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Probing the quantal identity of low-lying electronic states of CO^{2+} by quantum-chemical calculations and ion-translational-energy spectrometry

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Potential-energy curves of various electronic states of CO^{2+} and CO^{+} are computed using all-electron *ab initio* molecular-orbital methods. Configuration-interaction effects are treated by perturbative techniques (using Möller-Plesset perturbation theory to fourth order) and by variational methods (using the coupled-cluster approach). In the case of CO^{2+}, calculations indicate that the lowest-energy $^3\Pi$ and $^1\Sigma^+$ states are nearly degenerate in the Franck-Condon region but that only the latter is likely to be metastable; the former is expected to predissociate rapidly due to a curve crossing with a purely repulsive $^3\Sigma^-$ state. Experimental measurements have been carried out on the kinetic energy released when metastable CO^{2+} ions dissociate by a tunneling mechanism, using an ion-translational-energy spectrometer. The kinetic-energy spectra are measured of fragment ions produced when CO^{2+} dissociates via an intermediate highly excited (dissociative) CO^{+*} state populated in an electron-capture reaction in collision with He. The experimental results remain difficult to interpret within the framework of the computed potential-energy curves.

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I. INTRODUCTION

Metastable CO^{2+} ions were among the first multiply charged molecular species to be observed in mass-spectrometry experiments conducted as long ago as 1932 [1]. Since then a very large number of experimentalists and theoreticians have concentrated their attention on this ion. A compilation of pertinent references to earlier literature can be found in a number of recent papers [2–7] reporting the results of studies on this species conducted by means of ion-translational-energy spectrometry, photoion-photoion coincidence methods, Auger spectroscopy, inner-shell-photoionization experiments, and sophisticated *ab initio* quantum-chemical techniques. However, despite the enormous amount of attention that CO^{2+} has attracted, ambiguities regarding certain important aspects of its molecular properties continue to persist.

The first topic of continuing debate concerns the quantal identification of the lowest-energy metastable electronic state of the dication which can be accessed from the ground state of neutral CO by a Franck-Condon transition. The second major point of contention concerns the existence, or otherwise, of an excited electronic state of CO^{2+} which is metastable on the microsecond time scale.

Regarding the first question, the earliest attempt at constructing the potential-energy curve of the ground electronic state of CO^{2+} by theoretical means was made by Hurley [8] using a semiempirical approach. $^3\Pi$ symmetry was assigned to the lowest-energy state which was found to possess a potential barrier sufficiently deep to accommodate a number of vibrational levels and to give the dication a lifetime of the order of a few tens of microseconds. The results of a large number of subsequent, more refined, calculations produced somewhat divergent results. Both $^1\Sigma$ and $^3\Pi$ symmetry were suggested by different sets of *ab initio* molecular-orbital calculations carried out using a variety of sophisticated quantum-chemical techniques to account for configuration-interaction (CI) effects [9]. Moreover, many of these calculations fail to agree on the shapes of the potential-energy functions for low-lying CO^{2+} electronic states.

Regarding the question of whether or not CO^{2+} possesses a long-lived electronically excited state, the available information remains fragmentary and contradictory. The earliest evidence of a long-lived excited state of the dication emerged from studies conducted by Herman *et al.* [10] on state-diagnosed nondissociative electron-capture reactions of CO^{2+} with the rare gases:

$$CO^{2+} + X \longrightarrow CO^{+} + X^{+} + \Delta E \ , \qquad (1)$$

where X represents the different rare gases and ΔE is the energy defect for the electron-capture reaction which is experimentally determined by measuring the translational energy spectrum of CO^{+} product ions. By taking spectroscopically established values for the ionization energies of the rare gases and the energies of various electronic states of CO^{+}, known from photoelectron spectrosocopy, Herman *et al.* found that, for certain electron-capture reactions, their measured values of ΔE could only be made consistent with the law of energy conservation by postulating an excited CO^{2+} electronic state possessing a lifetime of at least 3 μs. In these experiments, the projectile CO^{2+} ions were produced in an electron-impact ion source of the type conventionally used in most commercial mass spectrometers. However, subsequent experiments conducted in the same laboratory [6], using an identical ion source coupled to a translational energy spectrometer having considerably enhanced energy resolution, yielded data on electron capture by, and excitation of, CO^{2+} ions, which could be interpreted without having to invoke the existence of a metastable, electronically excited CO^{2+} state. Mathur and Rajgara [3] have also reported the results of an ion-translational-energy spectrometric study of quantum-state-selected electron-capture reactions of 5-keV CO^{2+} ions with H_2, He, O_2 and Kr; they also found it necessary to suggest the existence of a long-lived excited state of CO^{2+} ions in the projectile beam in order to interpret their translational energy spectra of electron-capture products.

