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Citation: The Journal of Chemical Physics **97**, 162 (1992); doi: 10.1063/1.463616 View online: http://dx.doi.org/10.1063/1.463616 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/97/1?ver=pdfcov Published by the AIP Publishing

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Absolute state-selected and state-to-state total cross sections for the $Ar^+({}^2P_{3/2,1/2})+CO_2$ reactions

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(Received 13 January 1992; accepted 17 March 1992)

Absolute spin-orbit state-selected total cross sections for the reactions, Ar + $({}^{2}P_{3/2,1/2})$ + CO₂ \rightarrow CO₂⁺ + Ar [reaction (1)], CO + O + Ar [reaction (2)], $O^+ + CO + Ar$ [reaction (3)], $C^+ + 2O + Ar$ [reaction (4)], $ArC^+ + 2O$ [reaction (5)], $ArO^{+} + CO$ [reaction (6)], and $ArCO^{+} + O$ [reaction (7)] have been measured in the center-of-mass collision energy ($E_{\rm c.m.}$) range of 0.26–131 eV. The ratio of the charge-transfer cross section due to Ar + $({}^{2}P_{1/2})$ to that associated with Ar + $({}^{2}P_{3/2})$ varies in the range of 0.5-0.8. The appearance energies observed for CO $^+\,$ ($E_{\rm c.m.}=4.2\pm0.5$ eV), O $^+$ $(E_{\rm c.m.} = 3.7 \pm 0.5 \text{ eV})$, and C⁺ $(E_{\rm c.m.} = 12.6 \pm 0.5 \text{ eV})$ are in agreement with the thermochemical thresholds for reactions (2), (3), and (4), respectively. The comparison of the absolute cross sections for CO⁺, O⁺, and C⁺ from CO₂ by photoionization and by dissociative charge transfer [reactions (2)-(4)] is made. The kinetic-energy analysis of product CO₂⁺, CO⁺, O⁺, C⁺, ArO⁺, and ArC⁺ suggests that reactions (2)–(7) proceed via a charge-transfer predissociation mechanism. This experiment, together with the previous studies of Ar + $({}^{2}P_{3/2,1/2})$ + N₂ (O₂,CO), supports the conclusion that product ions formed by dissociative photoionization are also produced by dissociative charge transfer. We find that the absolute cross sections for product ions formed in the dissociative charge-transfer processes [reactions (2)-(4)] are substantially greater than those formed in the dissociative photoionization of CO_2 , a finding consistent with the general observation that photoionization cross sections are significantly smaller than charge-transfer cross sections. The relative cross sections for CO^+ , O^+ , and C^+ formed by reactions (2)–(4) are also found to be different from those for photoionization of CO_2 . This difference is attributed to the anisotropic interaction potential surface responsible for the Ar $^+$ ($^2P_{3/2,1/2}$) + CO₂ reactions.

I. INTRODUCTION

The rate constants for the Ar⁺ + CO₂ charge-transfer reaction in the center-of-mass (c.m.) collision energy $(E_{c.m.})$ range of ≤ 2.5 eV have been measured in many previous experiments using flow-tube and ion-cyclotron resonance techniques.¹⁻⁸ At thermal energies, the rate constant for the charge-transfer reaction Ar⁺ (${}^{2}P_{1/2}$) + CO₂ is reported to be significantly smaller than that for the Ar⁺ (${}^{2}P_{1/2}$) + CO₂ charge transfer.⁴ The collisions of Ar⁺ (${}^{2}P_{1/2}$) + CO₂ at thermal energies have been shown to be dominated by inelastic relaxation of Ar⁺ (${}^{2}P_{1/2}$) to Ar⁺ (${}^{2}P_{3/2}$).⁴ Fehsenfeld, Ferguson, and Schmeltekopf point out that the Ar⁺ + CO₂ reaction is of potential importance in the atmospheres of Mars and Venus.

Charge transfer has long been used as an experimental method for studies of the unimolecular dissociation dynamics of energy-selected ions.⁹ In recent experiments performed in our laboratory concerning the cross-section measurements of the Ar $+ (^{2}P_{3/2,1/2}) + N_{2}$ (CO,O₂) reactions, a charge-transfer predissociation mechanism has been proposed for the formation of N $+ (C^{+}, O^{+})$.¹⁰⁻¹⁴ Figures 1(a) and 1(b) compare the absolute cross sections for the formation of N + from N₂ and O + from O₂ by dissociative pho-

toionization¹⁵⁻¹⁸ (DP) and by the dissociative charge-transfer (DCT) processes^{11,12} involving Ar + (${}^{2}P_{3/2}$) in the $E_{c.m.}$ scale.¹⁹ The comparison of the DP (Refs. 15 and 20) and DCT cross sections^{10,13} for the formation of C^+ and O^+ from CO are shown in Figs. 2(a) and 2(b). It has been well established that $N^+(C^+,O^+)$ ions from $N_2(O_2,CO)$ by DP are produced via the predissociative excited states of $N_2^+(O_2^+,CO^+)$ indicated in Figs. 1(a), 1(b), 2(a), and 2(b).²¹ The appearance energies (AEs) observed for $N^+(C^+,O^+)$ formed in the DCT reactions Ar $({}^{2}P_{3/2}) + N_{2}(O_{2},CO)$ are found to agree with the thermochemical thresholds.¹⁰⁻¹³ This and the similar crosssection curves for N⁺ from N₂, O⁺ from O₂, and C⁺ and O⁺ from CO observed in photoionization and in Ar $({}^{2}P_{3/2}) + N_{2}(O_{2},CO)$ DCT collisions are evidence that the DCT N $^+$ (C $^+$,O $^+$) ions are also formed via predissociative excited states of N_2^+ (CO⁺, O_2^+) similar to those involved in DP of N_2 (CO,O₂). The formation of N⁺ from N_2 , O⁺ from O₂, and C⁺ and O⁺ from CO by DP at sufficiently high photon energies includes small contributions from the dissociation of doubly charged parent ion states. To our knowledge, the formation of doubly charged parent ions or population of dissociative doubly charged parent ion states has not been reported in DCT for these systems in the



FIG. 1. (a) (**•**) Absolute total cross sections for the formation of N⁺ from the reaction of Ar⁺ (${}^{2}P_{3/2}$) + N₂ in the $E_{c.m.}$ range of 8–131 eV; (—) absolute total cross sections for the formation of N⁺ from photoionization of N₂. (b) (**•**) Absolute total cross sections for the formation of O⁺ from the reaction of Ar⁺ (${}^{2}P_{3/2}$) + O₂ in the $E_{c.m.}$ range of 3–150 eV; (—) absolute total cross sections for the formation of O⁺ from photoionization of O₂.

 $E_{\rm c.m.}$ range of < 150 eV. It is well known that neutral Rydberg states play an important role in populating the excited states of parent molecular ions, but the involvement of Rydberg states in charge transfer has not been explored. It is interesting to note that the total cross sections for N⁺ from N₂, O⁺ from O₂, and C⁺ and O⁺ from CO due to DP are only about 2% of those arising from the corresponding DCT processes.

