Translational energy spectrometry
of quantum-state-selected electron capture by metastable CO^{2+} ions

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Results are reported of a translational energy spectrometric study of state-selected electron-capture reactions between metastable CO^{2+} ions and H_2, He, O_2, and Kr. The experimental data are interpreted within the framework of recent *ab initio* calculations of the potential-energy curves of low-lying electronic states of CO^{2+}. Electron capture is found to occur predominantly into moderately exoergic channels corresponding to avoided crossings of seams of potential-energy surfaces in the range of internuclear separations between 3 and 5 a.u. Some evidence is found that the CO^{2+} projectile beam may comprise not only the $^1\Sigma^+$ ground electronic state but may also possess a not-insignificant long-lived excited-state ($^3\Pi$) component.

I. INTRODUCTION

The quantal identification of the lowest-energy metastable electronic state of the molecular dication of carbon monoxide, CO^{2+}, has been the subject of some controversy. The earliest theoretical attempt at constructing the potential-energy curve of ground-state CO^{2+} was by Hurley,[1] who devised a semiempircial method utilizing the quantum-mechanical virial theorem to derive the dication potential-energy function from the self-consistent-field type of curves of the isoelectronic BN radical; $^3\Pi$ symmetry was assigned to the CO^{2+} potential energy curve generated by Hurley.[1] However, subsequent experimental studies, by Bearman and co-workers,[2] of photon emission from excited electronic states of CO^+ product ions produced in electron-capture collisions between CO^{2+} and H_2, yielded results that could not be reconciled with Hurley's potential function. Subsequent to Hurley's calculations, a number of modern *ab initio* quantum chemical computations have also indicated that $^3\Pi$ is the lowest energy metastable state of CO^{2+} (see Ref. 3 for a brief overview and compilation of pertinent references). However, there exists another body of theoretical information[4-7] which suggests that the lowest energy metastable CO^{2+} state possesses $^1\Sigma^+$ symmetry. Despite the prevailing lack of clarity, the results of all other experiments subsequent to those of Bearman *et al.*[2] conducted to date[8-10] on electron capture by CO^{2+} ions have continued to be interpreted on the basis of the $^3\Pi$ state being the lowest energy metastable state of the CO dication.

Another source of ambiguity concerns whether or not CO^{2+} possesses a metastable, electronically excited state. State-diagnosed nondissociative electron-capture reactions of 6 keV CO^{2+} ions with the rare gases were studied by Herman *et al.*[9] who found that capture into doublet states of CO^+ was the dominant charge transfer channel. Firm indications were also obtained in these experiments for the involvement of a long-lived electronically excited state of CO^{2+} in the projectile ion beam. However, subsequent experiments[10] conducted in the same laboratory,

using a different spectrometer but employing an identical electron-impact ion source, yielded higher energy resolution translation energy spectrometry data on electron capture by, and excitation of, CO^{2+} ions which was interpreted without recourse to a metastable, electronically excited dication state.

A third source of continuing ambiguity concerns the energetics of the CO^{2+} formation process. As this matter has been the subject of lengthy discussions in a number of recent reports (see Refs. 3, 10, and 11 and references therein) we refrain from making further comments. Thermochemical data used to interpret our present results is presented in Sec. III.

Recently, we have reported[3,7] the results of extensive *ab initio*, all-electron, molecular orbital calculations of the potential energy functions of low-lying electronic states of CO^{2+}, using large basis sets and employing configuration-interaction procedures. Our computations indicate that CO^{2+} possesses two low-lying metastable electronic states, of $^1\Sigma^+$ and $^3\Pi$ symmetry, with the former being the ground electronic state of the dication. In this paper, we report the results of state-diagnosed single-electron-capture reactions of CO^{2+} ions with H_2, He, O_2, and Kr at a collision energy of 4 keV and a scattering angle of 0° and interpret the experimental data obtained within the framework of our recent theoretical findings. The two lowest CO^{2+} states are considered metastable in the sense that there exists only a small potential barrier against dissociation into C^+ and O^+ fragments; the lifetime against dissociation is estimated to be several tens of microseconds, compared to the transit time of ca. 7 μs taken by CO^{2+} ions with 4 keV translational energy to traverse the distance between the ion source and the collision cell in our apparatus.

