

## CHARGE TRANSFER BETWEEN $\text{CO}_2^{2+}$ AND Ar OR Ne AT COLLISION ENERGIES 3–10 eV

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The beam scattering method was used to investigate non-dissociative single-electron charge transfer between the molecular dication  $\text{CO}_2^{2+}$  and Ar or Ne at several collision energies between 3–10 eV (centre-of-mass, c.m.). Relative translational energy distributions of the product ions showed that in the reaction with Ar the  $\text{CO}_2^+$  product was mainly formed in reactions of the ground state of the dication,  $\text{CO}_2^{2+}(\text{X}^3\Sigma_g^-)$ , leading to the excited states of the product  $\text{CO}_2^+(\text{A}^2\Pi_u)$  and  $\text{CO}_2^+(\text{B}^2\Sigma_u^+)$ . In the reaction with Ne, the largest probability had the process from the reactant dication excited state  $\text{CO}_2^{2+}(\text{X}^3\Sigma_g^-)$  leading to the product ion ground state  $\text{CO}_2^+(\text{X}^2\Pi_g)$ . Less probable were processes between the other excited states of the dication  $\text{CO}_2^{2+}$ , ( $^1\Delta_g$ ), ( $^1\Sigma_u^-$ ), ( $^3\Delta_u$ ), also leading to the product ion ground state  $\text{CO}_2^+(\text{X}^2\Pi_g)$ . Using the Landau–Zener model of the reaction window, relative populations of the ground and excited states of the dication  $\text{CO}_2^{2+}$  in the reactant beam were roughly estimated as  $(\text{X}^3\Sigma_g^-):(\text{X}^3\Sigma_g^-):(\text{X}^3\Sigma_g^-):(\text{X}^3\Sigma_g^-):(\text{X}^3\Sigma_g^-) = 1.0:0.6:0.5:0.25:0.25$ .

**Keywords:** Charge transfer; Dications; Energetics; Electronic state population; Beam scattering; Carbon dioxide; Noble gases.

Systematic interest of chemists and physicists in molecular dications dates several decades back. First, stability, structure and energetics of molecular multiply-charged ions, namely polyatomic organic dications, created a wave of interest among ion chemists<sup>1–4</sup>. Then the behaviour of molecular multiply-charged ions in collision with other particles started to attract increasing attention<sup>4,5</sup>. In particular, charge transfer including molecular dications has been investigated and numerous data on both non-dissociative and dissociative electron exchange processes were obtained from translational energy spectroscopy and scattering experiments<sup>4,6,7</sup>. The

first studies in the 1980's suffered from lack of data on exact ionization energies of even simple diatomic dications and on energetics and population of electronically excited states of these species. However, in a joint effort of both experimentalists and theoreticians, considerable amount of new data was collected so that the situation with diatomic dications is incomparably better now than it was fifteen years ago. In the mid 1990's reports on the occurrence of chemical, bond-forming reactions of molecular dications appeared for the first time<sup>8,9</sup>. Earlier information concerned only a few reports on chemical reactions of atomic, metal dications<sup>10-12</sup>. In recent years the interest in chemical reactivity of dications has been increasing. Bond-forming reactions, leading both to non-dissociative or various dissociative products with rearranged bonds, have been reported for several systems. Dynamics of these processes was investigated in detail<sup>13,14</sup> and models of dications reactivity, treating chemical reactions and charge transfer processes in competition, have been formulated<sup>12,14</sup>.

Detailed studies of chemical reactions require reliable information not only on the energetics of ground states of molecular dications, but also on their electronically excited states. In addition, data on relative populations of these states are needed to correctly assess the chemical reactivity. Useful information can be obtained from coincidence photoionization studies of dications<sup>15</sup>. The data provide probabilities of formation of various electronic states of molecular dications, but information on the stability of these states and on their relative concentrations in reactant beams is limited. A possible approach to this problem is to study the reactivity of molecular dications in charge transfer processes with simple targets like noble gases and to analyze the translational energy of the product formed. In this way, information on the ground and excited states of molecular dications can be obtained and from measurements at a series of collision energies, at least approximate information on the relative population of the states may be deduced.

In this communication, we report on a crossed-beam scattering study of non-dissociative charge transfer reactions



and



The scattering data on the translational energy distribution of the product ion  $\text{CO}_2^+$  from these reactions at several collision energies were used to obtain information on approximate populations of the electronic states in the reactant ion beam of  $\text{CO}_2^{2+}$ , by application of the Landau-Zener model and the reaction window concept.