In the present study, we focus attention on detailed calculations of the potential-energy curves of several low-lying electronic states of CO^{2+}. Due to the high density of electronic states, even close to the lowest-energy states, we have incorporated configuration-interaction effects into our all-electron *ab initio* molecular-orbital calculations not only by conventional perturbative means, using Möller-Plesset perturbation theory (up to fourth order), but also by using variational techniques, making use of the coupled-cluster approach. In order to have some assessment of the reliability of the shapes of our computed potential-energy curves, we have combined our theoretical efforts with recent ion-translational-energy spectrometry experiments on dissociation of metastable CO^{2+} ions. Such dissociation can occur following one of two distinct pathways. C^+ and O^+ ion pairs can be formed in a direct dissociation process

$$CO^{2+} \longrightarrow C^+ + O^+ + T\ , \tag{2}$$

where T is the center-of-mass kinetic-energy release accompanying ion-pair formation. This type of spontaneous (collisionless) process is attributable to tunneling through the barrier in the potential-energy curve of the metastable ground state of the dication. Dissociation of metastable CO^{2+} can also occur through a two-step process induced by collision with a neutral gas, such as He:

$$CO^{2+} + He \longrightarrow CO^{+*} + He^+ \pm \Delta E_1 \tag{3}$$

followed by

$$CO^{+*} \longrightarrow C^+ + O + \Delta E_2 \tag{4}$$

or

$$CO^{+*} \longrightarrow C + O^+ + \Delta E_3\ . \tag{5}$$

In the first step of this collision-induced process, electron-capture occurs to an excited, dissociative electronic state of CO^+ which, subsequently, fragments into either C^+ or O^+ ions. Each of these reactions has an associated center-of-mass energy defect which is determined in the laboratory frame in our experiments by means of translational energy measurements of product ions. We attempt to correlate the measured values of kinetic-energy releases with those expected by our calculated potential-energy curves. In order to carry out such comparisons, it becomes necessary to also have information on the potential-energy curves of highly excited electronic states of CO^+. Due to the acute paucity of such data, we have had to extend our calculations to excited CO^+ states, and theoretical data have also been generated on some high spin states of CO^+ in the present study.

II. ELECTRONIC STRUCTURE OF SINGLY AND DOUBLY CHARGED IONS OF CO

The ground electronic state of the neutral CO molecule has $^1\Sigma^+$ symmetry with the following electronic configuration: $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4$. CO^+ ions can be produced by removing an electron from the highest 5σ and 1π occupied orbitals. Some of the resulting electronic configurations and possible low-lying CO^+ electronic states are as follows: $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^4$ giving rise to $^2\Sigma^+$ states; $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^3$ giving rise to $^2\Pi$ states; $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^2\, 2\pi^1$ yielding $^4\Pi$ $3\,^2\Pi$ and $^2\Phi$ states; $1\sigma^2 2\sigma^2\, 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^3\, 2\pi^1$ yielding $^4\Sigma^+, ^4\Sigma^-, ^4\Delta$, $2\,^2\Sigma^+$, $2\,^2\Sigma^-$, and $2\,^2\Delta$ states; and $1\sigma^2\, 2\sigma^2\, 3\sigma^2\, 4\sigma^2 5\sigma^1 1\pi^2\, 2\pi^2$ yielding $^6\Sigma^+$, $2\,^4\Sigma^+$, $2\,^4\Sigma^-$, $2\,^4\Delta$,$4\,^2\Sigma^+$,$3\,^2\Sigma^-$,$4\,^2\Delta$, and $^2\Gamma$ states.

Similarly, CO^{2+} can be produced by removing two electrons from the high occupied orbitals giving rise to the following electronic configurations with the corresponding dication states: $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4$ giving rise to a $^1\Sigma^+$ state; $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^3$ yielding $^3\Pi$ and $^1\Pi$ states; $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^2$ giving rise to $^3\Sigma^-, ^1\Sigma^+$ and $^1\Delta$ states; and $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 5\sigma^1 1\pi^4$ giving rise to $^3\Sigma^+$ and $^1\Sigma^+$ states.

Low-lying electronically excited dication states may also be obtained by promoting one or two electrons to normally unoccupied 2π orbitals, such as $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^2 2\pi^1$ yielding $^5\Pi$, $4\,^3\Pi$, $3\,^1\Pi$, $^3\Phi$, $^1\Phi$ states.

Production of CO^{2+} in our ion source, by electron-impact double ionization of CO, is a process governed by the Franck-Condon principle. Consequently, only those parts of the potential-energy functions of dication electronic states will be initially accessed in our experiments which lie vertically above the classical Franck-Condon region of the lowest-energy vibrational level of the ground electronic state of neutral CO. From analysis of uv spectroscopic data it has been established [11] that the equilibrium internuclear distance for the $^1\Sigma^+$ ground electronic state of neutral CO is 1.128 Å; the classical inner and outer turning points for the zeroth vibrational level of this state are 1.083 and 1.179 Å, respectively.