II. EXPERIMENTAL METHOD

Ion translational energy spectrometry measurements on CO^+ products from single-electron-capture collisions of the type
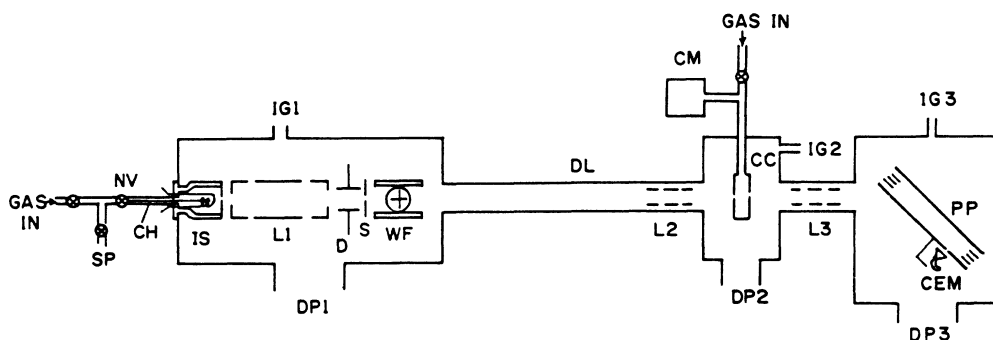
FIG. 1. Schematic diagram of the ion translational energy spectrometer used in the present measurements. IS: low-voltage arc ion source. SP, NV, and CH: sorption pump, needle valve, and solid charge holder in the ion source gas feed line. L1, L2, and L3: cylindrical electrostatic lenses. D: deflector plates. S and WF: entry slit and Wien-type mass filter. DL: 1.5-m drift length. CC: electrically isolated tungsten collision cell (can be heated to 2400 °C). CM: capacitance manometer. PP: electrostatic parallel-plate energy analyzer. CEM: channel electron multiplier. DP1, DP2, and DP3: diffusion pumps. IG1, IG2, and IG3: ionization gauges.

$$CO^{2+} + X \rightarrow CO^+ + X^+ + \Delta E \tag{1}$$

were carried out using a somewhat modified version of an apparatus which has been described in detail in a number of earlier reports.[12] A schematic diagram of the spectrometer is shown in Fig. 1. Briefly, ions produced in a low-voltage, high-pressure (10^{-1} Torr) arc are extracted by an accelerating potential in the 0.5–10-kV range and focused by a three-element cylindrical lens to the input slit of a region of crossed electric and magnetic fields (Wien filter) where separation on the basis of ion velocities occurs. As all ions emerging from the ion source are accelerated through the same potential, an ion velocity spectrum corresponds to a spectrum of mass-to-charge ratios. Mass-selected ions are passed through a differentially pumped static gas target maintained, in the present measurements, at room temperature. In the

postcollision region, the scattered ions are energy analyzed by a large electrostatic parallel-plate energy analyzer whose overall energy resolution is better than 0.1%. Ion detection is by a channel electron multiplier operating in the pulse counting mode.

Typical gas pressures are of the order of 10^{-1} Torr within the ion source, 5×10^{-7} Torr immediately outside the ion source and in the mass analysis region, and 1×10^{-7} Torr in the energy analysis and detection region. The scattered ions are detected with an angular resolution of the order of 10^{-2} deg. According to the uncertainty principle the classical concept of the impact parameter to be used in discussing results presented in this report can only be considered valid for scattering angles larger than a critical value θ_c:

$$\theta_c \sim h / \mu v b , \tag{2}$$

where b is the impact parameter, v is the collision velocity, and μ is the reduced mass of the collision system.[13] In the present experiments, at a collision energy of 4 keV and impact parameter of the order of 3.5 a.u., θ_c remains much smaller than the instrumental angular resolution.