In order to examine further the similarities and differences of the DCT and DP processes, we have decided to extend the DCT cross-section measurements to involve a triatomic molecule. The electronic states of CO_2^+ have been investigated extensively by photoelectron spectroscopy,²¹⁻³² (*e*,2*e*) spectroscopic techniques,³³⁻³⁵ and theoretical calculations.³⁶⁻³⁹ Furthermore, the photoionization and DP processes of CO_2 [processes (1)–(4)] have also been well studied by photoionization,^{20,40-46} photoelectron–photoion coincidence^{29,47} (PEPICO) and (*e*,*e* + ion) methods:³⁴

 $\rightarrow \operatorname{CO}_2^+(\widetilde{X}) + e^-, \qquad \Delta E = 13.788 \text{ eV} \quad (1)$

 $CO_2 + hv$

 $\rightarrow CO^{+}(\tilde{X}) + O(^{3}P) + e^{-}, \quad \Delta E = 19.466 \text{ eV}$ (2)

$$\rightarrow O^{+}(^{4}S) + CO(X) + e^{-}, \quad \Delta E = 19.067 \text{ eV}$$
 (3)

$$\rightarrow C^{+}(^{2}P) + 2O(^{3}P) + e^{-}, \quad \Delta E = 27.80 \text{ eV}.$$
 (4)

To our knowledge, the dissociative and reactive chan-



FIG. 2. (a) (**•**) Absolute total cross sections for the formation of C⁺ from the reaction of Ar⁺ (${}^{2}P_{3/2}$) + CO in the $E_{c.m.}$ range of 4.5–131 eV; (—) absolute total cross sections for the formation of C⁺ from photoionization of CO. (b) (**•**) Absolute total cross sections for the formation of O⁺ from the reaction of Ar⁺ (${}^{2}P_{3/2}$) + CO in the $E_{c.m.}$ range of 7–140 eV; (—) absolute total cross sections for the formation of O⁺ from photoionization of CO.

nels for the Ar⁺ + CO₂ reactions have not been examined. In addition to the exothermic charge-transfer channel [reaction (5)], the results of previous photoionization experiments on CO₂ suggest that we may find three DCT channels [reactions (6)–(8)], which are all endothermic,⁴⁸

$$Ar^{+}(^{2}P_{3/2}) + CO_{2}$$

$$\rightarrow CO_{2}^{+}(\widetilde{X}) + Ar, \qquad \Delta E = -1.984 \text{ eV} \quad (5)$$

$$\rightarrow CO^{+}(\widetilde{X}) + O(^{3}P) + Ar, \quad \Delta E = 3.708 \text{ eV} \quad (6)$$

$$\rightarrow O^{+}(^{4}S) + CO(X) + Ar, \quad \Delta E = 3.31 \text{ eV}$$
 (7)

$$\rightarrow C^{+}(^{2}P) + 2O(^{3}O) + Ar, \quad \Delta E = 12.066 \text{ eV}.$$
 (8)

The previous studies of the $Ar^+({}^2P_{3/2,1/2})$ + $N_2(CO,O_2)$ reactions reveal the formation of reactive ionic product ArN^+ (ArC^+ , ArO^+).⁹⁻¹³ Based on the results of these experiments and the open channels identified in the photoionization of CO_2 , we predict that product $ArCO^+$, ArC^+ , and ArO^+ ions may be formed in the reactive collisions of $Ar^+({}^2P_{3/2,1/2}) + CO_2$ via reactions (9)– (11),

$$Ar^{+}(^{2}P_{3/2}) + CO_{2} \rightarrow ArC^{+} + 2O$$
 (9)

$$\rightarrow ArO^{+} + CO \qquad (10)$$

$$\rightarrow \text{ArCO}^+ + \text{O.} \tag{11}$$

In accord with these predictions, we have positively identified reactions (5)-(11) in this experiment. The cross sec-

tions for the corresponding reactions involving the excited Ar $^+$ ($^2P_{1/2}$) state have also been measured.

II. EXPERIMENT

The triple–quadrupole double-octopole (TQDO) photoionization apparatus used in this study has been described in detail.^{12,49,50} The TQDO apparatus consists of a 0.2 m vacuum-ultraviolet (VUV) monochromator (McPherson 234), a discharge lamp, a tungsten photoelectric VUV light detector, three quadrupole mass filters (QMF), two radiofrequency (rf) octopole ion guide reaction gas cells, a supersonic free-jet production system, and a variant of the scintillation ion detector. The arrangement of the apparatus requires reactant ions formed by photoionization to pass through, in sequential order, the reactant QMF, the lower rf octopole ion guide reaction gas cell, and product QMF before their detection by the scintillation ion detector.

A. Absolute total cross-section measurements

The experimental procedures for these absolute total cross-section measurements are similar to those outlined previously.¹² Briefly, the Ar $^+$ reactant ions in the pure $^2P_{3/2}$ state or in a 2:1 mixture of ${}^{2}P_{3/2}$ and ${}^{2}P_{1/2}$ states are prepared by photoionization of an Ar free jet at 786 and 769 Å, respectively, using a wavelength resolution of 3.5 Å [full width at half maximum (FWHM)]. The reactant Ar + ions formed in the photoionization region are extracted perpendicular to the Ar free jet and mass selected by the reactant QMF before reacting with CO₂ in the upper rf octopole ion guide reaction gas cell. The CO₂ gas cell pressure is monitored with a Baratron manometer (MKS model 390HASP05) and a gas cell pressure of $(1-2) \times 10^{-4}$ Torr is used in this experiment. The Ar $^+$ reactant ions and CO₂ $^+$, CO $^+$, C $^+$, O $^+$, ArCO $^+$, ArO⁺, and ArC⁺ product ions formed in the upper rf octopole ion guide reaction gas cell are mass selected by the product QMF and detected by the scintillation ion detector.

The Ar⁺ reactant ion-beam laboratory energy ($E_{\rm lab}$) is measured by the retarding potential energy and the time-offlight methods.¹² At each $E_{\rm lab}$ the product ion collection efficiencies are maximized carefully by optimizing the ion transmission through the ion lenses and product QMF and the rf voltage applied to the upper octopole ion guide.

The precision or reproducibility of cross sections reported is 5%–10%. The accuracy of the absolute cross sections is estimated to be $\pm 25\%$. The uncertainties of the relative cross sections due to the Ar + (${}^{2}P_{3/2}$) and Ar + (${}^{2}P_{1/2}$) reactant states are better than $\pm 25\%$.

B. Retarding potential-energy analyses of product ions

The retarding potential-energy (RPE) curves for product CO_2^+ , CO^+ , C^+ , O^+ , ArO^+ , and ArC^+ ions are obtained using the same experimental arrangement and procedures as those employed for measuring the RPE curve of the reactant Ar^+ ion. Using the product QMF to select the product ion of interest, the RPE curves for various product ions at a given E_{lab} of reactant Ar^+ can be recorded individually.

III. RESULTS AND DISCUSSION

A. Absolute cross sections for charge transfer CO₂⁺

Figure 3(b) shows the absolute cross sections for product $CO_2^+ [\sigma_{3/2} (CO_2^+)]$ formed in the charge-transfer collisions of Ar⁺ (²P_{3/2}) + CO₂ [reaction (5)] in the $E_{c.m.}$ range of 0.26–131 eV. The cross section for reaction (5) exhibits a minimum of 1.4 Å² at $E_{c.m.} \approx 10$ –12 eV, and increases rapidly toward lower $E_{c.m.}$. At $E_{c.m.} = 0.26$ eV, $\sigma_{3/2} (CO_2^+)$ has a value of 54 Å². This observation of a rapid increase in cross section as $E_{c.m.}$ is decreased toward thermal energies, typical for an exothermic ion-molecule reaction process such as reaction (5), is in qualitative accord with the Langevin-Gioumousis-Stevenson orbiting complex model.^{51,52}

Two flow-tube measurements for the rate constants (k)of the Ar⁺ + CO₂ charge-transfer reaction in the $E_{c.m.}$ range of 0.04–2.5 eV have been reported previously.^{3,6} Since electron-impact ionization was used to prepare reactant Ar⁺ in the rate-constant measurements, it is most likely that



