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# Characterization of low-lying electronic states of $CO^{2+}$

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A new and elaborate set of high-level *ab initio* bound-state computations has been undertaken to obtain the various low-lying excited electronic states of doubly charged $CO^{2+}$ ion, using the multireference single and double excitations configuration interaction (MRDCI) method. The characteristics and shapes of the potential energy curves are discussed to elucidate the metastable character of $CO^{2+}$ ion. The results are discussed and compared with earlier theoretical and experimental results.

## Introduction

$CO^{2+}$ ion is perhaps the first among the doubly charged metastable species observed in mass spectrometry measurements in 1930's. Since then it has been investigated by a variety of experimental techniques and theoretical studies. It is now generally agreed that $CO^{2+}$ is metastable for at least a few microseconds (μs). However, the quantal characterization of the low-lying electronic states responsible for its metastability remained a debating issue in the literature. A brief historical account can be found in a recent review [1].

Short lifetimes, high reactivity, and relatively high energies required for $CO^{2+}$ formation (~ 40 eV) with respect to the neutral ground state) along with sparse bound electronically excited states, pose a challenging task for its experimental investigation. As a result, it has been explored mostly by techniques which are inherently of low resolution. Improved experimental information has become available in recent years by using ion-translational-energy spectrometer and monitoring the kinetic energy released (KER) when metastable $CO^{2+}$ ions dissociate by tunneling or predissociation mechanism. Most of the relevant experimental references are compiled in references 2 and 3.

The stability of such molecular ions is strongly correlated with the nature of their potential energy curves (PECs). Quite often these metastable species possess a high density of electronic states in a given range of energy and also exhibit near-degeneracies which make their assignments difficult from the available experimental data. Because of the increased nuclear charge (Coulombic) repulsion it becomes extremely important to compute the electronic energy as accurately as possible, taking into account the electron correlation. This still poses a challenging problem theoretically, and demands the use of high quality *ab initio* calculations.

The first attempt to construct the PECs for $CO^{2+}$ was based on a semiempirical approach. Hurley[4] identified the PEC of the ground electronic state of $CO^{2+}$as a $^3\Pi$ state which exhibited a potential minimum (with a barrier), and was sufficiently deep to support a number of vibrational levels. This could perhaps explain the lifetime of the dication of the order of μs. However, subsequent *ab initio* computations showed somewhat divergent results as regards the lowest electronic states as well as the shapes of PECs. In their calculations using a restricted contracted gaussian basis set and multireference configuration interaction (MRCI) method with self-consistent field (SCF) molecular orbitals (MO) Wetmore *et al.*[5] suggested a $^1\Pi$ to be the lowest state. Correia *et al.*[6], employing a multireference contracted configuration interaction (MRCCI) treatment with MOs obtained from complete active space SCF (CASSCF) and using a larger basis set, identified a $^1\Sigma^+$ state as the lowest state. The second state of $^1\Sigma^+$, which could be important, was described quite differently by these computations. Later, employing a larger basis set, Larsson *et al.*[2] computed the low-lying electronic states of $CO^{2+}$ using the CASSSCF and MRCCI approaches, and identified a $^1\Sigma^+$ state to be the lowest state. Their calculations also revealed that both $1\,^1\Sigma^+$ and $1\,^3\Pi$ states were nearly degenerate in the Franck-Condon (FC) regions, and thus both could be accessed during a FC excitation from the ground vibrational state (v=0) of the ground electronic state ($X\,^1\Sigma^+$) of neutral CO. However, the $1\,^3\Pi$ state was found to be the lowest state exhibiting a minimum at a slightly

larger internuclear distance ($r$). Krishnamurthi *et al.*[3] computed the various electronic states wherein the configuration interaction effects were treated by perturbative techniques, using MØller-Plesset perturbation theory upto fourth order, and by variational methods, using the coupled-cluster approach. Their calculations also indicated that the lowest energy $1^1\Sigma^+$ and $1^3\Pi$ states are nearly degenerate and that the latter is expected to predissociate rapidly due to a curve crossing with a purely repulsive $^3\Sigma^-$ state, which was in agreement with the findings of Larsson *et al.*[2]. It is to be noted that the earlier calculations of Wetmore *et al.*[5] had predicted that the $^3\Sigma^-$ state was bound showing a minimum. Lablanquie *et al.*[7] undertook valence electrons configuration interaction calculations. Interestingly, the ordering of PECs for $1^1\Sigma^+$ and $1^1\Pi$ states in the calculations of Wetmore *et al.* and Lablanquie *et al* were found to be reversed in comparison with that from MRCCI calculations[2,6] and as suggested by Auger spectroscopy[6].