III. THEORETICAL METHODS AND RESULTS

Calculations of the potential-energy curves of a number of electronic states of CO^{2+} and CO^{+*} have been carried out using all-electron, *ab initio*, molecular-orbital methods. Configuration-interaction effects were accounted for by different perturbative as well as variational techniques. These calculations were carried out using the GAUSSIAN 88 and GAUSSIAN 90 suites of programs, implemented on a MicroVAX computer. The basis set used comprised 6-311G** type orbitals, containing four *s*, three *p*, and one *d* functions for both C and O, with a total of 36 atomic orbitals.

As a first step, exploratory comparative calculations were carried out on the $^1\Sigma^+$ and $^3\Pi$ states of CO^{2+} at a fixed equilibrium internuclear distance of 1.25 Å. Configuration-interaction calculations using Möller-Plesset (MP) perturbation theory up to second order (MP2) [12] and third order (MP3) [13] include only double substitutions while the fourth-order (MP4) [14–16] method includes all single, double, triple, and quadruple substitutions. Variational calculations were carried out using the coupled-cluster approach. (A concise overview of various perturbative and variational CI procedures can be found in Ref. [19].) Configuration interaction with double substitutions (CID) [19] and CID plus single substitutions (CISD) [17] are conventional variational procedures which need size consistency correction [18]. Coupled cluster with double substitutions (CCD) [20], CCD plus single and triple substitutions using MP4 (ST4CCD) [21], quadratic CI including single and double substitutions (QCISD), and QCISD plus triple substitutions using MP4 [QCISD(T)] [22] procedures are different forms of the coupled-cluster method which meet the size consistency condition. In the QCISD(T) procedure the electron correlation energy calculation is carried out variationally with a trial wave function including all single and double substitutions. The resulting wave function is then used to evaluate the contribution from triple substitutions in a perturbative manner. The calculated values of the total energy for CO^{2+} using these different CI methods are shown in Table I. Using perturbative CI procedures it becomes clear that the correlation contribution to the total energy is high (particularly for the $^1\Sigma^+$ state) and, moreover, that this contribution oscillates as higher orders of perturbation are included. This indicates that there are many low-lying $^1\Sigma$ states close to the ground state and perturbation calculations carried out many orders higher than at the MP4 level would be necessary in order to obtain a reliable energy value for the $^1\Sigma^+$ state. The relative positions of $^1\Sigma^+$ and $^3\Pi$ were also found to interchange as higher and higher order perturbations were included. It is, consequently, clear that recourse to nonperturbative methods of incorporating CI effects is mandatory in order to generate reliable potential-energy functions of low-lying states of CO^{2+}. As indicated in Table I, various variational methods [CID, CISD, CCD, ST4CCD, QCISD, QCISD(T)] also show significant fluctuation in the magnitudes of the correlation contributions. Since the QCISD(T) method is the most sophisticated of the ones used, it may not be unreasonable to assume that the result obtained using this method yields the most reliable of the energy values shown in Table I. It is of interest to note that all the variational methods consistently indicate that $^3\Pi$ is lower in energy than $^1\Sigma$ at the internuclear distance of 1.25 Å.

It is pertinent to draw attention to the time required to carry out such calculations. On a MicroVAX II computer, the QCISD(T) method required 3 h for the calculation of a single point on the $^1\Sigma^+$ curve, and 4 h in the case of a point on the $^3\Pi$ curve. For larger molecules, or for calculations on diatomics carried out with larger basis sets, such a method would clearly be impractical. We have therefore carried out a series of CI calculations on CO^{2+} at the QCISD(T) level using a "window" which includes only the valence orbitals of C and O. The results of these computations [indicated as QCISD(W) in Table I], which are shown in Fig.1, show a significant reduction of correlation energy compared to the calculations carried out without a window. The effect of carrying out these calculations at different internuclear distances has also been studied. Although the global features describing the three low-lying states of CO^{2+} are the same whether a window is used or not, there is a significant difference in the relative positions of the curves, the heights of the potential barriers, and the crossing points between the curves in the two cases. This is contrary to the expectation that consideration of valence orbitals alone in CI calculations ought to be sufficient to predict accurate interaction curves for diatomic and polyatomic molecules. Indeed, this is the basic assumption in most multiconfiguration self-consistent-field (MCSCF) calculations using a discrete active space. The MCSCF technique, and other

TABLE I. Calculated total energies of $^1\Sigma$ and $^3\Pi$ states of CO^{2+} at $R_e = 1.25$ Å. HF are self-consistent-field calculations carried out at the Hartree-Fock level without configuration interaction (CI). All other calculations incorporate CI effects by either perturbative or variational methods (see text).