FIG. 3. (a) (•) Absolute total cross sections for the formation of CO⁺, O⁺, C⁺, ArO⁺, ArC⁺, and ArCO⁺ from the collisions of Ar⁺(²P_{3/2}) + CO₂ in the $E_{c.m.}$ range of 2.5–131 eV; (---) absolute cross sections for the formation of CO⁺, O⁺, and C⁺ from photoionization of CO₂. (b) (•) Absolute total cross sections for CO₂⁺ formed in the chargetransfer collisions of Ar⁺(²P_{3/2}) + CO₂ in the $E_{c.m.}$ range of 0.25–131 eV; (---) the sum of absolute cross sections for CO₂⁺, CO⁺, O⁺, C⁺, ArCO⁺, ArO⁺, and ArC⁺ in the $E_{c.m.}$ range of 4–131 eV; (·-·) effective total cross sections at $E_{c.m.} \approx 0.25$ –1.2 eV converted from rate constants for the Ar⁺ + CO₂ reaction (Ref. 3); (····) effective total cross sections at $E_{c.m.} \approx 0.1$ –2 eV converted from rate constant for the Ar⁺ + CO₂ reaction (Ref. 6); see text. (c) Values for the ratio $\sigma_{1/2}$ (CO₂⁺)/ $\sigma_{3/2}$ (CO₂⁺) in the $E_{c.m.}$ range of 0.1–131 eV.

the k values represent the cross sections due to a mixture of Ar + $({}^{2}P_{3/2})$ and Ar + $({}^{2}P_{1/2})$. The k values can be converted into effective cross sections (σ) using the approximate relation, $k \approx \sigma v$, where v is the average relative velocity of the Ar + + CO₂ colliding pair. As shown in Fig. 3(b), the σ values derived from the rate constants of Refs. 3 and 6 are in poor agreement, and the values for $\sigma_{3/2}$ (CO₂⁺) at $E_{c.m.} = 0.26-2$ eV obtained in this experiment fall in between the σ values of Refs. 3 and 6. We note that since the kinetic-energy spreads of reactants in this and the flow-tube experiments are different, a precise comparison of the results of these experiments is difficult.

The valence shell electronic configuration²² of CO_2 can be written as

$$(3\sigma_g)^2(2\sigma_u)^2(4\sigma_g)^2(3\sigma_u)^2(1\pi_u)^4(1\pi_g)^4;^1\Sigma_g^+$$

The removal of an electron from the $1\pi_g$, $1\pi_u$, $3\sigma_u$, or $4\sigma_g$ orbital leaves CO_2^+ in the $\tilde{X}\,^2\Pi_g$, $\tilde{A}\,^2\Pi_u$, $\tilde{B}\,^2\Sigma_u^+$, or $\tilde{C}\,^2\Sigma_g^+$ state, respectively. The $E_{c.m.}$ thresholds¹⁹ for the CO_2^+ ($\tilde{A}\,^2\Pi_u$, $\tilde{B}\,^2\Sigma_u^+$, and $\tilde{C}\,^2\Sigma_g^+$) states²² are 1.54, 2.31, and 3.62 eV, respectively. Studies of the binding-energy spectra of CO_2 obtained using He II (Ref. 26) and x-ray^{27,28} and (e,2e)³⁵ spectroscopic methods have identified electronic bands corresponding to multiple electron transitions (MET). The MET I–VI states are attributed to ionization of an electron from the $3\sigma_g$ or $2\sigma_u$ orbital along with other excitations.³⁴ The positions of the excited CO_2^+ ($\tilde{C}\,^2\Sigma_g^+$, MET I–VI) states are marked in Fig. 3(a).

The value for $\sigma_{3/2}$ (CO₂⁺) increases monotonically as $E_{\rm c.m.}$ is increased from $E_{\rm c.m.} \approx 12$ eV and reaches a value of 5 Å² at $E_{c.m.} = 131$ eV. It is interesting to note that the $E_{c.m.}$ dependence of the cross section of CO_2^+ formed in the O^+ (⁴S) + CO₂ charge-transfer reaction^{53,54} displays a profile similar to that observed for $\sigma_{3/2}$ (CO₂⁺) at $E_{c.m.} \approx 8-131$ eV. That is, the cross section for the $O^+({}^4S) + CO_2$ chargetransfer reaction has a minimum at $E_{\rm c.m.} \approx 10$ eV and increases as $E_{\rm c.m.}$ is increased from $E_{\rm c.m.} \approx 10 \, \rm eV$. This observation suggests that the electronic states of CO_2^+ , such as the $\tilde{C}^{2}\Sigma_{g}^{+}$ and MET I–VI states, appearing in this $E_{c.m.}$ range are mostly responsible to the profile of the cross sections for the Ar $^+$ + CO₂ and O $^+$ (⁴S) + CO₂ charge-transfer reactions. However, we note that the absolute charge-transfer cross sections for $O^+(^4S) + CO_2$ are significantly greater than those for reaction (5) at $E_{c.m.} > 10 \text{ eV}$.

Figure 3(c) shows the plot of the ratio $\sigma_{1/2}(CO_2^+)/$ $\sigma_{3/2}$ (CO₂⁺) vs $E_{c.m.}$. At $E_{c.m.} = 0.26-10$ eV, the ratio is found to be in the range of $\approx 0.5-0.6$. It increases from about 0.5 at $E_{c.m.} = 10 \text{ eV}$ to 0.7 at $E_{c.m.} = 20 \text{ eV}$ and then increases gradually from 0.7 to 0.8 as $E_{\rm c.m.}$ is increased in the of eV. 20-131 Energetically, range the Ar + $({}^{2}P_{3/2,1/2})$ + CO₂ states are in close energy resonance with the CO₂⁺ ($\tilde{X}^{2}\Sigma_{g}^{+}, v$) + Ar states for CO₂⁺ ($\tilde{X}^{2}\Sigma_{g}^{+}$) in highly vibrationally excited states. It is most likely that a high vibrational state of $\operatorname{CO}_2^+(\widetilde{X}\,^2\Sigma_g^+)$ exists, which is in closer energy resonance with the Ar⁺ ($^{2}P_{3/2}$) + CO₂ state compared to the Ar + $({}^{2}P_{1/2})$ + CO₂ state, favoring the formation of CO_2^+ by process (5).

At $E_{c.m.} > 3.7 \text{ eV}$, the DCT processes (6)–(8) and reac-

tive processes (9)–(11) are energetically allowed. The sum of the cross sections for these processes is plotted in Fig. 3(a). In the region of $E_{\rm c.m.} > 8$ eV, the values for the sum of the dissociative and reactive cross sections are comparable to those for charge transfer. The existence of extensive curve crossings and electronic state mixings, which leads to predissociation of excited CO_2^+ , are expected to reduce the energy resonance effect for charge transfer. The higher value for the ratio $\sigma_{1/2} (CO_2^+)/\sigma_{3/2} (CO_2^+)$ observed at $E_{\rm c.m.} > 10$ eV is consistent with this expectation.

Figure 3(b) also shows the sum of the cross sections for processes (5)–(11). At $E_{c.m.} = 20-100$ eV, this sum stays essentially constant and has a value of 5.3 Å².