The methodology adopted in the present measurements is the same as that in other recent translational energy spectrometry studies of electron-capture and electron-loss collisions conducted in our laboratory.[11,12,14] One particular aspect that needs emphasizing is that, in addition to relying on our Wien filter to pass CO^{2+} ions on the basis of their mass to charge ratio (m/q) being 14, an addition-
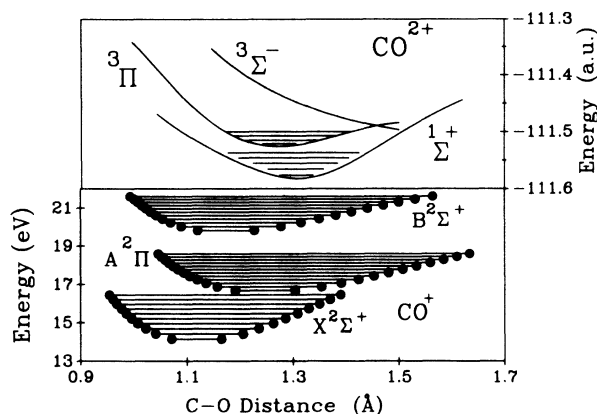

FIG. 2. Potential energy curves of CO^+ and CO^{2+}. The former are based on the calculations of Krupenie and Weissman (Ref. 15) and the latter on *ab initio* SCF MO CI calculations by Marathe and Mathur (Ref. 3). In the case of the CO^{2+} curves, the energy, in atomic units (1 a.u. = 27.2 eV), represents the sum of the binding energies of all the electrons in the dication. Spectroscopic data deduced by us from these curves are presented in Table I.

TABLE I. Spectroscopic data pertaining to the potential-energy curves of CO^+ and CO^{2+}.

State	r_e (10^{-8} cm)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})
CO^+ $X\,^2\Sigma^+$	1.1150	2214	15
CO^+ $A\,^2\Pi$	1.2436	1562	13
CO^+ $B\,^2\Sigma^+$	1.1686	1734	28
CO^{2+} $X\,^1\Sigma^+$	1.308	2487	61
CO^{2+} $A\,^3\Pi$	1.273	2194	216

al check was performed to ensure that experiments were not being conducted with a projectile beam of, for example, N^+ or metastable N_2^{2+} ions (also with $m/q=14$). Translational energy spectra were obtained of collision-induced dissociation (CID) products resulting from 4-keV collisions between ions possessing $m/q=14$ and He to establish that C^+ and O^+ fragments appeared at the appropriate energy analyzer voltages and to ensure the absence of N^+ products resulting from CID of contaminant N_2^{2+} ions. The absence of possible atomic impurities in the projectile beam, such as N^+, was established by scanning the postcollision energy analyzer voltage over a range which would transmit the N^{2+} product resulting from electron-loss (charge-stripping) collisions with the He target. Such translational energy spectra also provided useful confirmation of the fact that the Wien filter did not transmit ions whose mass-to-charge ratio had been altered (by autoionization, electron capture or loss, or by dissociation) in the region housing the ion acceleration and beam-formation optics.

III. RESULTS AND DISCUSSION

A. Quantal identification of CO^{2+} projectiles

Potential-energy curves of low-lying electronic states of CO^+ and CO^{2+} are an obvious prerequisite for interpreting the translational energy spectra of electron-capture product ions arising from reaction (1). Potential functions for the first three electronic states of each ion are shown in Fig. 2. The curves for the singly charged ions are taken from the calculations of Krupenie and Weissman,[15] who used a modified version of the Rydberg-Klein-Rees (RKR) method of obtaining the potential energy curves of diatomic species directly from observed vibrational and rotational levels of the system. The dication curves are from the large basis set, *ab initio* computations of Marathe and Mathur[3] using configuration-interaction procedures which account for all single, dou-
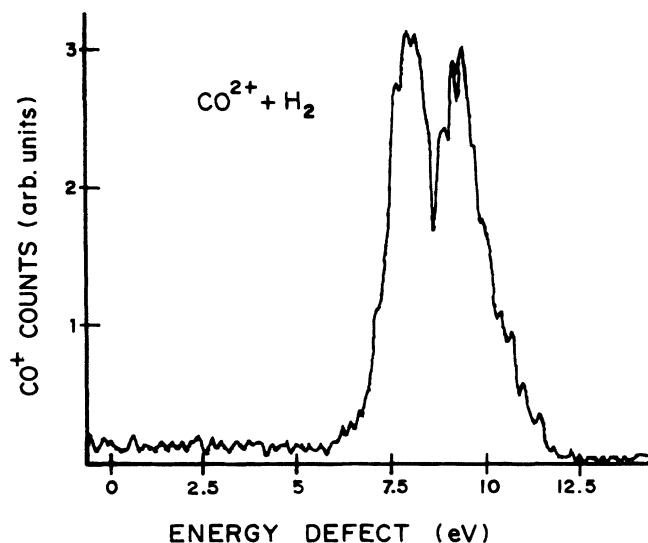