It is worth pointing out that most of the earlier experimental results are of low resolution in which the initial $CO^{2+}$ state distribution is mostly not known. Therefore, their interpretation depends heavily on theoretical calculations. In view of the fact that some of the electronic states show (near) degeneracy in the FC region, and that earlier theoretical calculations fail to agree on the shapes of the PECs, it becomes important to perform elaborate *ab initio* calculations for the low-lying electronic states of $CO^{2+}$. In the present study we report on high level bound-state *ab initio* multireference double-excitations configuration-interaction (MRDCI) calculations for the several low-lying electronic states of $CO^{2+}$. In the next section we discuss the characteristics and shapes of various PECs along with earlier theoretical and experimental results.

## Results and Discussion

*The basis set and MRDCI computations*

The present set of calculations was carried out using highly correlated wave functions using the MRDCI method. The method has been discussed several times in the literature[8-10] and was used previously by us on a similar problem[11]. Therefore, we only highlight the computational details here. The basis set chosen was cc-pVTZ (correlation consistent polarized valence triple zeta) suggested earlier by Dunning and coworkers[12,13]. The employed atomic basis set was 10s, 5p, 2d, 1f contracted to 4s, 3p, 2d, 1f, which led to 70 contracted GTO functions for the $CO^{2+}$ system.

In view of computational convenience molecular calculations were performed in $C_{2V}$ symmetry, and identification of electronic states for the $C_{\infty V}$ molecular geometry was done according to the usual correlation rules[15]. This means that the various species of $C_{2V}$ point group will correlate with the corresponding species of the $C_{\infty V}$ point group. That is, calculations for $\Sigma^+$ and $\Sigma^-$ states were done in the $A_1$ and $A_2$ symmetries (the irreducible representations of the $C_{2V}$ point group), respectively. The occurrences of $\Pi$ and $\Delta$ states were identified with the degeneracies of electronic energies in $B_1$ and $B_2$ symmetries ($B_1+B_2$), and in $A_1$ and $A_2$ symmetries ($A_1+A_2$), respectively. The MRDCI calculations for asymptotic atomic states were carried out in $D_{2h}$, wherein the $P_g$ and $P_u$ states correlate with $B_{1g}+B_{2g}+B_{3g}$ and $B_{1u}+B_{2u}+B_{3u}$ species, respectively. $S_g$ and $S_u$ atomic states were identified, respectively, with $A_g$ and $A_u$ species of the point group. The CI configuration space was generated by restricted Hartree-Fock (HF) calculations. For the spatial symmetry various open or closed shell SCF occupations were chosen, and the CI results were found to be insensitive to the choice. The present set of CI calculations were done with the HF-SCF configuration space of $^3\Pi$-state. Three of the MOs with extremely high orbital energies were excluded from the CI while the lowest two, essentially the core orbitals, were kept doubly occupied in the CI excitation process. These approximations are known to have negligible influence on the final interaction energies while producing substantial savings in the computational effort. Thus, in the CI treatment 65 MOs were available for the excitations. In the MRDCI method the dimension of final CI space depends upon a selection of threshold values in the configuration selection step. In a typical run, for most geometry and spatial symmetries about 35-60 optimized main configurations were used to generate $1.0\text{-}3.0\times10^5$ singly and doubly excited configurations out of which 14 000 were then selected by adopting a threshold of 2-12 microhartrees. The final Hamiltonian matrix in the selected configuration space was then diagonalized to give 5 lowest roots. Their eigenvalues were subsequently extrapolated to the full generated space corresponding to a selection threshold of zero, and also corrected for the effects arising from the higher excitations by the modified Davidson correction (for details see ref. 8-10). We report the extrapolated and corrected values here. The final CI wavefunctions were quite well represented by the reference space. The sum over the squared configuration coefficients was between 0.91 and 0.95 for

