Computed lifetimes of metastable states of CO$^{2+}$

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Highly correlated internally contracted multireference configuration interaction wave functions are used to calculate the potential energy and spin-orbit coupling functions for the lowest electronic states of CO$^{2+}$ dication. Using these functions, the positions and lifetimes of the corresponding vibronic states are evaluated by means of log-phase-amplitude, stabilization, and complex-scaling methods within the framework of a multichannel Schrödinger analysis. For the first time in the literature, the calculated lifetimes are in good agreement with the experiment, thereby proving the reliability of the predicted characteristics and adequacy of the used theory for a theoretical study of other molecular dications. © 2006 American Institute of Physics. [DOI: 10.1063/1.2198835]

I. INTRODUCTION

Small, multiply charged molecular ions are of topical interest in science, especially due to their roles in extreme environments, such as planetary atmospheres, circumstellar envelopes, and interstellar regions (for more details see, e.g., Refs. 1–5). Generally, due to the strong electrostatic repulsion of their charged centers, the multiply charged ions are thermochemically unstable. However, quite frequently, chemical bonding can overcome this repulsion and make these ions fairly stable or, at least, metastable. A key stability aspect concerns the relative positions of the potential energy asymptotes of the ions and the corresponding charge-separated fragments and the positions of the molecular vibronic levels. The stability of individual molecular states also depends strongly on the shape of the potential energy curves, their relative positions, and interstate electronic couplings. Consequently, the actual lifetimes acquire values which may vary over a fairly wide range of values. For instance, experimentally determined lifetimes of CO$^{2+}$ range from a few tenths of a nanosecond to several seconds.\textsuperscript{6–10}

From the dynamic point of view, the lifetimes are determined by the tunnelings through the potential barriers and by the predissociations mediated by the electronic couplings, such as the spin-orbit couplings (see, e.g., Ref. 8). The theoretical evaluation of the lifetimes is thus limited only by the knowledge of the potential energy and electronic coupling functions. In principle, these potentials can be derived from vibrationally resolved spectral data. Presently, such data are accessible mainly by means of the threshold photoelectron coincidence (TPEsCO) technique,\textsuperscript{10,11} the time-of-flight photoelectron-photoelectron coincidence (TOF-PEPECO) method,\textsuperscript{11} the time-of-flight Doppler-free kinetic energy release (DFKER) spectroscopy,\textsuperscript{7} the double charged transfer (DCT) technique,\textsuperscript{14} and, ideally, rotationally resolving optical spectroscopy.\textsuperscript{15–17} So far, however, mostly due to the scarcity and limited accuracy of the available experimental data, no experimental “multichannel” potentials have been derived from the experiment. A natural way of overcoming this situation is the theoretical modeling based on a highly accurate \textit{ab initio} evaluation of the molecular potentials and their critical testing by comparison with the experiment. Although it is extremely difficult to calculate these potentials with spectroscopic accuracy, the \textit{ab initio} approach has been adopted in a long series of theoretical studies and has been found to be useful in many respects. In the case of CO$^{2+}$, for instance, the comprehensive sets of potential energy functions (PEF’s) were published by Wetmore et al.,\textsuperscript{18} Larsson et al.,\textsuperscript{19} and Elgendy et al.\textsuperscript{20} The most accurate potentials are those of Elendt et al. who rely on a full valence multireference configuration interaction (MRCI) treatment. These potentials provide very good agreement between the experiment and the theory regarding spectroscopic constants, photo-double-ionization spectra, and band origins of the vibrational progressions of several quasibound electronic states. Veseth\textsuperscript{21} computed vibrationally resolved partial cross sections for photoionization of CO$^+$ and from these results deduced information on the equilibrium internuclear distance of the CO$^{2+}$ $^3\Pi$ ground state. The spin-orbit couplings (SOC’s) among the three lowest electronic states $X^3\Pi$, $a^1\Sigma^+$, and $b^1\Sigma^-$ of CO$^{2+}$ were calculated by Andersen et al.\textsuperscript{8} as residues of linear response functions of multiconfigurational self-consistent-field (SCF) states.\textsuperscript{22}