FIG. 3. Energy defect spectrum for CO^+ formation in 4-keV electron-capture collisions between CO^{2+} and H_2.
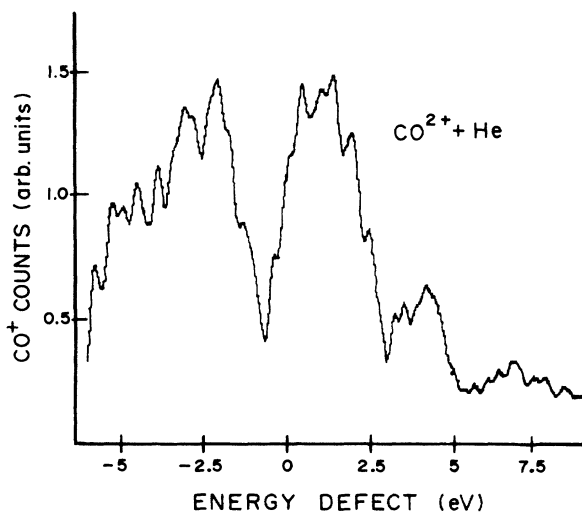
ble, triple, and quadruple excitations using Moller-Plesset perturbation theory up to fourth order. Some relevant spectroscopic information pertaining to these potential-energy curves is tabulated in Table I.

The computed dication potential-energy curves indicate that $^1\Sigma^+$ is the lowest CO^{2+} states accessible in vertical transitions from the lower vibrational levels of the ground electronic state of CO. This state is metastable to the extent that up to ten vibrational levels can be accommodated within its potential well; it "crosses" the purely repulsive $^3\Sigma^-$ at an internuclear separation of 1.5 Å. It has been postulated[3] that as a consequence of the not-insignificant amount of spin-orbit coupling in CO, a spin-nonconserving curve crossing process might result in predissociation of higher vibrational levels of the $^1\Sigma^+$ state. The $^3\Pi$ state is the second lowest metastable state of CO^{2+}. It possesses a potential well which can accommodate ca. six vibrational levels; higher vibrational levels would be expected to rapidly predissociate due to a curve crossing with the $^3\Sigma^-$ curve in the region of 1.4 Å. Vertical transitions from the $v=0$ level of the ground electronic state of CO will overwhelmingly populate the $v=2$ level of the $^3\Pi$ state and the $v=4$ level of the $^1\Sigma^+$ state of the dication. The vertical energy separation between these two levels is computed to be 1 eV. In case the relatively high gas pressure within our ion source leads to effective vibrational deexcitation of both the electronic states, the energy separation between the two $v=0$ levels becomes 1.5 eV.

In the case of the CO^+ curves, a sufficiently large body of photoelectron spectroscopy data exists[16] to demonstrate the reliability of the computed potential functions shown in Fig. 2.