B. Absolute cross sections for DCT processes

The absolute cross sections for the formation of CO⁺, O⁺, and C⁺ from the collisions of Ar⁺(${}^{2}P_{3/2}$) + CO₂ in the $E_{c.m.}$ range of 3–131 eV are depicted in Figs. 4(a), 5(a), and 6(a), respectively. The mass spectra observed at 5–200 eV reveal mass peaks corresponding to O₂⁺. Background O₂⁺ ions may arise from the charge-transfer reaction involving reactant Ar⁺ and ambient O₂. The thermochemical threshold for the formation of O₂⁺ from the Ar⁺(${}^{2}P_{3/2}$) + CO₂ reaction is 7.8 eV.⁴⁸ The absolute cross sections observed for O₂⁺ intensity rises in the $E_{c.m.}$ region of 6–7.8



FIG. 4. (a) (•) Absolute total cross sections for the formation of CO⁺ from reaction (6) in the $E_{c.m.}$ range $\approx 1.5-131 \text{ eV}$; (--) absolute cross sections for the formation of CO⁺ from photoionization of CO₂. (b) (\odot) Values for the ratio $\sigma_{1/2}$ (CO⁺)/ $\sigma_{3/2}$ (CO⁺) in the $E_{c.m.}$ range 1.5-131 eV. (c) (\odot) Absolute total cross sections for O₂⁺. The formation of O₂⁺ is attributed mainly to background reactions; see text.

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FIG. 5. (a) (\bullet) Absolute total cross sections for O⁺ formed by reaction (7) in the $E_{c.m.}$ range of 1.5–131 eV; (--) absolute cross sections for the formation of O⁺ by photoionization of CO₂. (b) (\odot) Values for the ratio $\sigma_{1/2}$ (O⁺)/ $\sigma_{3/2}$ (O⁺) in the $E_{c.m.}$ range of 5–131 eV.

eV, an observation which seems to support the conclusion that the majority of O_2^+ ions are produced from the $Ar^+({}^2P_{3/2}) + CO_2$ reaction. If the O_2^+ ions indeed originate from the collisions of $Ar^+({}^2P_{3/2}) + CO_2$, we expect that O_2^+ ions thus formed have kinetic energies greater than those of the charge-transfer ions. Contrary to this expectation, the retarding potential analysis indicates that O_2^+ ions are overwhelmingly slow ions. Based on this analysis, to-



FIG. 6. (a) (•) Absolute total cross sections for C⁺ formed by reaction (8) in the $E_{c.m.}$ range of 8–131 eV; (---) absolute cross sections for the formation of C⁺ by photoionization of CO₂. (b) (\odot) Values for the ratio $\sigma_{1/2}$ (C⁺)/ $\sigma_{3/2}$ (C⁺) in the $E_{c.m.}$ range of 14–131 eV.

gether with the fact that O_2^+ is not identified as a product in the photoionization of CO_2 , we believe that the O_2^+ ions observed here are unlikely to be the products of the $Ar^+({}^2P_{3/2}) + CO_2$ reaction.

1. Absolute cross sections for CO+

The CO⁺ ion is the dominant fragment compared to O⁺ and C⁺. The experimental onset for CO⁺ is determined to be 4.2 \pm 0.5 eV [Fig. 4(a)], which is slightly higher than the thermochemical threshold of 3.71 eV for reaction (6). The cross section for CO⁺ [$\sigma_{3/2}$ (CO⁺)] formed by reaction (6) rises gradually from the onset, reaches a maximum of 2.2 Å² at $E_{c.m.} \approx 20$ eV, and then decreases to a broad minimum of 1.0 Å² at $E_{c.m.} \approx 65$ –100 eV.

The partial DP cross sections^{15,34,46} for CO⁺ from CO₂ are also plotted in Fig. 4(a) for comparison with the DCT cross sections for CO⁺ from reaction (6). The absolute cross sections for CO⁺ formed by the DP process (2) are nearly 100-fold smaller than those by the DCT reaction (6). Unless specified, the DP cross sections given here are average values reported by Refs. 34 and 46.15 These studies suggest that CO⁺ is produced by predissociation via the $\tilde{C}^{2}\Sigma_{e}^{+}$ and MET states. The DP cross-section curve exhibits two peaks, a strong one at $E_{c.m.} = 15 \text{ eV}$ and a weak one at 40 eV. The strong DP peak is close to the maximum of the DCT cross-section curve for CO⁺. Ignoring the fine structure of the DP cross sections, the profiles for the DCT and DP cross sections have a similar kinetic-energy dependence. This suggests that CO⁺ ions observed here may also be produced by predissociation via excited CO_2^+ in the $\tilde{C}^2\Sigma_g^+$ and MET states initially populated in the charge-transfer collsions of Ar + $({}^{2}P_{3/2}) + CO_{2}$.

Figure 4(b) shows the ratios $\sigma_{1/2}$ (CO⁺)/ $\sigma_{3/2}$ (CO⁺) in the $E_{\rm c.m.}$ range of 5–131 eV. In the $E_{\rm c.m.}$ region (5–10 eV) close to the threshold of reaction (6) the ratio is greater than one. The ratio drops to a value below one at $E_{c.m.} > 12 \text{ eV}$ and has a value of ≈ 0.9 at $E_{\rm c.m.} = 15-131$ eV. According to the charge-transfer predissociation model, we expect to find the values for the ratios $\sigma_{1/2}$ (CO $^+$)/ $\sigma_{3/2}$ (CO $^+$) to be similar to those for $\sigma_{1/2}$ (CO₂⁺)/ $\sigma_{3/2}$ (CO₂⁺). Therefore, the observation that $\sigma_{1/2}$ (CO⁺) is greater than $\sigma_{3/2}$ (CO⁺) at $E_{\rm c.m.} \approx 5-10$ eV is surprising. In the absence of any accurate theoretical interpretations, we tentatively attribute this finding to an energetic effect. Since the formation of CO + from the $Ar^+ + CO_2$ is an endothermic process, the CO⁺ threshold due to Ar + $({}^{2}P_{1/2})$ should be lower than that associated with Ar⁺ (${}^{2}P_{3/2}$). The shift to lower $E_{c.m.}$ for the CO⁺ threshold due to Ar⁺ (${}^{2}P_{1/2}$) would account for the observation of $\sigma_{1/2}$ (CO ⁺)/ $\sigma_{3/2}$ (CO ⁺) > 1 at $E_{c.m.}$ close to the onset for the formation of CO +. However, one may argue that the spin-orbit state separation of 0.178 eV for Ar $({}^{2}P_{J})$ is too small to cause a significant difference in the production of CO⁺.

2. Absolute cross sections for O⁺

Taking into account the experimental uncertainties, the onset of 3.7 ± 0.5 eV determined for O⁺ [Fig. 5(a)] agrees

with the thermochemical threshold of reaction (7). The profile for the $E_{c.m.}$ dependence of the cross section for O⁺ formed by reaction (7) $[\sigma_{3/2} (O^+)]$ is similar to that for $\sigma_{3/2} (CO^+)$. The value for $\sigma_{3/2} (O^+)$ is peaked at $E_{c.m.} \approx 15$ eV and is about six times smaller than that for $\sigma_{3/2} (CO^+)$.

The DP cross sections for O⁺ from CO₂ are compared to $\sigma_{3/2}(O^+)$ in Fig. 5(a). The DP cross-section curve also displays two peaks with the position of the major peak is at $E_{\rm c.m.} \approx 23 \, {\rm eV}$. The maximum cross section for O⁺ formed in the DCT process (7) is about tenfold higher than that resulting from the DP process (3). The threshold for the formation of O⁺ (^{4}S) + CO(X) by process (3) is very close to the ionization energy (IE) of CO₂ to CO₂⁺ ($\tilde{C}^{2}\Sigma_{g}^{+}$). For photon energies between the thresholds of processes (2) and (3), the previous PEPICO studies^{29,47} indicate that the CO_2^+ ($\bar{C}^2\Sigma_g^+$, v = 0-2) states are 100% predissociative to form $O^+({}^4S) + CO(X)$. This, together with the high Franck-Condon factors for the formation of CO₂⁺ $(\tilde{C}^{2}\Sigma_{s}^{+}, v = 0-2)$ by photoionization results in the relatively rapid rise of the DP cross section for O⁺ at the threshold. For higher photon energies, the previous (e,e+ion)study³⁴ suggests that the MET states also contribute to the formation of O^+ . We note that the maximum of the DCT cross-section curve lies in the $E_{c.m.}$ region of the MET states [see Fig. 5(a)].