Information on energetics of the ground and excited states of the  $\text{CO}_2^{2+}$  dication has been available both from experimental<sup>16</sup> and theoretical<sup>17</sup> studies. The values of  $\text{IE}(\text{CO}_2 \rightarrow \text{CO}_2^{2+})$  come from a recent photoionization study and theoretical calculations<sup>16</sup> that give for the IE of the ground state  $\text{CO}_2^{2+}(\text{X}^3\Sigma_g^-)$  a value of  $37.7 \pm 0.3$  eV. On the basis of a comparison of a series of photoionization and electron impact values, we adopt here the value  $\text{IE}(\text{CO}_2 \rightarrow \text{CO}_2^{2+}) = 37.4$  eV. The values and assignment of electronic excited states of  $\text{CO}_2^{2+}$  originate from the above mentioned paper<sup>16</sup> and also from an excellent theoretical study<sup>17</sup>. The non-dissociative excited states are located 1.35 ( $^1\Delta_g$ ), 1.93 ( $^1\Sigma_g^+$ ), 2.87 ( $^1\Sigma_u^-$ ), and 3.25 eV ( $^3\Delta_u$ ) above the ground state. Ionization energies of the cation  $\text{CO}_2^+$  are well known<sup>18</sup>; the ground state  $\text{CO}_2^+(\text{X}^2\Pi_g)$ , lies at 13.79 eV, and the excited states  $\text{CO}_2^+(\text{A}^2\Pi_u)$  and  $\text{CO}_2^+(\text{B}^2\Sigma_u^+)$  3.52 and 4.3 eV, respectively, above the ground state. The third excited state,  $\text{CO}_2^+(\text{C}^2\Sigma_g^+)$ , 5.6 eV above the ground state, is known to be dissociative<sup>19</sup>.

## EXPERIMENTAL

The experiments were carried out on a crossed-beam scattering apparatus EVA II. The apparatus and its application to measurements of doubly-charged ion processes were described earlier<sup>6,13</sup>. Briefly, reactant  $\text{CO}_2^{2+}$  ions were produced by impact of 140-eV electrons on carbon dioxide in a low-pressure ion source. The ions were extracted, mass-analyzed, and ions of  $m/z$  22 were decelerated with a multi-element electrostatic lens system to a desired laboratory energy. The ion reactant beam had an energy spread of about 0.4 eV (full width at half maximum, fwhm) and an angular spread of about  $1.5^\circ$  (fwhm). The reactant beam crossed at right angles with a collimated thermal beam of the rare gas atoms emerging from a multi-channel jet (angular spread of  $10^\circ$ , fwhm). The two beams could be rotated about the collision centre in the plane of the detector. Reactant and product ions passed through a detection slit, and were energy-analyzed with a stopping-potential analyzer; then they were accelerated to 1 keV, mass-analyzed in a magnetic mass spectrometer, further accelerated to 2.5 keV, and detected with a Galileo multiplier. Modulation of the neutral reactant beam, phase-sensitive detection, and signal averaging were used to deal with background problems. Velocity profiles of the ion product  $\text{CO}_2^+$  were obtained from energy profiles recorded at specific laboratory scattering angles.

For the scattering diagrams, the raw data consisted of angular distributions and sets of energy profiles of the reactant and product ions at a series of scattering angles. The scattering diagrams were constructed using the well-established procedure<sup>20,21</sup>; they show the contours of the Cartesian probability density of the ion product in dependence on the velocity and

scattering angle. Relative differential cross-sections,  $P(\vartheta)$  vs  $\vartheta$ , and relative translational energy distributions of products,  $P(T')$ , plotted here in dependence of reaction exoergicity  $\Delta E = T' - T$  ( $T$  and  $T'$  are the relative translational energies of reactants and products, respectively) were obtained by appropriate integration of the scattering diagrams<sup>20,21</sup>.

For the reaction with neon, energy profiles of  $\text{CO}_2^+$  were measured only at the laboratory angular maximum. The velocity profiles obtained from them were plotted in the framework of the respective Newton diagrams. The  $P(T')$  vs  $\Delta E$  plot was then obtained from these velocity profiles at the angular maximum.