Method	Energy (hartrees) $^1\Sigma$	$^3\Pi$
HF	−111.181 457	−111.342 398
MP2	−111.577 851	−111.566 170
MP3	−111.491 575	−111.572 448
MP4	−111.653 904	−111.597 167
CID	−111.529 182	−111.578 718
CISD	−111.559 154	−111.593 346
CCD	−111.529 424	−111.576 254
ST4CCD	−111.590 750	−111.597 510
QCISD(T)	−111.588 481	−111.602 670
QCISD(W)	−111.383 967	−111.417 764

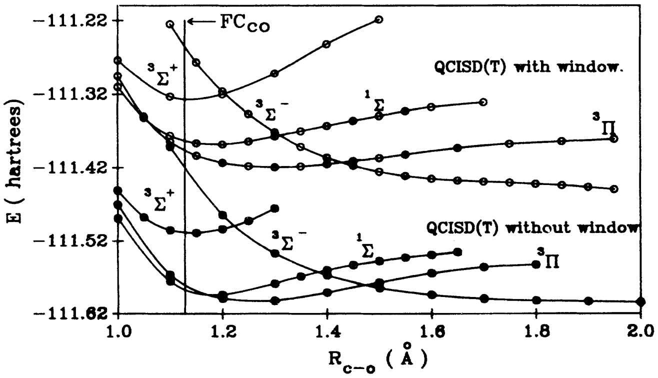

FIG. 1. Potential-energy curves of some low-lying electronic states of CO^{2+} calculated using the QCISD(T) procedure with and without a window (see text). The vertical line marked FC_{CO} indicates the center of the Franck-Condon zone from the zeroth vibrational level of the ground electronic state of neutral CO.

similar methods in which only valence orbitals are considered for purposes of incorporating CI effects, have been used in a number of recent studies [4, 5] of the potential-energy curves of diatomic dications, including CO^{2+}.

Our calculated values for Franck-Condon excitation energies from the ground electronic state of CO to the lowest electronic states of CO^+ and CO^{2+}, computed using the QCISD(T) procedure at an equilibrium internuclear distance of 1.128 Å, are given in Table II. The first vertical ionization energy (E_{I1}) of CO, giving rise to CO^+ ($^2\Sigma^+$), was calculated to be 13.66 eV. This value agrees very well with the experimental value of 13.99 eV determined from photoelectron spectroscopy [23]. Our calculated value of the lowest vertical double ionization energy (E_{I2}) of CO, giving rise to CO^{2+}, was 41.03 eV. This value is also in extremely good accord with the most recent experimental determinations of E_{I2} (41.25 ± 0.1 eV obtained in photionization and ion kinetic-energy coincidence experiments carried out by Dujardin *et al.* [24] and 40.75 ± 0.5 eV obtained in the photoion-photoion coincidence experiments of Lablanquie *et al.* [4]). The relative positions of the other electronic states of CO^+ and CO^{2+} can be visualized in Table II. The asymptotic energy values for C^+ and O^+ ions in various electronic states are also tabulated; they were also computed using QCISD(T) procedures. It is pertinent to reinforce the point that in making comparisons between our calculated energy values and experimental data, no energy normalization or recalibration has been performed. Recent valence CI calculations [4], on the other hand, have required the computed energy scale to be calibrated with reference to experimental E_{I1} and E_{I2} data, with the implicit assumption that the potential-energy curves are calculated with the same accuracy over a range of internuclear distances.

TABLE II. Calculated total energies and excitation energies of various electronic states of CO, CO^+, and CO^{2+} and different dissociation limits.

Electronic state	Energy (hartrees)	Excitation energy (eV) from CO ($^1\Sigma$, 1.128 Å)
	CO molecule	
$^1\Sigma^+$	−113.093 70	0.0
	CO^+ ion	
$^2\Sigma$	−112.591 85	13.66
$^2\Pi$	−112.476 11	16.80
$^4\Sigma^+$	−112.322 05	21.00
$^4\Delta$	−112.281 26	22.11
$2\,^2\Pi$	−112.238 65	23.27[a]
$^4\Pi$	−112.120 46	26.48
$3\,^2\Pi$	−112.080 71	28.07[a]
$^6\Sigma^+$	−112.041 36	28.63
$C^+(^2P) + O(^3P)$	−112.296 50	21.69
$C(^3P) + O^+(^4S)$	−112.234 75	23.37
	CO^{2+} dication	
$^1\Sigma^+$	−111.585 87	41.03
$^3\Pi$	−111.579 84	41.19
$^1\Pi$	−111.566 15	41.57 [b]
$^3\Sigma^+$	−111.508 47	43.13
$^3\Sigma^-$	−111.422 92	45.46
$2\,^1\Sigma^+$	−111.385 00	46.50 [b]
$2\,^3\Sigma^+$	−111.379 03	46.66 [b]
$^5\Pi$	−111.305 79	48.65
$C^+(^2P) + O^+(^4S)$	−111.820 56	34.64

[a] Calculated value using the MCSCF-FOCI (first-order configuration-interaction) procedure (Ref. [34]), calibrated to the lowest-energy $^2\Pi$ state calculated by us.