The relative values of the DCT cross sections for O⁺ due to the spin-orbit Ar + $({}^{2}P_{3/2,1/2})$ states are shown in Fig. 5(b). As expected, $\sigma_{1/2}$ (O⁺) is less than $\sigma_{3/2}$ (O⁺), similar to the trend observed for the spin-orbit cross sections of the Ar $^+$ ($^2P_{3/2,1/2}$) + CO₂ charge-transfer reaction. The values observed for the ratio $\sigma_{1/2}$ (O⁺)/ $\sigma_{3/2}$ (O⁺) at $E_{c.m.} = 5-$ 131 eV are in the range of $\approx 0.82-0.95$. It seems that the $\sigma_{1/2}$ (O ⁺)/ $\sigma_{3/2}$ (O ⁺) ratio increases as $E_{c.m.}$ is decreased toward the threshold for reaction (7). However, the low intensities of O⁺ observed near the threshold for reaction prevent accurate measurements of the (7) $\sigma_{1/2}$ (O ⁺)/ $\sigma_{3/2}$ (O ⁺) ratio at $E_{\rm c.m.} < 5$ eV.

3. Absolute cross sections for C+

The onset for the formation of C⁺ is determined to be 12.3 \pm 0.3 eV [Fig. 6(a)], in agreement with the thermochemical threshold of 12.07 for reaction (8). This observation indicates that the formation of C⁺ + O₂ in the collisions of Ar⁺ + CO₂ is not probable. The DCT cross section for C⁺ from reaction (8) peaks at $E_{c.m.} \approx 40$ eV with a value 0.72 Å², which is about 35% greater than the maximum cross section observed for the formation of O⁺ from reaction (7).

As shown in Fig. 6(a), the profiles of the DP cross sections for C⁺ and O⁺ are similar except for the shift in threshold. The position of the the maximum for $\sigma_{3/2}$ (C⁺) coincides with that of the minor peak of the DP cross-section curve for C⁺. The maximum DP cross section for C⁺ at $E_{\rm c.m.} \approx 22$ eV is about 35 times lower than that by DCT at $E_{\rm c.m.} \approx 40$ eV. The formation of C⁺ by DP is suggested to result from fragmentation of excited CO₂⁺ in the MET states at photon energies > 30 eV ($E_{\rm c.m.} > 14.2$ eV). The values observed for $\sigma_{1/2}(C^+)/\sigma_{3/2}(C^+)$ in the $E_{\rm c.m.}$ range of 13.5–131 eV are shown in Fig. 6(b). The profiles of the kinetic-energy dependence of the spin–orbit ratios for the formation of C⁺ and CO⁺ are similar. That is, $\sigma_{1/2}(C^+)$ is greater than $\sigma_{3/2}(C^+)$ near the threshold region ($E_{\rm c.m.} = 13.5-21$ eV) and the trend is reversed at $E_{\rm c.m.} > 30$ eV, where the ratio $\sigma_{1/2}(C^+)/\sigma_{3/2}(C^+)$ is in the range of $\approx 0.86-0.96$. Similar to the argument given above, we attribute the higher $\sigma_{1/2}(C^+)$ compared to $\sigma_{3/2}(C^+)$ to the energetic effect.

C. Absolute cross sections for reactive processes

The absolute cross sections for the formation of ArCO⁺, ArO⁺, and ArC⁺ (Fig. 7) are approximately 3 orders of magnitude smaller than that for charge transfer CO_2^+ . The maximum value for $\sigma_{3/2}$ (ArC⁺) is about three times those for $\sigma_{3/2}$ (ArO⁺) and $\sigma_{3/2}$ (ArCO⁺). Within the sensitivity of this experiment, ArO₂⁺ was not found, in accord with the conclusion than O₂⁺ is not formed in the collisions of Ar⁺ + CO₂. Due to the very low intensities of these reactive ions, their cross sections due to Ar⁺ (²P_{1/2}) were not measured. For the same reason, the experimental onsets for ArC⁺, ArO⁺, and ArCO⁺ from reactions (9)–(11) cannot be determined with accuracy.

The binding energies^{12,13,55-58} for Ar–O⁺ and Ar–C⁺ are low and have been estimated to have a value of 0.7 and 0.9 eV, respectively. Based on the ionization energy for ArCO to CO⁺ (\tilde{X}) ·Ar determined in a vacuum-ultraviolet photoionization experiment,⁵⁹ a value of 0.70 ± 0.06 eV is calculated for the binding energy of Ar–CO⁺ (\tilde{X}), in fair agreement of the theoretical estimate of 0.82.⁶⁰ The fact that the onsets for ArO⁺, ArC⁺, and ArCO⁺ are similar to those for O⁺, C⁺, and CO⁺ from Ar⁺ (²P_{3/2}) + CO₂ are in accord with the low binding energies for ArO⁺, ArC⁺,

FIG. 7. \Box , \odot , and \triangle are absolute total cross sections for the formation of ArCO⁺, ArO⁺, and ArC⁺ from reactions (11), (10), and (9), respectively.



and ArCO⁺. Similar to the previous observation of ArN⁺, ArO⁺, and ArC⁺ formed in the reactions of Ar⁺ + N₂ (O₂,CO), the formation of the reactive product ions ArCO⁺, ArO⁺, and ArC⁺ are only found in specific $E_{c.m.}$ ranges. This observation may be rationalized that ArO⁺, ArC⁺, and ArCO⁺ formed at higher $E_{c.m.}$ contain internal energies greater than the dissociation energies of these reactive ions.

D. Translational energy distributions of product ions

As pointed out in previous experiments,¹¹⁻¹³ the RPE analyses of product ions provide information about the ion translational energy distributions along the central axis of the rf octopole ion guide reaction gas cell. The RPE curves of product ions CO_2^+ , CO^+ , O^+ , ArO^+ , and ArC^+ formed in the collisions of $Ar^+(^2P_{3/2}) + CO_2$ at $E_{lab} = 5-200 \text{ eV}$ have been examined. Typical RPE curves for reactant $Ar^+(^2P_{3/2})$ and product ions at nominal $E_{lab}(Ar^+) = 10$, 25, and 100 eV are depicted in Figs. 8, 9, and 10, respectively.

To facilitate the discussion concerning the interpretation of the RPE curves, the Newton diagram for the formation of $ArO^+ + CO$, $CO^+ + ArO$ (or Ar + O), and $O^+ + ArCO$ (or Ar + CO) in the collisions of $Ar^+({}^2P_{3/2}) + CO_2$ at a nominal $E_{lab} = 25 \text{ eV}$ is shown in Fig. 11. At a nominal E_{lab} (Ar⁺) = 25 eV, the actual E_{lab} (Ar⁺) is determined to be 27.7 eV [$E_{\text{c.m.}} = 14.5 \text{ eV}$] by the RPE curve of reactant Ar + [see Fig. 8(a)]. The z axis coincides with the central axis of the rf octopole ion guide reaction gas cell. The scattering products are expected to have a cylindrical symmetry around the z axis. The RPE analysis is sensitive to the velocity component of a product ion projected along the z axis. Here, $\mathbf{v}_{c.m.}$, $\mathbf{v}_{c.m.}$ (CO₂), and $v_{c.m.} (Ar^+)$ are the c.m. velocities of the Ar $+ ({}^{2}P_{3/2}) + CO_{2}$ system, the reactant CO₂, and the reactant Ar + $({}^{2}P_{3/2})$, respectively. Based on the known thermochemical thresholds⁴⁸ for the formation of CO $^+$ (\tilde{X}) + ArO $[or Ar + O({}^{3}P)], O^{+}({}^{4}S) + ArCO [or Ar + CO(X)],$ and ArO⁺ + CO(X), we have calculated the maximum c.m. velocity circles for CO⁺ (\tilde{X}) [$v_{c.m.}$ (CO⁺)], O⁺ (⁴S) $[v_{c.m.} (O^+)]$, and ArO⁺ $[v_{c.m.} (ArO^+)]$ as shown in Fig.