## RESULTS AND DISCUSSION

Figure 1 shows the scattering diagram of the product ion  $\text{CO}_2^+$  from reaction (1) at the collision energy  $T = 4.88$  eV. It exhibits a dominant maximum and a weak side maximum at a higher velocity. Dashed concentric lines about the center-of-mass (c.m.) indicate exoergicities of processes leading from the reactant ion ground state  $\text{CO}_2^{2+}(\text{X})$  to the product ion excited states  $\text{CO}_2^+(\text{A})$ ,  $\text{CO}_2^+(\text{B})$ , and  $\text{CO}_2^+(\text{C})$  (dissociative), assuming that all particles are in vibrationally ground states. Figure 2 gives the relative differential cross section,  $P(\vartheta)$ , of the product  $\text{CO}_2^+$  ( $\vartheta$  is the c.m. scattering angle). The angular dependence decreases rather quickly from the maximum at  $\vartheta = 0^\circ$  and reaches 50% of the maximum intensity at about  $7.5^\circ$ .

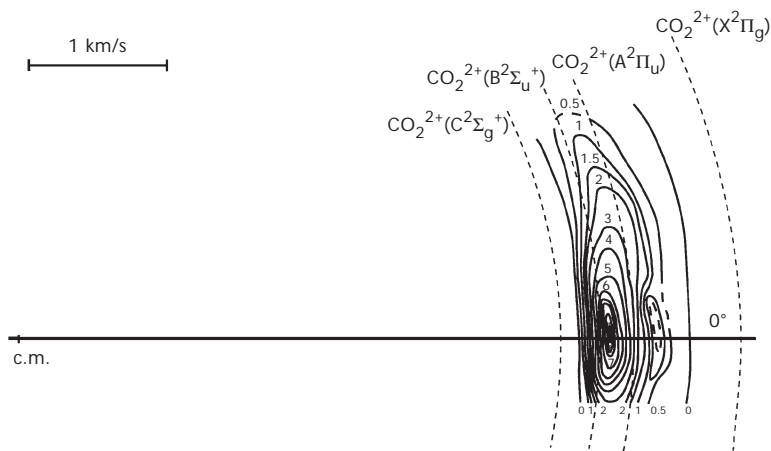


FIG. 1

Scattering diagram of the product  $\text{CO}_2^+$  from reaction (1) with Ar at  $T = 4.88$  eV. Concentric dashed circles about c.m. (tip of the center-of-mass vector) indicates *loci*, where product would be expected from a reaction of the ground-state dication reactant to the indicated states of the product  $\text{CO}_2^+$  (assuming no vibrational excitation of molecular species)

The relative translational energy distribution of the products,  $P(T')$ , was obtained by the usual integration of the scattering diagram<sup>20,21</sup>. It is plotted in Fig. 3 in dependence on the reaction exoergicity,  $\Delta E = T' - T$ , as a solid line. The scales in the figure show product energy thresholds for the indicated (electronic) state-to-state processes. The product translational energy distribution is a rather unresolved broad peak which evidently originated as an overlap of several processes. As the  $\text{CO}_2^+(\text{C})$  state is known to be dissociative, the dominant role in the product  $\text{CO}_2^+$  formation is played by the transitions between the ground state of the reactant  $\text{CO}_2^{2+}(\text{X})$  and the product excited states  $\text{CO}_2^+(\text{A})$  and  $\text{CO}_2^+(\text{B})$ , the probability of formation of the product ground state  $\text{CO}_2^+(\text{X})$  being negligible. The reactions of the excited states of the reactant ion  $\text{CO}_2^{2+}(^1\Delta_g)$  (transitions to  $\text{CO}_2^+(\text{B})$  and  $\text{CO}_2^+(\text{A})$ ) and  $\text{CO}_2^{2+}(^1\Sigma_g^+)$  (transitions to  $\text{CO}_2^+(\text{B})$ ) contribute considerably less to the formation of the product.