the lower roots and for most of the geometry considered here. It is worth pointing that using the same basis set employed here the computed dissociation energy of CO with respect to v=0($X^1\Sigma^+$) was 11.015eV (compared to the experimental value[15] of 11.09eV). The computed equilibrium distance ($r_e$) was found to be 2.130 bohr, which was again in excellent agreement with the experimental value[15] of 2.132 bohr.

*Comparison with theoretical and experimental results*

Figure 1 displays the PECs as a function of internuclear distance ($r$) for the lowest $^1\Sigma^+$ and $^1\Sigma^-$ states of $CO^{2+}$. Note that for the sake of convenience the PEC of the ground electronic state of CO ($X^1\Sigma^+$) is also displayed in the lower panel, and the energies of the electronic states are shown (hereafter in eV) with respect to the energy value corresponding to $r_e$ of the ground state PEC of neutral CO ($X^1\Sigma^+$). There is an avoided crossing between $2^1\Sigma^+$ and $3^1\Sigma^+$ curves around $r$ = 2.3 bohr and also between $1^1\Sigma^+$ and $2^1\Sigma^+$ around $r$ = 2.9 bohr. The PEC for the $1^1\Sigma^-$ (line connecting the crosses) is also shown in the figure. Interestingly, the $3^1\Sigma^+$ state becomes degenerate (within the associated computational accuracy) with the $1^1\Sigma^-$ at lower values of $r$ (< 2.3 bohr), while $2^1\Sigma^+$ and $1^1\Sigma^+$ become degenerate with $1^1\Sigma^-$ state at intermediate (2.3 < $r$ < 2.9 bohr) and at large $r$ ($r$ > 2.9 bohr) values, respectively. As discussed above, the computations were carried out in $C_{2v}$ point group where the $\Sigma^+$ and $\Sigma^-$ states of the diatom correlate with $A_1$ and $A_2$ symmetries of the point group, and a $\Delta$ state is identified as the state having the same energy in both $A_1$ and $A_2$ symmetries, that is, when $\Sigma^+$ and $\Sigma^-$ states become degenerate. Here, we see that $1^1\Sigma^-$ state becomes degenerate with $^1\Sigma^+$ states in different intervals of $r$. Therefore, we identify the $1^1\Sigma^-$ state as $^1\Delta$ state. Accordingly, the $^1\Sigma^+$ states get modified and are shown in Fig.2.

We used a cubic spline[16] to interpolate the PECs. We see that the (2,3) $^1\Sigma^+$ state (hereafter mentioned as $2^1\Sigma^+$ state) thus exhibits a potential minimum around $r$=2 bohr and another potential minimum around $r$ = 3 bohr. The existence of a double minimum has also been predicted in earlier calculations[2]. While Auger spectroscopy[6] supports the minimum at $r_e$ = 2.073 bohr, the existence of the second minimum is yet to be confirmed experimentally. Another low lying PEC of $1^1\Pi$ state is also shown in Fig.2. The PECs for the lowest singlet and triplet states are shown in Fig.3. Unlike the earlier findings of Wetmore *et al.*[5] and Larsson *et al.*[2], we did not encounter any difficulty in getting the convergence for selected