B. Translational energy spectra

Translational energy spectra for CO^+ ions formed in 4-keV collisions with light targets, H_2 and He, and with heavy targets, O_2 and Kr, are shown in Figs. 3–6, respec-

FIG. 4. Energy defect spectrum for CO^+ formation in 4-keV electron-capture collisions between CO^{2+} and He.
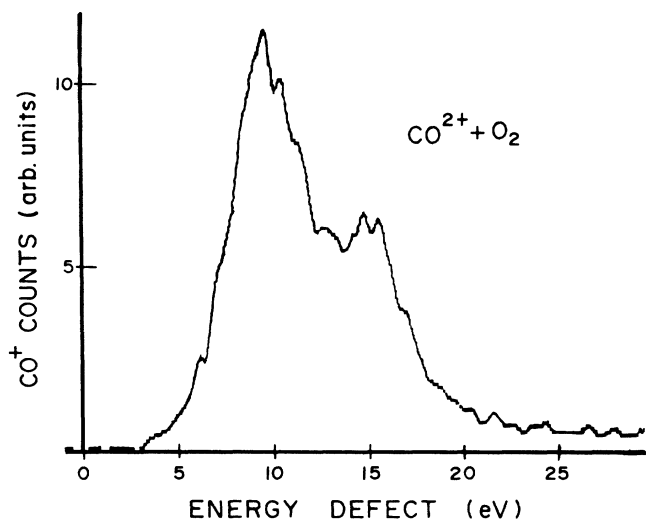
FIG. 5. Energy defect spectrum for CO^+ formation in 4-keV electron-capture collisions between CO^{2+} and O_2.

tively. In each instance the abscissa scale is expressed in terms of the energy defect ΔE for reaction (1). All measurements were conducted under experimental conditions which ensured that the amount of energy released in the collision which is imparted to the target as recoil energy is negligible. Assuming that there is no scattering in the incoming channel in reaction (1) and that the outgoing channel is dominated by a purely Coulombic interaction, the target recoil energy is of the order of 88 meV in the worst case of a light target (H_2), for an exoergic energy defect of 10 eV.

Discussion of the various electron-capture channels is greatly simplified by adopting the Hasted notation[17] in which Roman numerals I and II represent the ground and excited electronic states of the CO^{2+} projectile ions, the Greek letters $\alpha, \beta, \ldots$ represent the ground and higher-lying electronic states of the CO^+ products and X and D designate, respectively, the ground state and dissociative states (for the molecular targets) of the target ions, X^+, in reaction (1).

We consider, first, the global features of the energy-defect spectra measured in the present experiments. Figure 3 shows a typical spectrum for the electron-capture reaction

$$CO^{2+} + H_2 \rightarrow CO^+ + H_2^+ + \Delta E \ . \tag{3}$$
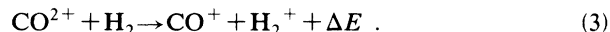
The exoergic energy defects ΔE computed for various possible reaction channels are indicated in Table II. ΔE values have been calculated on the basis that the vertical double ionization energy[3,7] of CO is 39.6 eV and that the $v=2$ vibrational level is predominantly populated in the H_2^+ formed in reaction (3); vertical ionization energies for the three lowest electronic states of CO^+, as deduced from photoelectron spectroscopy measurements[16] have been utilized.

Comparison of Fig. 3 with the contents of Table II indicates that nondissociative electron capture by CO^{2+}

[reaction (3)] occurs predominantly, and with almost equal partial cross sections, into the $X\,^2\Sigma^+$ and $A\,^2\Pi$ electronic states of CO^+. Dissociative electron capture, leading to formation of $H^+ + H$ appears to be an unimportant channel. Unfortunately, the measured spectrum does not allow an unambiguous deduction to be made about the importance, or otherwise, of the $II\beta X$ channel which would arise if there was a substantial $^3\Pi$ component in the CO^{2+} projectile beam.

In the case of electron capture from He, the overall cross section was found to be extremely small. The typical, relatively noisy, spectrum shown in Fig. 4 indicates that the main exoergic channel leads to formation of CO^+ in the ground electronic state. The first excited state of CO^+ is also formed with approximately the same partial cross section, even though this channel is endoergic by ca. 2 eV (see Table III). Clearly, the relatively weak $CO^{2+} + He$ electron-capture reaction proceeds with equally (low) efficiency both via an avoided crossing of potential-energy surfaces as well as by Demkov-type of noncrossing mechanisms.[18] Endoergic reaction channels are also found in the case of $CO^{2+} + Kr$ reactions (see below). The energy defect spectrum for the $CO^{2+} + He$ reaction has also been measured by Herman et al.[9] Although the magnitudes of the energy defects in the two experiments are different, due to significant differences in the value assumed for the double ionization energy of CO, there is qualitative agreement that electron capture proceeds through the $I\alpha X$ and $I\beta X$ channels (see Table III).