Figure 4 gives velocity distributions of the product  $\text{CO}_2^+$  from reaction (2) with Ne. Because of low intensity, the profiles were determined only at one laboratory scattering angle of  $-1.5^\circ$  (close to the angular maximum) at two collision energies of 3.31 and 9.67 eV. They are plotted in the framework of

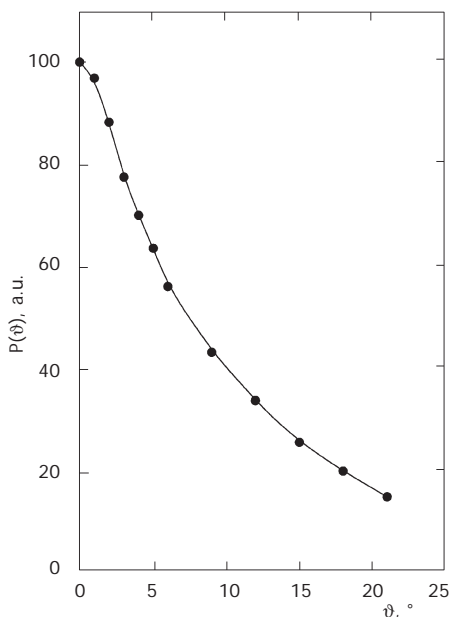


FIG. 2

Relative differential cross-sections,  $P(\phi)$ , (c.m. angular distribution) of the product  $\text{CO}_2^+$  from reaction (1) at  $T = 4.88$  eV

the respective Newton diagrams. The concentric dashed lines show the *loci* of velocity, where the product is expected to appear for processes of the given exoergicity  $\Delta E$ . It can be seen that the product  $\text{CO}_2^+$  is formed with highest probability with exoergicity 3–6 eV. The velocity distributions were then transformed into relative translational energy distributions and plotted – similarly as for Ar in Fig. 3 – against the reaction exoergicity,  $\Delta E = T' - T$ , in Fig. 5 (solid line). Again, the scales in the figure indicate exoergicities of the respective state-to-state processes. It can be seen that the product is formed in measurable amounts in reactions of the excited states of the reactant  $\text{CO}_2^{2+}$  leading to the ground state of the product  $\text{CO}_2^+(\text{X})$  at both collision energies. While the  $P(T')$  curve at  $T = 3.31$  eV shows a certain structure, any structure in the curve at  $T = 9.67$  eV is smeared, presumably because of a lower resolution of the experiment at the higher collision energy.

An approximate estimation of the relative population of the electronic states of the dications in the reactant beam can be made, assuming that the charge transfer transition probability is determined by the Landau-Zener model of non-adiabatic transitions. The Landau-Zener formalism leads to

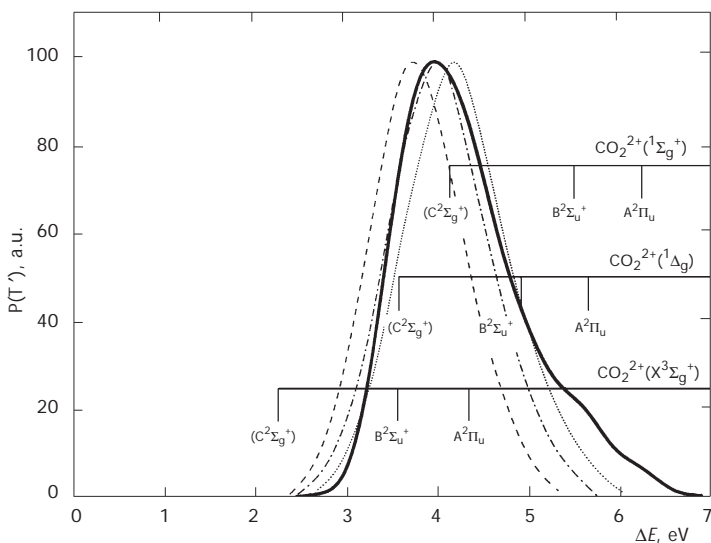


FIG. 3

Relative translational energy distribution,  $P(T')$ , of products of reaction (1) at  $T = 4.88$  eV, plotted against reaction exoergicity  $\Delta E$ . Solid line, experimental data. Reaction windows: dashed, ground state  $\text{CO}_2^{2+}(\text{X}^3\Sigma_g^-)$ ; dash-and-dotted,  $\text{CO}_2^{2+}(^1\Delta_g)$ ; dotted,  $\text{CO}_2^{2+}(^1\Sigma_g^+)$

the “reaction window” concept (LZRW)<sup>22,23</sup>. In the approximation of a two-state model, the cross section can be then formulated as<sup>22,23</sup>

$$\sigma_{\text{int}} = \pi R_C^2 [1 - U_1(R_C)/T] G(\gamma), \quad (3)$$

where  $G(\gamma)$  is a tabulated integral

$$G(\gamma) = 2 \int_0^1 \exp(-\gamma/\sqrt{x}) [1 - \exp(-\gamma/\sqrt{x})] dx. \quad (4)$$