[b] Calculated using the CIS procedure in GAUSSIAN 90, calibrated to the $^1\Sigma^+$ state calculated by us using the QCISD(T) procedure.

Figures 1 and 2 show the potential-energy curves computed in the present study for CO^{2+} and CO^+, respectively, using the QCISD(T) procedure. We found that the variational methods employed failed to produce convergence at those internuclear distances where an excited-state electronic configuration happened to be degenerate with, or lie lower than, other configurations of the same symmetry [as computed by the Hartree-Fock self-consistent-field (SCF) procedure]. Consequently, all our computed potential-energy curves do not cover the same range of internuclear distances. Nevertheless, it is clear from the data shown that the following conclusions can be drawn in a fairly unambiguous manner. Firstly, it is clear that the two lowest $^1\Sigma^+$ and the $^3\Pi$ curves both possess substantial potential barriers. This is consistent with earlier theoretical results, even those carried out with perturbative CI procedures [9]. However, the present results also indicate that, in the Franck-Condon region of neutral CO, both these electronic states are nearly degenerate. Secondly, the $^3\Sigma^-$ state is found to be purely repulsive. This result is contrary to that obtained in early *ab initio* molecular-orbital calculations, carried out by Wetmore, Roy, and Boyd [25], which yielded an extrememly large (approximately 4.5 eV deep) potential well; later computations carried out by Mazumdar *et al.* [26] indicated that this large well was an artifact generated by the type of Hartree-Fock procedures used by Wetmore, Roy, and Boyd.

In spite of the near degeneracy of the lowest $^1\Sigma^+$ and $^3\Pi$ electronic states, examination of the calculated potential-energy curves indicates that the $^3\Pi$ electronic

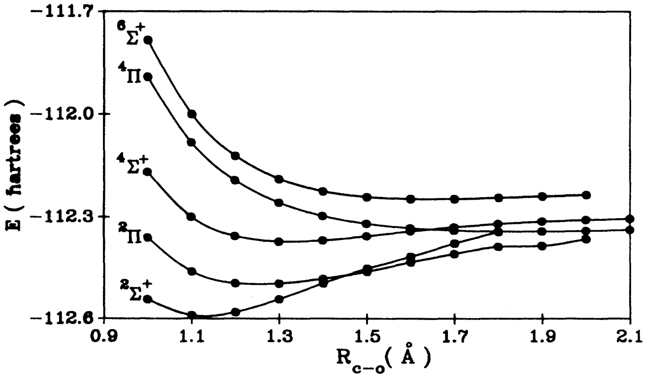

FIG. 2. Potential-energy curves of some doublet, quartet, and sextet electronic states of CO^+.

state will be unlikely to yield metastable CO^{2+} ions in all situations where the dication state is populated via a Franck-Condon transition from neutral CO. As can be seen in Fig.1, a curve crossing occurs between the $^3\Pi$ and $^3\Sigma^-$ states which will result in very rapid predissociation into C^+ and O^+ ion pairs. The $^1\Sigma^+$ state, on the other hand, is expected to present a substantial barrier towards dissociation. Even the higher vibrational levels in this state are likely to be fairly long lived, as a crossing with the $^3\Sigma^-$ is forbidden on two grounds: firstly, dipole selection rules prohibit a crossing between singlet and triplet states and, secondly, even if spin-orbit coupling is considered to be substantial enough to circumvent the above rule, the spin-orbit operator will be ineffective in the case of a two-electron transition such as $^1\Sigma^+ \rightarrow ^3\Sigma^-$. Consequently, our theoretical results indicate, in fairly unequivocal terms, that the lowest-energy metastable CO^{2+} state, which is vertically accessible from the ground electronic state of CO, can only be a $^1\Sigma$ state. During the course of this work, results of complete active space SCF and multireference contracted configuration-interaction calculations on CO^{2+} states were published by Larsson, Olsson, and Sigray [5] which have yielded potential-energy curves which are in very good accord with those shown in Fig.1. It is of interest to note that both sets of calculations also indicate that there exists an excited state of $^1\Sigma^+$ symmetry which is vertically accessible from the ground state of CO and which possesses a potential barrier deep enough to accommodate a number of quasibound vibrational levels. However, a curve crossing with a $^3\Sigma^-$ state occurs in the region of 1.25 Å. It appears likely that vibrational levels $\nu > 0$ will predissociate rapidly; at present it is not clear whether the $\nu = 0$ level will possess a sufficient lifetime in order to account for the observations made in the ion-translational-energy spectrometry experiments of Herman *et al.* [10] and Mathur and Rajgara [3]. Comparison of our potential-energy curves with those obtained in recent valence CI calculations carried out by Lablanquie *et al.* [4] is precluded by the large uncertainties associated with the reported internuclear distances in the latter computations. (It may also be pointed out that, for reasons which remain unclear, the Franck-Condon region chosen by Lablanquie *et al.* to intersect the CO^{2+} potential-energy curves pertains not to the lowest vibrational level of the ground $^1\Sigma^+$ state of neutral CO but to some higher vibrational level.)