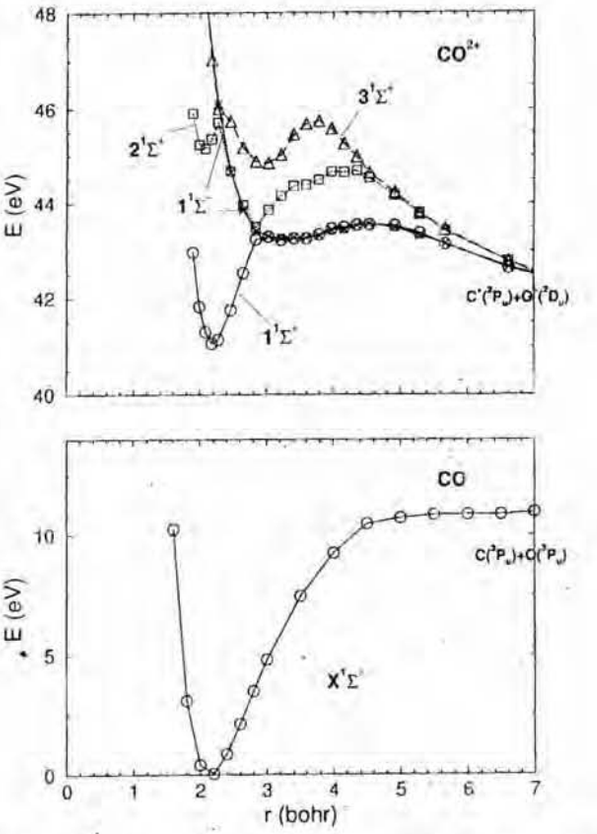


Fig 1 - Potential energy curves (PEC) for the lowest single $\Sigma^+$ and $\Sigma^-$ states of $CO^{2+}$. The PEC of the ground electronic state of CO ($X^1\Sigma^+$) is also displayed in the lower panel, and the energies of the electronic states are shown with respect to $E(r_e)$ of the ground state PEC of the neutral CO ($X^1\Sigma^+$). Note the avoided crossing between the $\Sigma^+$ states, and that the $\Sigma^-$ state becomes (nearly) degenerate with the $\Sigma^+$ states. The $\Sigma^-$ state is identified as a $\Delta$ state (see text).

roots for $r$ beyond 5 bohr. It was pointed out that due to near-degeneracy and crossing of different singlet and triplet states, it was difficult to get convergence for a selected root for larger $r$ values. One can see in Fig.2 that the PECs display a $1/r$ behavior beyond $r$=5 bohr. The computed energy difference between the lowest asymptotic limits $C^+(^2P_u)+O^+(^4S_u)$ and $C^+(^2P_u)+O^+(^2D_u)$ was 3.43eV. The present value is in better agreement with experimental value[17], and is higher only by 0.11eV than the latter. The $1^3\Pi$ and $1^1\Sigma^-$ states correlate to the lowest asymptotic limit $C^+(^2P_u)+O^+(^4S_u)$, while the rest of the states shown in the figure correlate to the next higher asymptotic limit, $C^+(^2P_u)+O^+(^2D_u)$.

The present PECs shown in Fig.2 and Fig. 3 are in good agreement with those obtained by Larsson *et al.*[2]. A comparison of $r_e$ and $T_e$ (vertical energy difference from the equilibrium distance) values of different elec-

Table 1 - Equilibrium constants for electronic states of $CO^{2+}$.

| State | Ref. | $r_e$ (Å) | $T_e$ (eV) |
|---|---|---|---|
| $^3\Pi$ | This work | 1.238 | 0.0 |
| | 2 | 1.261 | 0.0 |
| | 5 | 1.180 | 0.0 |
| | 7 | 1.2782 | 0.0 |
| $^3\Sigma^+$ | This work | 1.1446 | 2.46 |
| | 2 | 1.142 | 2.60 |
| | 5 | 1.238 | 7.09 |
| | 7 | 1.1149 | 2.88 |
| $1^1\Sigma^+$ | This work | 1.160 | 0.14 |
| | 2 | 1.170 | 0.25 |
| | 5 | 1.125 | 0.92 |
| | 6 | 1.170 | |
| | 7 | 1.1736 | 1.29 |
| $2^1\Sigma+$ | This work | 1.083 | 4.22 |
| | 2 | 1.097 | 4.37 |
| | 5 | 1.5 | 4.62 |
| | 7 | 1.10 | 5.58 |
| $^1\Pi$ | This work | 1.248 | 0.51 |
| | 2 | 1.264 | 0.52 |
| | 5 | 1.170 | 0.62 |
| | 6 | 1.257 | |
| | 7 | 1.275 | 0.71 |