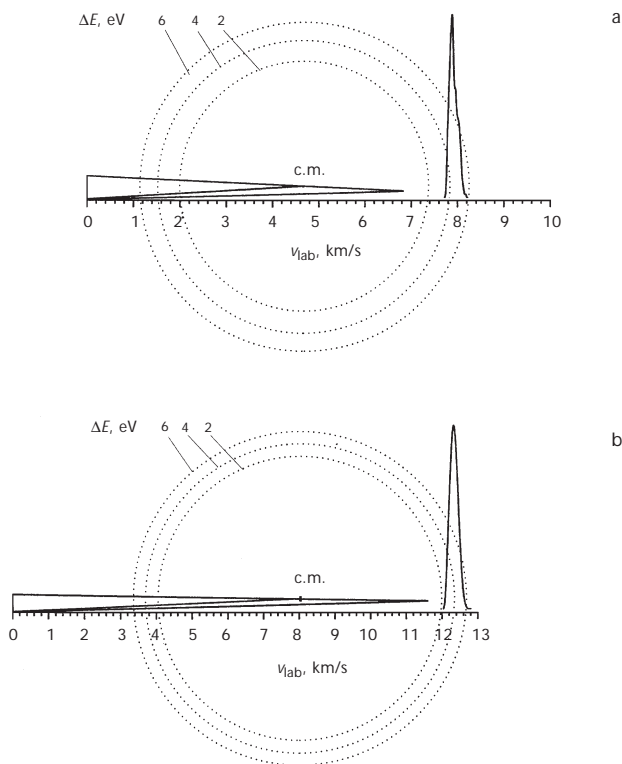


FIG. 4

Velocity profiles of the product  $\text{CO}_2^+$  from reaction (2) with Ne at two collision energies a 3.31 eV and b 9.67 eV, respectively, at the laboratory scattering angle  $-1.5^\circ$ , plotted in the framework of the Newton diagram





Assuming that the ion-induced dipole interaction between reactants may be neglected and only the Coulomb repulsion between products considered,  $\gamma$  can be expressed as

$$\gamma(R_C, T) = (2\pi\mu)^{1/2} R_C^{5/2} U_{12}(R_C)^2 (R_C T + 1)^{-1/2}. \quad (5)$$

Here,  $R_C$  is the position of the crossing between the reactant ( $U_1$ ) and product ( $U_2$ ) potential energy terms,  $T = \mu v_{\text{rel}}^2/2$  is the c.m. collision energy,  $U_{12}$  is the coupling matrix term between  $U_1$  and  $U_2$ , which can be expressed as<sup>22</sup>

$$U_{12}(R_C) = \frac{\sqrt{I_1} + \sqrt{I_2}}{\sqrt{2}} R_C \sqrt{I_1 I_2} \exp(-0.86 \frac{\sqrt{I_1} + \sqrt{I_2}}{\sqrt{2}} R_C). \quad (6)$$

For charge transfer in molecular systems, where potential hypersurfaces rather than potential energy curves have to be considered, the LZRW model, as developed for atomic systems, holds only approximately<sup>24</sup>.

TABLE I

Estimation of the relative abundance  $N_{\text{rel}}$  of CO<sub>2</sub><sup>2+</sup> ground and excited states in the reactant beam