The calculated potential-energy curves for the lowest $^2\Sigma^+$ and $^2\Pi$ states of CO^+ are consistent with experimental information obtained from photoelectron spectroscopy. The curves for higher spin states, $^4\Sigma^+$, $^4\Pi$, $^4\Delta$, and $^6\Sigma$, are discussed in relation to the dissociative electron-capture results below.

IV. EXPERIMENTAL METHOD AND RESULTS

The present experiments on kinetic-energy measurements on dissociation products of 5-keV collisions between metastable CO^{2+} ions with He were carried out using a translational energy spectrometer which has been described in detail in a number of earlier reports [3, 26, 27]. Briefly, a high-pressure plasma type of ion source is used to produce CO^{2+} ions. The relatively high gas pressures (approximately 1–10^{-1} Torr) used in the ionization region ensure that collisional deactivation of any ions produced in excited states proceeds very efficiently. Background pressures in the region immediately outside the ion source are typically about 1×10^{-6} Torr, and 10^{-7} Torr elsewhere in the apparatus. The ions extracted from such a source are therefore expected to be overwhelmingly in their ground electronic state. Ions produced in our source are extracted by a nominal accelerating voltage of 2.5 kV (the exact value being 2530.5 V). The extracted beam is then focused, by a three element cylindrical electrostatic lens, onto the entrance slit of a Wien filter, a region of crossed electric and magnetic fields, where the ions are separated on the basis of their mass to charge ratios. This beam then passes through a collision chamber maintained with a target gas pressure of approximately 10^{-4} Torr. The beam emerging with a scattering angle of 0° is energy analyzed by a parallel-plate electrostatic analyzer and ion detection is by a channel electron multiplier operating in the particle counting mode, coupled to conventional pulse counting electronics and a multichannel analyzer. The angular resolution in our experimental configuration is very high, of the order of 0.001° for detection of post-collision ions.

A typical raw 0° translational energy spectrum of CO^{2+} ions colliding with He at an impact energy of 5 keV is shown in Fig.3. In the spectrum, the central peak *a* is the elastic scattering peak. Peaks b_1 and b_2 are due to C^+ dissociation fragments. In the first approximation the dissociation products are produced in a variety of center-of-mass angles; the rigid constraint on ion detection imposed by the angular resolution in our apparatus ensures that only those fragment ions are detected which

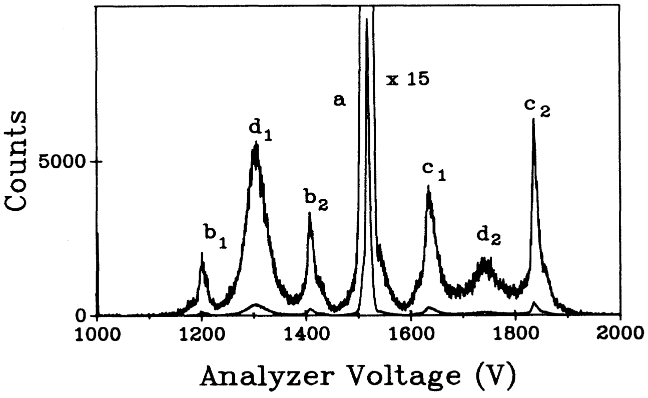

FIG. 3. Typical raw translational energy spectrum of 5-keV metastable CO^{2+} ions dissociating into C^+ and O^+ fragments. *a* indicates the elastic scattering peak. Pairs of peaks marked *b* and *c* represent C^+ and O^+ ions, respectively, formed upon spontaneous (collisionless) dissociation of metastable CO^{2+}. Peaks d_1 and d_2 correspond to formation of C^+ and O^+ ions, respectively, by electron-capture-induced dissociation of metastable CO^{2+}.

are scattered such that their velocity vectors are either in the same or the opposite direction as the incoming CO^{2+} beam velocity (forward or 0° scattering and backward or 180° scattering, respectively). Clearly, in the former case the velocity vectors of the fragment ions and the projectile CO^{2+} ions would add, whereas in the latter case there is a subtraction. In the spectrum shown in Fig.3, peak b_2 corresponds to forward-scattered C^+ ions and peak b_1 is due to the backward-scattered component. Similarly, peaks c_2 and c_1 correspond to forward- and backward-scattered O^+ fragments.