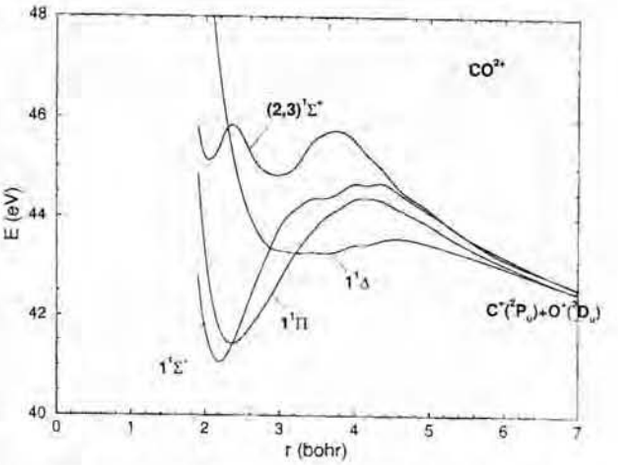


Fig 2 - Potential energy curves for the lowest singlet states of $CO^{2+}$. The energies of the electronic states are shown with respect to $E(r_e)$ of the ground state PEC of the neutral CO ($X^1\Sigma^+$).

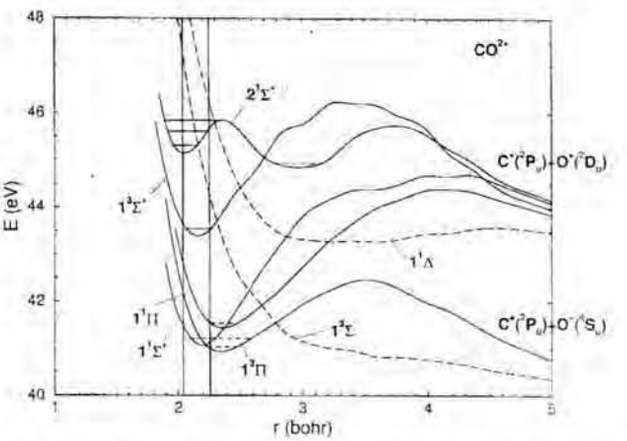


Fig 3 - Potential energy curves for the lowest singlet and triplet states of $CO^{2+}$. The energies of the electronic states are shown with respect to $E(r_e)$ of the ground state PEC of the neutral CO ($X^1\Sigma^+$). The $^3\Pi$ and $^3\Sigma^-$ curves correlate to the lowest asymptotic limit, $C^+(^2P_u)+O^+(^4S_u)$, while the rest of the curves correlate to the next higher asymptotic limit, $C^+(^2P_u)+O^+(^2D_u)$. The lowest vibrational energy levels are marked by horizontal lines, and the Franck-Condon region is highlighted with the two vertical lines. Note that the energy levels for v=0($1^1\Sigma^+$) and v=1($^3\Pi$) are coincident.

tronic states is given in Table 1 along with other earlier theoretical results. The present elaborate calculations using a larger basis set appear to yield better results. It also settles the issue that $^3\Pi$ state is the ground state of $CO^{2+}$ in confirmation with earlier calculations[2,3,6]. It is to be noted that a reverse order was predicted for $^1\Sigma^+$ and $^1\Pi$ states by Wetmore *et al.*[5] and Lablanquie *et al.*[7] as compared to that suggested by Auger spectroscopy[6]. Also, one finds a little resemblance among the present PECs and those of Wetmore *et al.*[5] for $2^1\Sigma^+$, $^3\Sigma^+$ and $^3\Sigma^-$ states. The $^3\Sigma^+$ state was predicted by Wetmore *et al.* to lie about 7eV above the $^3\Pi$ state, which appears to be unusually large. Another point of difference is that Wetmore *et al.* found $^3\Sigma^-$ state to be bound in contrast to its purely repulsive nature found in the present and earlier calculations[2,3,6].