No.	Target $T^a$ , eV	Transition	$\Delta E^b$ eV	$P(T)_{\Delta E}$	$\sigma_{\Delta E}$	$N$	$N_N$	$(N_N)_{\text{av}}$	$N_{\text{rel}}$
1	Ar, 3.44	(X <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> )→(B <sup>2</sup> Σ <sub>u</sub> <sup>+</sup> )	3.55	71	91	0.78	2.34	2.34	1.00
2	Ar, 4.88	(X <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> )→(A <sup>2</sup> Π <sub>u</sub> )	4.33	86	55	1.56			
3	Ar, 4.88	( <sup>1</sup> Δ <sub>g</sub> )→(B <sup>2</sup> Σ <sub>u</sub> <sup>+</sup> )	5.68	43	29	1.48	1.48	1.47 ± 0.20	0.56 ± 0.09
4	Ne, 3.31	( <sup>1</sup> Δ <sub>g</sub> )→(X <sup>2</sup> Π <sub>g</sub> )		74	49	1.51	1.22		
5	Ne, 9.67	( <sup>1</sup> Δ <sub>g</sub> )→(X <sup>2</sup> Π <sub>g</sub> )		89	42	2.12	1.72		
6	Ar, 4.88	( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )→(B <sup>2</sup> Σ <sub>u</sub> <sup>+</sup> )	5.48	22	12	1.83	1.83	1.13 ± 0.50	0.48 ± 0.20
7	Ne, 3.31	( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )→(X <sup>2</sup> Π <sub>g</sub> )		82	95	0.86	0.70		
8	Ne, 9.67	( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )→(X <sup>2</sup> Π <sub>g</sub> )		96	91	1.05	0.85		
9	Ne, 3.31	( <sup>1</sup> Σ <sub>u</sub> <sup>-</sup> )→(X <sup>2</sup> Π <sub>g</sub> )		40	43	0.93	0.75	0.61 ± 0.15	0.26 ± 0.06
10	Ne, 9.67	( <sup>1</sup> Σ <sub>u</sub> <sup>-</sup> )→(X <sup>2</sup> Π <sub>g</sub> )		36	63	0.57	0.46		
11	Ne, 3.31	( <sup>3</sup> Δ <sub>u</sub> )→(X <sup>2</sup> Π <sub>g</sub> )		24	24	1.00	0.81	0.61 ± 0.20	0.26 ± 0.09
12	Ne, 9.67	( <sup>3</sup> Δ <sub>u</sub> )→(X <sup>2</sup> Π <sub>g</sub> )		20	39	0.51	0.41		

<sup>a</sup>  $T$ , collision energy; <sup>b</sup>  $\Delta E$ , reaction exoergicity.

The reaction windows for the particular electronic states of the reactant are shown in Figs 3 and 5 by dashed, dotted and dash-and-dot, and dash-double-dot lines (see Figure captions).

To estimate approximately the relative abundance of the ground and excited states of the  $\text{CO}_2^{2+}$  dication in the reactant ion beam, we made the following simplifications:

1. The value of  $P(T')$  at a specific value of exoergicity  $\Delta E$  (exoergicity of a process),  $P(T')_{\Delta E}$ , may be expressed as a product of the population of that state,  $N_S$ , and the cross-section of the particular process  $\sigma_{\Delta E}$ , as calculated using the LZRW model,  $P(T')_{\Delta E} = N_S \sigma_{\Delta E}$ .

2. We assume that transitions occur between the ground vibrational states of the reactant and production, *i.e.* the effect of population of vibrationally excited states of the reactant and product ion is neglected. This is at least approximately acceptable, as theoretical calculations<sup>17</sup> indicate that the Franck–Condon factors for producing the lowest three states of  $\text{CO}_2^{2+}$  are very similar and thus one may expect that these states would behave similarly also in the charge transfer process.

Table I summarizes the values estimated from Figs 3 (Ar) and 5 (Ne) and the relative populations of various electronic states of the reactant ion. The ratio of the ground state  $\text{CO}_2^{2+}(\text{X}^3\Sigma_g^-)$  (sum of the transitions to the B and A states of  $\text{CO}_2^+$ ) and the first excited state ( ${}^1\Delta_g$ ) was obtained from the data with Ar, lines 1, 2, 3 in Table I). The Ne data were then normalized to the Ar data by multiplying with the factor  $2 \times 1.48/(1.51 + 2.12)$  to obtain  $N_N$ ; the factor comes from normalization of the Ne for ( ${}^1\Delta_g$ ) (lines 4, 5) to Ar data (line 3). An average of the normalized Ar and Ne data,  $(N_N)_{\text{av}}$ , was then calculated for all states as well as its standard deviation. The final data for  $N_{\text{rel}}$  show a scatter, but they are consistent. By averaging the data, one can roughly estimate the population of the ground and excited states of  $\text{CO}_2^{2+}$  in the reactant beam as  $(\text{X}^3\Sigma_g^-):({}^1\Delta_g):({}^1\Sigma_g^+):({}^1\Sigma_u^-):({}^3\Delta_u) = 1.0:0.6:0.5:0.25:0.25$ .

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