Obtaining such spectra at different pressures of helium in the collision cell and observing that the intensities of b and c peaks relative to the elastic scattering peak remain independent of collision gas pressure lead us to deduce that these pairs of peaks arise from spontaneous (collision-less) dissociation of metastable CO^{2+} ions [Eq. (1)]. The kinetic energy released, T, when CO^{2+} dissociates in a spontaneous (collisionless) fashion, is deduced using the relation

$$\mathrm{T} = \frac{\Delta E_{\mathrm{lab}}^2 M^2}{16 m_C m_O E} \tag{6}$$

where ΔE_{lab} is the laboratory-frame energy difference between the forward- and backward-scattered fragments of C^+ or O^+, M is the total mass of the projectile ions, m_C and m_O are the masses of carbon and oxygen, respectively, and E is the kinetic energy of the incident CO^{2+} ions (the exact value for the spectrum shown in Fig. 1 was 5061 eV). In the case of the spectrum shown in Fig.3, T was determined to be 5.6 ± 0.2 eV.

There have been a few other measurements of T with which our value can be compared. Kupriyanov [28] was the first to estimate the kinetic energy released (T) upon spontaneous dissociation of CO^{2+}; values of approximately 2 to 3 eV were deduced for each fragment, leading to a total T value in the range 4 to 6 eV. In later studies, Newton and Sciamanna [29] used a Dempster-type mass spectrometer, and reported a value of 5.75 ± 0.2 eV for T. Measurements of the T value have also been carried out using ion kinetic energy spectrometry conducted on commercial mass spectrometers. Beynon, Caprioli, and Richardson [30] used a RMH-2 double focusing mass spectrometer to determine a T value of 5.59 ± 0.07 eV, and, more recently, Boyd and co-workers [31, 32] have used reversed-geometry instruments to deduce a T value of 5.3 ± 0.1 eV.

There is reasonable accord between these earlier measurements and our value for T, with excellent agreement being obtained with the results of Newton and Sciamanna as well as Beynon, Caprioli, and Richarson. In all these measurements, dissociation of CO^{2+} occurs from the electronic state (or states) which are long-lived enough to enable the dications to survive the passage from the ion source region into the mass filtering region, although earlier studies have not been able to unambiguously attribute the measured value to T to a particular electronic state of CO^{2+}. In all the above experiments the typical transit time would be of the order of 1 μs. (In our apparatus, for 5-keV CO^{2+} ions, the time required to emerge from our mass filtering region is approximately 0.7 μs.) Any dissociations which occur on time scales which are much shorter than this will not be observed in these experiments. [It is of interest to note that dissociation occurring on much faster time scales has recently been studied using the photoion-photoion coincidence (PIPICO) method [4, 24, 33]].

It is of interest to attempt a correlation between the measured value of T and that which would be expected from the calculated potential-energy curves of metastable CO^{2+}. In a conventional electron-impact ion source CO^{2+} electronic states will be accessed at the equilibrium separation of CO due to the Franck-Condon principle. It can be seen from Fig.1 that both the $^1\Sigma$ and the $^3\Pi$ states of the dication can be populated by electron-impact double ionization of CO because of their near degeneracy in the Franck-Condon region. It can also be seen that the $^3\Pi$ state thus accessed will predissociate rapidly, into C^+ and O^+ fragments. This argument therefore suggests that the projectile dication beam in our experiments will consist predominantly of CO^{2+} ions in the $^1\Sigma$ state. But a comparison of the experimentally observed and theoretically calculated T values suggests otherwise. The kinetic energy released when CO^{2+} spontaneously dissociates from this state, by tunneling through the potential barrier, is determined from our calculated potential-energy curves to be 2.2 eV. This value appears to be considerably smaller than that determined experimentally (5.6±0.2 eV). On the other hand, the T value calculated for the dissociation of the dication from the ground vibrational level of the $^3\Pi$ state, 5.8 eV, is in much better agreement with the experimental value. This suggests that the projectile contains a fair amount of CO^{2+} in the $^3\Pi$ state which, in turn, implies that the state itself has a lifetime of at least a few μs.