In most of the experiments the metastable $CO^{2+}$ ions are produced by low energy electron impact or photon absorption of neutral CO mostly from its ground vibrational state v=0 ($X^1\Sigma^+$). Therefore, one would expect that excited electronic states of $CO^{2+}$ would be populated through the FC excitations. Larsson *et al.*[2] have discussed in detail about possible electronic states which

could give rise to metastabilty. Since the present PECs are in good qualitative agreement with those of Larsson *et al.* we will not discuss this aspect in detail. In the following section we discuss only qualitatively the likelihood of states responsible for the metastability of $CO^{2+}$.

The FC excitation region is shown by two vertical lines in Fig.3. The lowest vibrational energy levels of the electronic states were obtained by solving the radial Schrödinger equation numerically using the Le Roy program[18]. The vibrational energy levels are also marked by horizontal lines in the figure. It can be seen that all the shown states can be populated in various vibrational states and predissociation through tunneling (Herzberg case III[14]) is possible for all of them. However, such a mechanism would be effective only for vibrational levels close to barrier maximum, and thus loss by tunneling would be very little for lower vibrational states. The $1^1\Sigma^+$ state is expected to be mostly populated in lower vibrational state with v=0 having the largest population, and one would expect little contribution from tunneling since there is a substantial barrier for dissociation. Likewise, the $1^3\Sigma^+$ state would be mostly populated in v=0 state. The lower vibrational levels of $1^3\Pi$ and $1^1\Pi$ would also have little effect from tunneling. The first (inner) well of $2^1\Sigma^+$ state supports three vibrational levels and their tunneling lifetime has been estimated[2] to be of the order of 14ns. Overall, tunneling mechanism appears to be insignificant except for $2^1\Sigma^+$state, and lower vibrational levels of other states are expected to survive for longer time. Thus one would expect emission spectra arising from $2^1\Sigma^+ \rightarrow 1^1\Sigma^+$, $2^1\Sigma^+ \rightarrow 1^1\Pi^+$, and $1^3\Sigma^+ \rightarrow 1^3\Pi$ transitions. However, there is no experimental evidence for these as yet. There are some experimental hints[2] about the possibility of $1^3\Sigma^+ \rightarrow 1^3\Pi$ emission, but a conclusive experimental evidence is yet to come.

We see that $^3\Sigma^-$ state crosses with all the bound electronic states in Fig.3. Thus, predissociation (Herzberg case I[14]) of lower vibrational levels is possible by the repulsive $^3\Sigma^-$ state, and it would depend on the coupling between the different electronic states and $^3\Sigma^-$ state. The interaction between discrete vibrational and continuum levels can be given in terms of Fano theory[19] as $\Gamma_v = 2\pi |H_{v,E}|^2$, where $\Gamma_v$ is the width of the bound vibrational level, $H_{v,E}$ is the matix element between discrete vibrational wavefunction and energy-normalized continuum wavefunction. In the case of potential crossing $H_{v,E}$ can be separated[20] in terms of one electron spin-orbit coupling and the FC factor $\langle \chi_v | \chi_E \rangle$, where $\chi_v$ and $\chi_E$ are the vibrational and continuum wavefunctions. Larsson *et al.*[2] numerically estimated the predissociation lifetime of the low vibrational levels of the considered electronic states: ~40ns and ~80μs, respectively, for v=0 and v=1 states of $^3\Pi$ state, ~3ns for v=0 state of $^1\Pi$ state, ~1μs for v=0 state of $^1\Sigma^+$ state, and ~14ns for v=0 state of $2^1\Sigma^+$ state. They argued that the v=0 level of $1^1\Sigma^+$ state could be considered to be infinitely lived since its overlap with the dissociating $^3\Sigma^-$ state was practically zero. Therefore, they concluded that v=0 level of $1^1\Sigma^+$ was responsible for the observation of $CO^{2+}$ in the mass spectrometry. Considering the window-time in mass spectrometry of the order of ~μs they argued that the observed KER was due to v=0 of $^3\Pi$ state. However, they noted that these lifetimes would be sensitive to the exact location of the potential crossing between $^3\Pi$and $^3\Sigma^-$ state and an order of magnitude error in the respective lifetimes could be possible. For example, in their MRCCI computations with a "selection threshold" of 0.1 the v=0 state yielded a lifetime of 20μs while with "selection threshold" of 0.05 the lifetime increased to 80μs. Overall, there is good agreement between the present PECs and those of Larsson *et al.*[2], but a quantitative picture may emerge differently if the present PECs are employed. Although we do not compute the associated lifetimes in the present study we feel that it is the v=1($1^3\Pi$) state which would undergo predissociation at microsecond timescale, and survival time for v=0($1^3\Pi$) state would be even more than 80μs, as we will see in the following discussion when we compare the computed values of KER with the experimental values.