FIG. 9. Nominal $E_{lab} = 25$ eV. Retarding potential-energy curves for (a) reactant Ar⁺ (---) and product CO₂⁺ (---), (b) product CO⁺ (---) and product ArO⁺ (---), and (c) product O⁺ (---) and product C⁺ (---). E_h and E_{fb} have the same meanings as indicated in Fig. 8. The marked position for E_{max} (ion) is the maximum laboratory kinetic energy for the ion allowed by energy conservation.

11. Since the bond dissociation energies for ArO and ArCO are expected to be low, but not known, they are assumed to be zero in the calculation. The maximum laboratory velocities are $v_{\rm c.m.} + v_{\rm c.m.} (\rm CO^{+})$ for $CO^+(\tilde{X}),$ $v_{\rm c.m.} + v_{\rm c.m.} (O^+)$ for $O^+ ({}^4S)$, and $v_{\rm c.m.} + v_{\rm c.m.} (ArO^+)$ for ArO⁺. The corresponding maximum laboratory energies E_{max} are calculated and indicated in Figs. 9(a)-9(c). The intensities for CO_2^+ , CO^+ , O^+ , C^+ , and ArO^+ are in the noise level as the RPEs are greater than the corresponding $E_{\rm max}$ values, an observation in accord with the conservation of energy. The values for E_{max} for CO₂⁺, CO⁺, O⁺, C⁺, and ArO⁺ formed in the collisions of Ar⁺ (${}^{2}P_{3/2}$) + CO₂ at $E_{lab} = 11.6$ and 105 eV have also been calculated. These $E_{\rm max}$ values, which are not shown here, are also found to be in accord with the RPE curves depicted in Figs. 8 and 10 from the consideration of energy conservation.

The positions for E_{fb} (CO₂⁺), E_{fb} (CO⁺), E_{fb} (O⁺), E_{fb} (C⁺), and E_{fb} (ArO⁺) indicated in Figs. 8, 9, and 10 correspond to E_{lab} of CO₂⁺, CO⁺, O⁺, C⁺, and ArO⁺ moving with projected velocities equal to $\mathbf{v}_{c.m.}$. Depending on whether the laboratory energies of product ions are higher or lower than these E_{lab} values, the product ions are scattered in the forward or backward hemispheres with respect



FIG. 8. Nominal $E_{lab} = 10 \text{ eV}$. Retarding potential-energy curves for (a) reactant Ar⁺ (---) and product CO₂⁺ (---) and (b) product CO⁺ (---) and product O⁺ (---). The marked position for E_{h} (ion) is the RPE at which the ion intensity has a half of that at RPE = 0 eV. The position for E_{fb} (ion) is the laboratory energy of the ion when it is traveling at an velocity equal to $\mathbf{v}_{c.m.}$.



FIG. 10. Nominal $E_{lab} = 105 \text{ eV}$. Retarding potential-energy curves for (a) reactant Ar⁺ (---), product CO₂⁺ (---), and product CO⁺ (---), (b) product O⁺ (---) and product C⁺ (---). E_h and E_{fb} have the same meanings as indicated in Fig. 8.



FIG. 11. Newton diagram for the collision of Ar^+ and CO_2 at E_{tab} (Ar^+) = 27.7 eV. The z axis coincides with the central axis of the octopole ion guide reaction gas cell. Here, $v_{c.m}$, $v_{c.m}$ (Ar^+), and $v_{c.m.}$ (CO_2) are the c.m. velocities for the $Ar^+ + CO_2$ system, reactant Ar^+ , and reactant CO_2 , respectively. The $v_{c.m}$ (ArO^+), $v_{c.m}$ (CO^+), and $v_{c.m.}$ (O^+) circles mark the maximum c.m. velocities for ArO^+ , CO^+ , and O^+ , respectively, allowed by energy conservation.

to $\mathbf{v}_{c.m.}$ (Ar⁺). Also indicated in the figures are RPEs (E_h) at which the intensity of a product ion falls to a half of that at RPE = 0 V. For a given RPE curve, if E_h (ion) is greater (lower) than E_{fb} (ion), we may conclude that the majority of the product ions are scattered forward (backward) with respect to $\mathbf{v}_{c.m.}$ (Ar⁺).

The RPE curves for charge-transfer CO_2^+ in Figs. 8(a), 9(a), and 10(a) show that the intensity for CO_2^+ drops sharply at RPE > 2 V, indicating that CO_2^+ ions are slow and that they are scattered predominantly backward with respect to $v_{c.m.}$ (Ar⁺). This observation is consistent with the expectation that in this $E_{c.m.}$ range, the overwhelming majority of CO₂⁺ is formed via a long-range electron-transfer mechanism with little momentum transfer. At low $E_{c.m.}$, where the binding energy is comparable to $E_{c.m.}$, the collision complex mechanism may play an important role in charge transfer. If the lifetime of such a complex is longer than the rotational period, the scattering pattern of CO_2^+ product ions is anticipated to display forward-backward symmetry. According to the RPE curve for CO₂⁺ observed at E_{lab} (Ar⁺) = 5.8 eV, which is not shown here, we find that the forward:backward ratio for charge-transfer CO_2^+ is about 2:3. At E_{lab} (Ar⁺) = 11.6 eV ($E_{c.m.}$ = 6.1 eV) and $E_{\rm lab}$ (Ar ⁺) = 27.7 eV ($E_{\rm c.m.}$ = 14.5), the fractions of forward-scattered CO₂⁺ represent about 20% [Fig. 8(a)] and 10% [Fig. 9(a)] of the total CO_2^+ . This fraction decreases as E_{lab} (Ar⁺) or $E_{c.m.}$ is increased. As shown in Fig. 10(a), essentially all CO₂⁺ ions are backward scattered at E_{lab} (Ar⁺) = 104 eV ($E_{\text{c.m.}}$ = 54.5 eV).

The RPE curves for O⁺ and CO⁺ plotted in Fig. 8(b) show that both O⁺ and CO⁺ formed by reactions (7) and (6) at $E_{\rm c.m.} = 6.1$ eV, respectively, are scattered predominantly in the forward hemisphere with respect to $\mathbf{v}_{\rm c.m.}$ (Ar⁺). As $E_{\rm lab}$ (Ar⁺) is increased, the backward-scattered component increases at the expense of the forward

component. At $E_{\text{lab}}(\text{Ar}^+) = 27.7 \text{ eV}$, product O⁺ and CO⁺ remain slightly forward scattered [Figs. 9(a) and 9(b)], whereas both species become overwhelmingly backward scattered at $E_{\text{lab}}(\text{Ar}^+) = 104 \text{ eV}$ [Figs. 10(a) and 10(b)].