In the case of O_2 target, our energy defect spectrum (Fig. 5) indicates that the dissociative electron-capture channel (leading to $CO^+ + O^+ + O$ products) is again negligible (see Table IV). The dominant channel leads to nondissociative capture into the $A\,^2\Pi$ state of CO^+. There is also a contribution from the channel leading to capture into the ground state of CO^+. Spin-allowed transitions leading to electron capture accompanied by excitation of O_2^+ into the lowest $^4\Pi_u$ state (channel $I\alpha A$, Table IV) may also be occurring, although our present
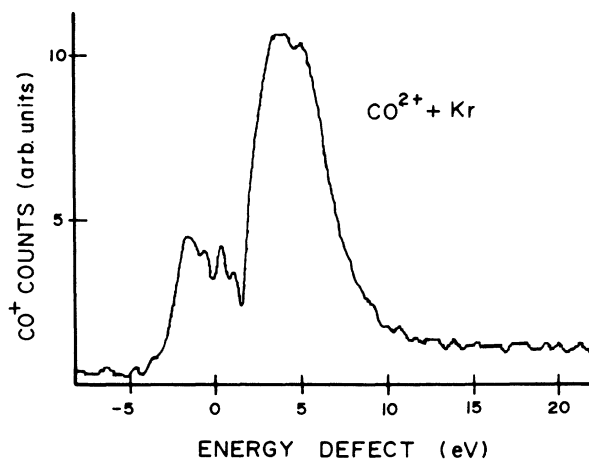

FIG. 6. Energy defect spectrum for CO^+ formation in 4-keV electron-capture collisions between CO^{2+} and Kr.

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TABLE II. Energy defects (ΔE) for electron capture by CO^{2+} from H_2. H_2^+ product ions are assumed to be predominantly formed in the $v=2$ vibrational level. Values of impact parameter b are given for the dominant channels observed in the measured energy defect spectrum (Fig. 3). See text for a description of the Hasted notation used in describing the reaction channels.

Channel	ΔE^a (eV)	b (a.u.)	Channel	ΔE (eV)
IαX	9.62	2.8	IαD[b]	6.97
IIαX	10.62		IIαD	8.47
	(11.12)			
IβX	6.72	4		
IIβX	7.72	3.5		
	(8.22)	3.3		
IγX	3.91			
IIγX	4.91			
	(5.41)			

[a]The ΔE values in parentheses pertain to the $v=0$ level of $CO^{2+*}(^3\Pi)$.
[b]Dissociation energy, $D_0(H_2)=2.65$ eV.

energy resolution precludes separation of this channel from the IβX channel. Structure observed in the energy defect region of 15 eV is difficult to explain other than by postulating the existence of a substantial component of long-lived $^3\Pi$ states in the dication projectile beam. If this is indeed the case, then the IIβX and IIγX channels may also be contributing to the reaction process.

In the case of Kr target (Fig. 6), electron capture occurs overwhelmingly into the $B\,^2\Sigma^+$ state of CO^+ with an exoergicity of ca. 5.8 eV (Table V). In the earlier studies of Herman and co-workers,[9] the dominant channel for this electron-capture reaction was also observed to have an energy defect in the region of 5 eV. However, a somewhat different interpretation was offered, in terms of capture into quartet states of CO^+. On the basis of the energetics deduced from the potential-energy curves shown in Fig. 2, we prefer not to invoke capture into the hitherto-little studied quartet states. The shape of our measured spectrum does, however, indicate that capture into higher-lying electronic states of CO^+, such as $C\,^2\Delta$ and $D\,^2\Pi$, may be of significance in the $CO^{2+}+Kr$ reaction. Furthremore, although comparison of the measured energy defect spectrum with Table V enables us to rule out capture into the IαX and IβX channels, the shape of the dominant peak in the ΔE region between 5–10 eV may indicate the existence of the IIγX channel brought about by a long-lived excited state ($^3\Pi$) component in the CO^{2+} projectile beam. The small structures observed on either side of $\Delta E=0$ may be due to target excitation (channels such as IαA, see Table V) resulting in formation of excited target ion states such as $Kr^{+*}\,^2S_{1/2}$. As in the case of the endoergic channels observed in the $CO^{2+}+He$ reaction, Demkov-type of noncrossing processes might be occurring which involve electron-capture transitions at internuclear distances where the coupling strength between the initial and final states is comparable with the separation between the corresponding potential surfaces. It is also possible that capture into states such as $^2S_{1/2}$ can occur via avoided crossings at extremely small internuclear separations where potential-energy surfaces become difficult to describe.