In this connection it is of interest to draw attention to the recent calculations of Larsson, Olsson, and Sigray [5], whose potential-energy curves yield a value of T of 5.98 eV, close to the value expected from our calculations. These calculations also indicate that the $^3\Pi$ state of the dication is nearly degenerate with the $^1\Sigma^+$ in the Franck-Condon region with respect to CO. The $^3\Pi$ and the $^3\Sigma^-$ states cross each other at an internuclear separation of approximately 1.46 Å (the corresponding crossing point in our calculations is 1.47 Å).

So, there exists a rather curious situation in that we have the following.

(a) There is fair agreement between different experiments that the value of the total kinetic energy released when CO^{2+} dissociates in a collisionless fashion is in the region of 5.6 eV.

(b) The two most recent sets of calculations of potential-energy curves indicate that although $^1\Sigma^+$ is the lowest-energy metastable electronic state of the dication, the value of T resulting upon collisionless dissociation of this state is expected to be of the order of only 2.2 eV. On the other hand, although the nearly degenerate $^3\Pi$ state is not expected to be metastable, the value of the kinetic energy released when this state dissociates (rapidly, due to a curve crossing with the purely repulsive $^3\Sigma^-$ state) is 5.8 eV, in remarkably close agreement with the experimentally measured value. The contradiction remains unresolved at present.

In the spectrum shown in Fig.3, the additional peaks, marked d_1 and d_2, correspond, respectively, to C^+ and O^+ fragments which are formed as a result of the collision-induced dissocation of CO^{2+} via an electron-capture channel involving an intermediate highly excited (dissociative) state of CO^{+*} [Eqs. (2) and (3)]. The energy defects for these electron-capture-induced dissociation (ECID) reactions indicate an overall exoergicity; the measured values were 4.5 ± 1.0 and 11 ± 1.5 eV for formation of C^+ and O^+ fragments, respectively. The kinetic energy released in the case of C^+ products of the ECID reaction was measured to be approximately 0.3 eV.

In order to interpret the ECID spectrum it is necessary to have information on the energies of various electronic states of CO^{+*} ions which are populated in the intermediate electron-capture stage of the dissociation process. The excited states of CO^+ which are of interest are those which will spontaneously dissociate into either $\mathrm{C}^+ + \mathrm{O}$ or $\mathrm{C} + \mathrm{O}^+$ fragments. Clearly this means only those CO^{+*} states in which vibrational levels lying very close to the dissociation limit are populated in a vertical transition from the original CO^{2+} state, and others which are either purely repulsive or which undergo rapid predissociation by a curve crossing with a purely repulsive state. Information about such states from conventional uv emission spectroscopy and photoelectron spectroscopy is extremely scarce. Consequently we have to take recourse to energy calculations which we have carried out for a number of dissociative electronic states of CO^{+*}; our results are tabulated in Table II.

Table III indicates the calculated values of kinetic-energy release from various doublet, quartet, and sextet states of CO^{+*}. From the theoretical data, it is clear that the lowest $^4\Delta$ state of the singly charged ion is the most probable candidate for the intermediate CO^{+*} state participating in the dissociative electron-capture process, yielding an expected C^+ kinetic-energy release of 0.23 eV. Energy releases expected from other dissociative states are much higher than the measured value.

TABLE III. Calculated values (in eV) of kinetic energy released (KER) upon dissociation of various excited electronic states of CO^+.

CO^+ state	Total KER	C^+ KER	O^+ KER
$^4\Delta$	0.4	0.23	
$2\,^2\Pi$	1.58	0.9	
$^4\Pi$	4.79	2.74	
$3\,^2\Pi$	6.38	3.65	
$^6\Sigma$	5.26		2.25

Regarding formation of O^+ fragments in the ECID process, higher-lying $^4\Delta$ states lead to dissociation fragments $\mathrm{C}(^1\mathrm{D}) + \mathrm{O}^+\ (^4\mathrm{S})$; however, such high-energy states are unlikely to yield the overall exoergicity measured for the ECID process leading to O^+ formation. Moreover, theoretical information on such states remains nonexistent at present. The lowest-energy $^6\Sigma$ state can also yield O^+ fragments, with an expected kinetic-energy release of 2.25 eV. However, transitions of CO^{2+} (which may be in either a singlet or a triplet state) to CO^{+*} in the sextet state ($^6\Sigma$) are forbidden by spin conservation rules. The maximum spin that the CO^{+*} ion can possess through such a transition, involving He as a collision gas, is 3/2; this disallows transitions to any CO^+ state with spin multiplicity higher than quartet. O^+ fragments can also be produced by dissociation of the $F\,^2\Pi$ state of CO^+. Recent photoelectron spectroscopy measurements [35] indicate that this state lies 12–14 eV above the ground electronic state of CO^+; however, pertinent potential-energy curves for this state are currently unavailable.

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