The maximum energy releases observed for CO⁺ and O⁺ are greater than that for C⁺ at E_{lab} (Ar⁺) = 27.7 eV [see Figs. 9(b) and 9(c)], while the reverse is found at E_{lab} (Ar⁺) = 104 eV [Figs. 10(a) and 10(b)]. The lowerenergy release for C⁺ compared to O⁺ and CO⁺ at low $E_{c.m.}$ can be attributed to the energy constraint. As discussed above, C⁺ ions are most likely produced by reaction (8), which has a significantly higher threshold than those for reactions (6) and (7). Therefore, the total energy available to be distributed between the internal and kinetic energies of the products is smaller for the process [reaction (8)] responsible for the formation of C⁺ than those for the formation of CO⁺ + O [reaction (6)] or O⁺ + CO [reaction (7)].

Due to the low intensity for the reactive product ions, we have only measured the RPE curves for ArO⁺ and ArC⁺ at E_{lab} (Ar⁺) = 27.7 and 43 eV, respectively. Based on the RPE curve for ArO⁺ shown in Fig. 9(b), we conclude that ArO⁺ ions are scattered predominantly backward with respect to \mathbf{v}_{cm} (Ar⁺).

Table I summarizes the observed values for $E_h(ion)$ and predicted values for E_{fb} (ion) at $E_{c.m.} = 6.1-114$ eV $(E_{\text{lab}} = 11.6-218 \text{ eV})$. In this $E_{\text{c.m.}}$ range, the $E_h(\text{CO}_2^+)$ values are $\leq 2 \text{ eV}$, which are significantly lower than the values for E_{fb} (CO₂⁺) at the corresponding $E_{c.m.}$. This finding is consistent with the conclusion that charge-transfer product CO_2^+ ions are slow and are scattered overwhelmingly backward. The E_h values for CO⁺ and O⁺ decrease from E_h (CO⁺) = 5–6 V and E_h (O⁺) = 4 V at $E_{c.m.}$ = 6–15 eV to ≈ 2.5 V at $E_{\rm c.m.} = 114$ eV, respectively. The scattering patterns for CO⁺ and O⁺ change from predominantly forward at $E_{\text{c.m.}} = 6-15 \text{ eV}$ to backward at $E_{\text{c.m.}}$ 22-114 eV. The $E_h(C^+)$ value increases from 3.5 V at $E_{c.m.} = 14.5$ to 5-6.5 eV at $E_{c.m.} = 28-114$ eV. Although both ArO⁺ and ArC⁺ are found to be backward scattered at $E_{c.m.} = 14.5$ and 22.1 eV, respectively, the E_h value for ArC⁺ is significantly greater than that for ArO⁺.

E. Comparison of the DP and DCT processes

Figure 3(a) compares the sum of the DP cross sections⁴⁶ for CO⁺, O⁺, and C⁺ from CO₂ and the sum of $\sigma_{3/2}$ (CO⁺), $\sigma_{3/2}$ (O⁺), $\sigma_{3/2}$ (C⁺), $\sigma_{3/2}$ (ArCO⁺), $\sigma_{3/2}$ (ArO⁺), and $\sigma_{3/2}$ (ArC⁺). Disregarding the fine structure of the DP cross-section curve, the profiles observed for the sum of the DP cross sections and that of the DCT cross sections are similar and both are peaked at $E_{\rm c.m.} \approx 20$ eV. This, along with similar comparisons made in Figs. 1(a), 1(b), 2(a), 2(b), 4(a), 5(a), and 6(a), suggests that similar predissociative excited states of the parent CO₂⁺ ions can be populated efficiently by charge transfer as well as by photoionization.

The sum of the DP cross sections is approximately 2

TABLE I. Summary of the observed values for E_h and predicted values for E_{fb} at $E_{\rm c.m.}=6{-}114~{\rm eV.^{a,b}}$

	E_{h} (eV)					
$E_{\rm c.m.}$ (eV)	CO ₂ ⁺	CO +	0+	C +	ArO +	ArC +
6.1	2 (3.5)	5.0 (2.2)	3.8 (1.3)			•••
9.2	2 (5.3)	6.3 (3.4)	4.0 (1.9)		•••	•••
11.3	1.7 (6.5)	5.8 (4.1)	3.9 (2.4)			
14.5	2 (8.4)	6.5 (5.3)	4.0 (3.0)	≈3.5 (2.3)	2.5 (10.6)	
22.1	1.6 (12.7)	4.7 (8.1)	2.7 (4.6)	4.6 (3.5)		10 (15)
28.3	2 (16.3)	4.0 (10.4)	2.9 (5.9)	6.5 (4.4)		
41.3	1.7 (23.8)	2.7 (15.2)	2.0 (8.7)	6.0 (6.5)		
55	2 (31.7)	2.5 (20.2)	2.5 (11.5)	6.0 (8.6)	•••	
114	2 (65.8)	2.0 (41.9)	2.5 (23.9)	5.0 (17.9)	•••	•••

^a The value for E_h (ion) is the RPE at which the ion intensity is half of that at RPE = 0 eV. The value for E_{fb} (ion) is the laboratory energy of the ion when it is traveling at a velocity equal to $v_{c.m.}$. The values for E_{fb} (ion) are in parentheses.

^b When $E_h > E_{fb}$ ($E_h < E_{fb}$), the product ion is scattered mainly in the forward (backward) hemisphere with respect to $\mathbf{v}_{c.m.}$ (Ar⁺).

orders of magnitude lower than that for the DCT cross sections. The DP cross sections for CO^+ , O^+ , and C^+ from CO₂ are similar in magnitude, whereas the magnitude of the DCT $\sigma_{3/2}({\rm CO^+}) \gg \sigma_{3/2}({\rm O^+})$ cross section are $\approx \sigma_{3/2}$ (C⁺). Due to the different nature of photoionization and charge-transfer processes, differences observed in the DP and DCT processes are anticipated. The photoionization cross sections are usually substantially lower than those for charge transfer. The necessity to conserve energy and momentum in the collisions of $Ar^+ + CO_2$ requires finite momentum transfer. Furthermore, the interaction potential surfaces which govern the reaction dynamics for $Ar^{+} + CO_{2}$ are expected to be anisotropic and may favor collisions at particular geometries, which in turn favor the production of specific channels.

F. Reaction dynamics and mechanisms for the $\rm Ar^+ + \rm CO_2$ system

The comparison of the DP cross sections for CO⁺, O⁺, and C⁺ from CO₂ with the corresponding DCT cross sections for the formation of CO⁺, O⁺, and C⁺ [processes (6)-(8)] strongly suggests that predissociative states of CO_2^+ responsible for the DP processes also play an important role in the DCT reactions. The overwhelming majority of the charge-transfer CO_2^+ ions are produced via the longrange electron jump mechanism, involving little momentum transfer. The relatively high values observed for $\sigma_{3/2}$ (CO⁺), $\sigma_{3/2}$ (O⁺), and $\sigma_{3/2}$ (C⁺) may also be attributed to the long-range charge-transfer mechanism as an effective means for populating the predissociative states of CO_2^+ .

According to the experimental thresholds for the formation of CO⁺, O⁺, and C⁺, and the relative values for $\sigma_{3/2}$ (CO₂⁺), $\sigma_{3/2}$ (CO⁺), $\sigma_{3/2}$ (O⁺), and $\sigma_{3/2}$ (C⁺) observed here, it is most likely that a stepwise mechanism involving the dissociation of charge transfer CO₂^{*+},

is responsible for the formation CO⁺ and C⁺. Here, CO₂^{*+} are excited predissociative states populated in the chargetransfer collisions of Ar⁺ (²P_{3/2}) + CO₂. A similar mechanism has also been suggested for the formation of CO⁺ and C⁺ in the reaction of O⁺ (⁴S) + CO₂.⁵³ As pointed out above, at a given $E_{c.m.}$ close to the threshold for the formation of C⁺, the total available energy for distribution to the internal and kinetic energies of C⁺ + 2O is lower than that of CO⁺ + O. This may account for the lower average laboratory kinetic energy observed for C⁺ compared to that for CO⁺. However, at a sufficiently high $E_{c.m.}$, the further dissociation of excited CO^{*+} ions has the effect to increase the kinetic-energy spread for C⁺. The higher average laboratory kinetic energy observed for C⁺ in comparison with that observed for CO⁺ is consistent with this rationalization.