There are two aspects which need to be discussed while making comparison with experimental data: first, the unimolecular dissociation of metastable $CO^{2+}$ into $C^+$ and $O^+$ and measurement of their KER, and, second, the observation of $CO^{2+}$ itself which does not dissociate and travels from the production region to the ion-detection region in the mass spectrometer. Experiments[21,22] show that electron impact appearance potentials (threshold energies) for both $CO^{2+}$ and the dissociated fragments ($C^+$ and $O^+$ ions) are equal at 41.5eV. Photoionization experiments of Dujardin *et al.*[23] show a threshold of 41.25±0.05eV for production of metastable (>20μs) $CO^{2+}$. Single photon double ionization experiments of Lablanquie *et al.*[7,24] yielded threshold values of 40.75±0.5eV[7] and 40.5±0.5 eV[24] for $CO^{2+}$ production, and a threshold energy of 38.5±0.5eV[24] for $C^+ + O^+$ formation. Considering a typical transit time of the ions in the mass spectrometer of the order of 1μs, there appears to be two sets of lifetimes of the electronic states: first,

in which the $CO^{2+}$ predissociates on the time scale of the order of 1μs or even less, and second, in which it survives for more than a few microseconds (or even longer). There have been several measurements of KERs, when $CO^{2+}$ undergoes unimolecular dissociation, which range from 5.2 to 5.9 eV (5.75±0.2eV[21], 5.8±0.1 eV[23], 5.59±0.07eV[25], 5.3±0.1eV[26],). In a recent experiment, Krishnamurthi *et al.*[3] measured the KER to be 5.6±0.2eV. In their experiments the mass spectrometer window time was approximately 0.7μs, and disssociation processes occurring at much shorter time than this could not be observed. Following the discussion above, one would expect that only those elctronic states would contribute to the observed KER processes which predissociate in approximately 1μs time scale. Thus, we focus attention on the v=0 and v=1 state of $^3\Pi$ state which predissociates through the $^3\Sigma^-$ state to the lowest asymptotic level, $C^+(^2P_u)+O^+(^4S_u)$. From the present computations we find that v=0 and v=1 states of $^3\Pi$ lie, respectively, 5.72eV and 5.89eV above the asymptotic limit, $C^+(^2P_u)+O^+(^4S_u)$. Thus, predissociation from these vibrational states would give KER values of 5.72eV and 5.89eV, respectively, which is in excellent agreement with the experimental value of 5.6±0.2eV of Krishnamurthi *et al.*[3]. Since $v=0(^3\Pi)$ state is expected to survive for longer time (~80μs), presumably, it is the $v=1(^3\Pi)$ state which is largely responsible for the observed KER in the experiments. We also see that $v=0(^3\Pi)$ and $v=0(^1\Sigma^+)$ states lie 40.88eV and 41.05eV, respectively, above the $v=0(X^1\Sigma^+)$ state of the neutral CO. These values are in excellent agreement with experimentally deduced values by Hamdan and Brenton[27] (40.8eV and 41.1eV, respectively) and Herman *et al.*[28] (41.0 eV for $v=0(^1\Sigma^+)$. We further see in Fig. 3 that the energies of $v=0(1^1\Sigma^+)$ and $v=1(^3\Pi)$ states are coincident, lying 41.05eV above the $v=0(X^1\Sigma^+)$ state of CO. As discussed previously the $v=0(1^1\Sigma^+)$ state is one of the accessible states through FC excitations, which could possess practically an infinite lifetime. Although the $1^3\Pi$ state crosses with the $1^1\Sigma^+$ state, however the change in mutliplicity would seriously hinder the $1^1\Sigma^+ \rightarrow 1^3\Pi$ transition processes. This explains why the threshold energies (appearance potentials) for both the dissociated products ($C^+$ and $O^+$) and $CO^{2+}$ were experimentally observed to be the same[6,19,20].