Leaving aside electron capture from He, which occurs with an extremely small cross section, in all other cases the dominant electron-capture channels appear to be those which can be interpreted in terms of avoided crossings of potential-energy surfaces at internuclear separations in the region of 3 a.u. This situation, whereby selective electron capture occurs into only a limited number of excited states of the product ions—corresponding to certain favored impact parameters—is analogous to the well-established pattern in electron-capture reactions involving multiply charged atomic ions which has given rise to the concept of a reaction window.[19] Reaction channels which are accessible at impact parameters which fall within the reaction window (which extends over the range ca. 2–5 a.u.) are populated with much higher probability than those which occur at lower and higher impact parameters.

Although there is a relative paucity of experimental, state-diagnosed electron-capture data (earlier systematic studies were conducted by Herman et al.[9] with CO^{2+} projectiles and by Mathur et al.[20] using $CS_2^{2+,3+}$ ions), the available information tends to indicate that notwithstanding the generally higher density of states existing in triatomic collision systems (such as $CO^{2+}X$) and the more complex avoided crossings of seams of potential-energy surfaces, the reaction window type of picture appears to be also applicable to electron capture by multiply charged molecular species.

TABLE III. Energy defects (ΔE) for electron capture by CO^{2+} from He.

Channel	ΔE (eV)	Channel	ΔE (eV)
IαX	1.0	IIαX	2.5
IβX	−1.9	IIβX	−0.4
IγX	−4.7	IIγX	−3.2

TABLE IV. Energy defects (ΔE) for electron capture by CO^{2+} from O_2. Ground-state $(^2\Pi_g)O_2^+$ product ions are assumed to be predominantly formed in the $v=1$ vibrational level. Excited-state O_2^+ ions in the $^4\Pi_u$ states are assumed, on the basis of photoelectron spectroscopy data (Ref. 16) to be predominantly in the $v=5$ vibrational level (Kimura et al.). Values of impact parameter b are given for the dominant channels observed in the energy defect spectrum (Fig. 5).

Channel	ΔE^a (eV)	b (a.u.)	Channel	ΔE (eV)
IαX	13.3	1.8	IαD[b]	6.8
			IαA	9.0
IIαX	12.3	2.2	IIαD	8.3
	(14.8)	1.8		(7.8)
IβX	9.0	3.0		
IIβX	8.0	3.4		
	(10.5)	2.6		
IγX	8.1		IIγX	7.1 (9.6)
IδX	7.4		IIδX	6.4 (8.9)

[a]The ΔE values in parentheses pertain to the $v=0$ level of $CO^{2+*}(^3\Pi)$.
[b]$D_e(O_2^+ \, X \, ^2\Pi_g)=6.5$ eV.

C. Comparison of experimental data with computed potential energy curves

As noted above, within the framework of the reaction window picture, the overall quantal description of the CO^+ product ions that are produced in electron capture by CO^{2+} will, to a good approximation, be determined by the impact parameter at which the reaction takes place. However, the vibrational level distribution within the actual CO^+ electronic state that is populated will be governed by the relative positions along the internuclear axis of the potential-energy curves of singly and doubly charged CO ions shown in Fig. 2. Studies with much higher energy resolution are required in order to make quantitative comparisons of experimental energy defect spectra with the computed potential-energy curves. However, on the basis of present data, we make the following qualitative observations.

