^-)\) states has been observed\(^{21,40}\), particularly from CO\(_a\) and \(d\), but no absolute yields have been reported. For CO\(_a\)' emission, from \(v = 3\) – 11 has been reported, peaking at \(v = 5\); for CO\(_d\), \(v = 0\) – 6 are observed, with the peak at \(v = 1.21,40\). At present there appears to be no direct information concerning the populations of levels \(v = 0\) – 2 of the CO\(_a\) state. CO\(_a\) \(~a\) bands from these low-lying levels occur in the ir beyond the spectral detection region of Tsuji et al.\(^{84}\).

Interpretation of the data is complicated by two interesting phenomena. First, cascade emission from CO\(_a\) \(d, \text{ and } e\) contributes to the population of the CO\(_a\) state. Using the reported vibrational distributions and relative populations in these two states, the relative vibrational distribution in the CO\(_a\) \(v = 0\) – 3 levels arising from the \(\left(a'\ a\right)\) and \(\left(d\ a\right)\) transitions was calculated and found to be comparable to that observed in the present study. It is possible therefore that cascade emission contributes significantly to the observed CO\(_a\) population.

Second, these triplet states are connected also by collisional crossing between CO\(_a\) \(v \geq 4\) and the CO\(_a\) \((a')\) state and between CO\(_a\) \(v \geq 8\) and the CO\(_d\) state (see Fig. 1). Ottinger et al.\(^{50}\) have studied CO\(_a\) emission resulting from collisions of He with a beam of CO\(_a\) molecules with a vibrational temperature of about 6400 K and find a vibrational distribution in the \(a'\) state which is comparable to that reported by Tsuji et al.\(^{21}\). We have obtained preliminary evidence for the occurrence of CO\(_a\) \(a\) collision-induced transitions in the CO\(_2^+\) recombination system by detection of weak emission from CO\(_a\) \(v = 4\) – 7 \(\text{[which have similar}\)
energies to CO(a′, v = 0–4)]. These emissions decay down the flow tube significantly more rapidly than CO(a,v = 0–3), as expected if an additional loss process is available. Under the experimental conditions of the present study and of that of Tsuji et al., CO(a→a′) and, where energetically possible, CO(a→d) collision-induced transfer is expected to be a major loss process for CO(a,v ≈ 4), while the reverse processes are expected to be less dominant because of the lower radiative lifetimes of the CO(a′) and CO(d) states. We conclude that it is possible that CO(a→a′) transitions contribute to the observed CO(a′) [and CO(d)] emissions in CO₂⁺ + e⁻ recombination under flow tube conditions. Further studies are planned to clarify the pathways leading to formation of the CO triplet states in this reaction system.

Our results, combined with those of Gutchek and Zipf, show that about one-third of CO₂⁺ + e⁻ recombination events form singlet and triplet excited states of CO. We expect that the remainder gives rise to CO(X 1Σ⁺) + O(P, 1D, 3Σ) products. Recombination occurs by capture of an electron to form a repulsive electronic state of CO₂, possibly via an intermediate bound Rydberg state. Potential-energy surfaces of CO₂ are not known sufficiently well for the exact path or paths to be determined. Also, because of the very large number of electronic states of CO₂ which correlate with CO(a 1Π, a′ 3Σ⁺, and d 3Δ) + O(P), it is difficult to predict which state or states are involved.

It is interesting, however, to compare the dissociation pathways from CO₂⁺ + e⁻ recombination with those from photodissociation of CO₂. In separate studies, the absorption coefficient of CO₂ up to (and beyond) the first ionization limit and the cross sections for photodissociation to CO(a 1Π), CO(a′ 3Σ⁺, and d 3Δ), and CO(A 1Π) (Ref. 56) have been measured. For photoexcitation at 90.0 nm, close to the ionization energy, the results agree qualitatively with those for CO₂⁺ + e⁻ recombination. First, the measured yield of CO(a) from CO₂ photodissociation is about 60%, compared to about 30% from CO₂⁺ recombination. As in our experiments, this figure includes formation via cascade from higher-energy triplet states. Second, CO(a′ 3Σ⁺) and CO(d 3Δ) are important products but their yield at 90.0 nm appears to be somewhat smaller than that of CO(a). Finally, the vibrational distributions in CO(a, a′, and d) are similar to those resulting from CO₂⁺ recombination. One possible reason for this similarity in behavior is that both CO₂(X) and CO₂⁺(X) are linear molecules and have very similar bond lengths. Thus similar regions of the potential energy surfaces will be accessed initially in the two processes.

It cannot, however, be assumed that identical excited states of CO₂ are involved in photodissociation and CO₂⁻ recombination, because of the specific selection rules for the former process. The absorption and photodissociation spectra are highly structured, showing that several electronic states contribute to each dissociation channel. It would be interesting to compare the CO₂⁻ recombination products with those from HCO⁺ + e⁻, because far fewer valence excited states are expected to be accessible in this latter system.

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