Herman *et al.*[28] also found "conclusive" evidence of a non-dissociative excited state 1.7 eV above the $^3\Pi$ state. Our calculations show that $v=0(^3\Sigma^+)$ state lies 2.46eV above the $v=0(^3\Pi)$ state (see Table 1), and does not explain the experimental value. However, as mentioned above that the estimated[2] lifetime of the $v=0(^3\Pi)$ state was of the order of 1μs (or even below), and it could be considered to be a likely candidate for unimolecular dissociation to be observed in mass spectrometer. In the measurements of KER Dujardin *et al.*[23] and Curtis and Boyd[22] also observed a peak at 7.8±0.1eV and 7.9eV, respectively. The computed $v=0(^3\Sigma^+)$ state lies 8.18eV above the lowest asymptotic limit, $C^+(^2P_u)+O^+(^4S_u)$. The experimental values of KER could be attributed to be arising from this state.

There have been a few measurements of threshold energy for the formation of metastable $CO^{2+}$ ions using double electron capture reaction of the type: $H^+(3keV) + CO \rightarrow H^- + CO^{2+}$. These experiments help us locate[29] the singlet states of $CO^{2+}$ because of the spin selection rule, $\Delta S=0$. Experiments of Lablanquie *et al.*[7] gave a value of 41.3eV, while experiments of Mazumdar *et al.*[30] yielded values of 39.45±0.20eV[30] and 39.6eV[31]. However, using the technique of ion translational spectroscopy in collisions of $CO^+$ with He, Mazumdar *et al.*[30] measured the double ionization energy of CO to be 40.21±0.35eV, which they assigned to a metastable state. The lower energy values of 39.45eV and 39.6eV were assigned, respectively, to a predissociating state and the $1^1\Sigma^+$ state.

The lower threshold of 38.5±0.5eV for $C^+ + O^+$ production through single photon ionization[24] of CO cannot be explained by the present calculations. It was proposed that it is due to an indirect process wherein a highly excited electronic state of $CO^+$ autoionizes into $CO^{2+}(^1\Sigma) + e$ (continuum), thus being responsible for $C^+ + O^+$ production below the energetic threshold for metastable $CO^{2+}$ formation[32]. Krishnamurthi *et al.*[3] also studied the dissociation of $CO^{2+}$ in a proposed two step process in the presence of He:

$$CO^{2+} + He \rightarrow CO^{+*} + He^+ \pm \Delta E \qquad ...(1)$$

followed by

$$CO^{+*} \rightarrow C^+ + O \pm \Delta E_1 \qquad ...(2)$$

or

$$CO^{+*} \rightarrow C + O^+ \pm \Delta E_2 \qquad ...(3)$$

where $\Delta E$'s are the corresponding energy defects. They also computed PECs for some of the highly excited electronic states of $CO^+$. However, there still remains uncertainty about the exact location of these excited PECs. To explain their KER values obtained in this collision pro-

cess and the observed threshold energy in double electron capture reaction it is necessary to compute the excited state PECs of $CO^{+}$ on the same footing. Such a study is currently being undertaken in our laboratory. Just recently, measurements with high KER resolution (better than 250meV) have been performed at Grand Accélérateur National d'Ions Lourds facility (GANIL, Caen, France). We have studied the fragmentation dynamics of $CO^{2+}$ using the present PECs and a time-dependent wavepacket dynamics method. We obtained a good agreement between the experimentally observed and calculated KER distribution. The experimental and theoretical study is reported together elsewhere[33].

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