Considering the shapes and positions of the CO^+ and CO^{2+} potential-energy curves (Fig. 2) and the associated spectroscopy data (Table I), it is possible to deduce that if, within our ion source, CO^{2+} ions are formed in the $v=4$ level of the $^1\Sigma^+$ (as would be the case for a vertical

transition from the $v=0$ level of the $^1\Sigma^+$ ground state of neutral CO), then electron capture into the $X\,^2\Sigma^+$ state of CO^+ will populate a range of vibrational levels from $v=0-10$, with largest Franck-Condon overlaps for the highest vibrational levels. Capture into the $A\,^2\Pi$ state of CO^+, on the other hand, will predominantly populate the $v=0$ level. The manifestation of this in the energy defect spectrum would be a relatively broad peak for the IαX and a sharper one for the IβX channel. If the somewhat high gas pressure in our ion source (ca. 10^{-1} torr) results in effective collisional deactivation of higher vibrational levels, then the $^1\Sigma^+ \, CO^{2+}$ state produced in the $v=0$ level will capture an electron such that, for the IαX channel, a narrower distribution of vibrational levels will be expected (from $v=3-6$, with largest Franck-Condon factors for the $v=4,5$ levels). The IβX will still produce a narrow energy defect peak, with only the $v=0$ level being populated.

An analogous situation will prevail for the metastable excited state of CO^{2+} in that for production of the $^3\Pi$ state in the $v=2$ level, a broad vibrational distribution will be obtained for the CO^+ product ions for the IIαX channel (extending from $v=1-7$, with a maximum at

TABLE V. Energy defects (ΔE) for electron capture by CO^{2+} from Kr. Ground-state $(^2P_{3/2})Kr^+$ product ions are assumed to be predominantly formed. Values of impact parameter b are given for the dominant channels observed (Fig. 6). The ΔE values in parentheses pertain to the $v=0$ level of $CO^{2+}(^3\Pi)$.

Channel	ΔE^a (eV)	b (a.u.)	Channel	ΔE (eV)
IαX	11.6		IIαX	12.6 (13.1)
IβX	8.7		IIβX	9.7 (10.2)
IγX	5.88	4.6		
IIγX	6.88	3.9		
	(7.38)	3.7		
IαA[a]	-2.9		IIαA[a]	-1.9 (-1.4)

[a]Target excitation to $Kr^+ \, ^2S_{1/2}$.

$v=4$), whereas for CO^{2+} ion formation in the $v=0$ level of the $^3\Pi$ level, the electron-capture channel IIαX will have a narrower energy defect peak with only three vibrational levels of the ground state of CO^+ being populated ($v=2-4$). In both instances, the IIβX channel will give rise to narrower energy defect peaks with $v=0$ being the dominant vibrational level populated.

In our measured spectra, capture into the ground and first excited states of CO^+ occurs most prominently in the case of H_2 and O_2 targets. Although both spectra were obtained under conditions of only modest energy resolution in which the full width at half maximum of the elastic CO^{2+} peak was of the order of 1.5 eV, we make the following tentative observations. In the case of capture from O_2, comparison of the energy defect spectrum (Fig. 5) with the calculated values of ΔE (Table IV) indicates that, for the IIβX channel, the expected values of ΔE are 8.0 eV (for no vibrational deexcitation within the ion source) and 10.5 eV (when collisional deexcitation of vibrational levels proceeds efficiently). The shape of the measured spectrum tends to indicate that the latter situation prevails. In the case of H_2 target (Fig. 3), ΔE values

for the IIβX are calculated to be 7.7 eV and 8.2 eV for the case of the $^3\Pi$ state being in the $v=2$ and $v=0$ levels, respectively. The measured spectra once again indicates that the latter situation (i.e., efficient vibrational deexcitation within the ion source) dominates.

Due to the experimental constraints of only modest energy resolution (and a natural limitation imposed by a fairly high density of available states), these observations can only be regarded as being of a somewhat tentative nature. Further measurements with enhanced energy resolution will go a long way towards enabling meaningful comparison to be made between experimental state-selected electron-capture data and state-of-the-art computations of the quantal properties of electronic states of singly and doubly charged molecular ions.

ACKNOWLEDGMENTS

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