Excited CO^{*+} produced in the DCT collisions of Ar⁺ (²P_{3/2,1/2}) + CO₂ may also dissociate to form O⁺ + C. Such a channel cannot be identified unambiguously in this experiment. We note that the cross section for C⁺ is more than 20 times greater than that for O⁺ formed in the Ar⁺ (²P_{3/2,1/2}) + CO reactions.¹³ If a significant fraction of O⁺ results from the further dissociation of excited CO^{*+}, we expect that the average laboratory kinetic energy for O⁺ should increase in a fashion similar to that observed in the case of C⁺. The observation that E_h for O⁺ decreases as $E_{c.m.}$ is increased (Table I) can be taken as evidence that the dissociation of CO^{*+} to O⁺ + C is not a major channel.

The observation of the predominantly backward-scattered pattern for ArO⁺ and the forward-scattered patterns for CO⁺ and O⁺ is in accord with the near-colinear chargetransfer predissociation mechanism, which has been proposed for the formation of ArN⁺ (ArO⁺, ArC⁺) from the reaction of Ar₊ (²P_{3/2,1/2}) + N₂ (O₂, CO).¹¹⁻¹³ In the ground state, CO₂ has a linear geometry. As was argued previously, at $E_{c.m.}$ close to the ArO⁺, CO⁺, and O⁺ thresholds, the most effective collision geometry to convert kinetic energy into internal energies of CO₂ and to induce the formation of ArO⁺ + CO and CO⁺ + ArO (or Ar + O), etc. is the colinear Ar⁺-O-C-O configuration. The formation of ArO⁺, CO⁺, and O⁺ may proceed with a sequence of steps summarized below:

$$Ar^{+} + O - C - O \xrightarrow{(a)}{\rightarrow} Ar \cdots (O - C - O)^{*+}$$

$$\xrightarrow{(b)}{\rightarrow} Ar \cdots O^{+} \cdots CO(Ar \cdots O \cdots CO^{+},$$

$$Ar \cdots OC^{+} \cdots O, \text{ or } Ar \cdots OC \cdots O^{+}),$$
(13)

$$\operatorname{Ar} \cdots \operatorname{OC} \cdots \operatorname{O}^+ \rightarrow \operatorname{O}^+ + \operatorname{Ar} \operatorname{CO}$$
 (or $\operatorname{Ar} + \operatorname{CO}$), (14)

$$\operatorname{Ar} \cdots O^{+} \cdots CO \xrightarrow{(a)} \operatorname{Ar} O^{+} + CO \xrightarrow{(o)} O^{+} + \operatorname{Ar} + CO, \quad (15)$$

$$Ar \cdots O \cdots CO^+ \rightarrow CO^+ + ArO \text{ (or } Ar + O), \tag{16}$$

$$\operatorname{Ar} \cdots \operatorname{OC}^{+} \cdots \operatorname{O}^{(a)} \rightarrow \operatorname{Ar} \operatorname{OC}^{+} + \operatorname{O}^{(b)} \operatorname{CO}^{+} + \operatorname{Ar} + \operatorname{O}.$$
(17)

Step 13(a) involves the formation of a nearly colinear $Ar \cdots (O-C-O)^{*+}$ intermediate by charge transfer as Ar^+ approaches an O end of CO_2 . The CO_2^{*+} moiety thus formed may be in a predissociative state. As the dissociation of CO_2^{*+} proceeds [process 13(b)], the charge may reside on the O atom or be associated with CO, forming intermediates $Ar \cdots O^+ \cdots CO$, $Ar \cdots O \cdots CO^+$, $Ar \cdots OC^+ \cdots O$, or $Ar \cdots OC^+ \cdots O^+$. The dissociation of the $ArOC-O^+$ intermediate [process (14)] may lead to $O^+ + COAr$ (or CO + Ar) with O^+ scattered mainly forward. The breaking of the ArO^+ -CO bond in a nearly colinear geometry [process 15(a)] results in the scattering of ArO^+ in the backward hemisphere. Process 15(b) indicates that ArO^+ formed with sufficiently high internal excitation may dissociate into $O^+ + Ar$.

Similar dissociation processes [processes 17(a) and (16)] involving the intermediates $ArOC^+ -O$ and $ArO-(CO)^+$ are expected to yield and $ArOC^+$ and CO^+ scattered in the backward and forward hemispheres, respectively. Process 17(b) represents the further dissociation of internally excited $ArOC^+$ to $CO^+ + Ar$. According to the theoretical study, the most-stable geometry for $ArCO^+$ is a linear (Ar-C-O)⁺ structure.⁶⁰ Therefore, the formation of (Ar-O-C)⁺ according to process 17(a) may not be the most favorable pathway. The formation of (Ar-C-O)⁺ may involve the sideway attack of Ar^+ toward the center C atom in CO_2 .

The formation of ArC⁺ may also proceed by a sideway attack of Ar⁺ at the C atom of the CO₂ molecule. Such a pathway may account for the relative high laboratory kinetic energy observed for ArC⁺ at $E_{c.m.} = 22$ eV. The finding that the majority of ArC⁺ ions are backward scattered indicates that product ArC⁺ results mostly from small impact parameter collisions. The production of ArC⁺ may involve the further dissociation of excited (Ar-C-O)* initially formed by a sideway attack.

At $E_{\rm c.m.}$ higher than the thresholds for the reactive ions, the charge-transfer predissociation mechanism is not limited to near-colinear encounters of Ar⁺ and CO₂ because the energy constraint no longer applies.

IV. SUMMARY AND CONCLUSION

This experiment is designed to test the predictions of the predissociative charge-transfer mechanism for endothermic DCT processes, proposed previously in studies of the $Ar^+({}^2P_{3/2,1/2}) + N_2(O_2,CO)$ reactions. The identification of reactions (5)-(11), together with the kinetic-energy distribution analyses of product ions of these reactions, is in total conformity with the predictions of the predissociative charge-transfer mechanism. The observation that at higher $E_{\rm c.m.}$ product CO₂⁺, CO⁺, O⁺, and C⁺ are predominantly scattered in the backward hemisphere with respect to $v_{c.m.}$ (Ar ⁺) suggests that CO ⁺, O ⁺, and C ⁺ are produced by the subsequent predissociation of excited CO_2^{+*} initially populated by long-range charge transfer of $\operatorname{Ar}^+({}^2P_{3/2,1/2}) + \operatorname{CO}_2.$

The cross sections for the formation CO⁺, O⁺, and C⁺ from CO₂ by DP and by the DCT reactions (6)–(8) are found to have similar profiles in the $E_{c.m.}$ scale, suggesting that the predissociative excited CO₂⁺ states responsible for the DP processes also play a role in the DCT reactions. The substantially lower cross sections observed in DP compared to those in DCT can be attributed to the different nature of photoionization and charge-transfer interactions. The potential-energy surfaces responsible for the reaction dynamics of Ar⁺ + CO₂ collisions also favor specific DCT product channels.

ACKNOWLEDGMENTS

This research has been supported by the National Science Foundation Grant No. CHE 8913283. Acknowledgment is also made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.

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