Using their \textit{ab initio} data, Andersen et al.\textsuperscript{8} have completed their study by evaluating the electronic predissociation rates of the vibrational levels of the $X^3\Pi$ and a $^1\Sigma^+$ electronic states from the solution of the exterior complex dilated multichannel Schrödinger equation, describing nuclear motion. The same \textit{ab initio} data were also used by Bouhmik et al.\textsuperscript{9} in an approximate evaluation of the sought rates by

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means of the Fermi-Wentzel golden rule formula (the vibrational wave functions used in these calculations were obtained using the log-amplitude-phase method\textsuperscript{23}). Interestingly, the approximate values of the rates were found in close agreement with their “exact” counterparts. Both sets of the theoretical data, however, are in striking disharmony with the experiment. Therefore, aiming to resolve this confusion, we find it desirable to calculate the predissociation rates once again, using a more accurate theoretical procedure and involving a more extended set of electronic states. The required potential energy and spin-orbit coupling functions are evaluated using internally contracted multireference configuration interaction (icMRCI) wave functions. The approximate “one-dimensional” tunneling rates/lifetimes are evaluated using the log-amplitude-phase method,\textsuperscript{23} and the numerically exact (multichannel) predissociation rates/lifetimes accounting for the spin-orbit interactions are calculated using the stabilization\textsuperscript{24–26} and complex-scaling methods.\textsuperscript{27,28} The latter computational approaches have proved to be fairly reliable in our previous treatment of the quasibound states of van der Waals molecules\textsuperscript{29–31} and predissociation resonances of diatomic molecules.\textsuperscript{32} All the mentioned methods are described briefly in Sec. II.

II. COMPUTATIONAL METHODS

A. Potential energy curves and spin-orbit couplings

Ab initio calculations were carried out using the MOLPRO suite of \textit{ab initio} programs.\textsuperscript{33} The atomic orbital basis sets were cc-pVXZ, $X=5, 6$.\textsuperscript{34} The molecular orbitals for the CI treatment of CO$^{2+}$ were obtained in both the one-state and the state-averaged complete-active-space SCF (CASSCF) calculations with equal weights for the participating states of the same spin multiplicity in $C_{2v}$ symmetry. With the cc-pV6Z basis set, the full active space consisted of $1\sigma-6\sigma$, $1\pi$, and $2\pi$ orbitals with all electrons (AE) correlated. This led to a total of 5220 configuration state functions (CSFs) in the $X^1\Pi$, 5154 in the $A^3\Sigma^+$, and, e.g., 5196 in the $3\Sigma^{-}$ state. The PEF’s were calculated using the icMRCI method.\textsuperscript{35,36} The number of uncontracted configurations was about $4.1 \times 10^{5}$–$7.9 \times 10^{5}$. In calculating excitation energies and KER, a generalized Davidson correction\textsuperscript{37} was employed.

For the sake of comparison, some PEF’s of CO$^{2+}$ were calculated, using the spin-restricted coupled cluster method with singles, doubles and a perturbative estimate of triple excitations [RCCSD(T)].\textsuperscript{38,39} The SO integrals were evaluated with the icMRCI wave functions, using the Breit-Pauli operator, as implemented in the MOLPRO code. Due to the limitation of this program, only the $spdf$ orbital subset of the cc-pV5Z basis set with the valence electrons correlated was employed in the SO calculations.

B. Resonance calculations

The energies of vibronic states were obtained by numerical integration of the Schrödinger equation of the system Hamiltonian $\hat{H}$. The positions and lifetimes of the quasibound levels of CO$^{2+}$ were evaluated using three different approaches: the log-amplitude-phase method for solving one-dimensional problems (SO interaction disregarded) and the stabilization and complex-scaling methods based on the coupled treatment of the electronic states by means of SO interaction.

The log-amplitude-phase method of Sidky and Ben-Itzhak\textsuperscript{25} is a modification of the earlier Milne method.\textsuperscript{40} This approach which takes advantage of the oscillatory structure of the wave function provides an efficient way for locating resonances; the local maxima in the energy derivative of a phase are identified as resonance peaks, the resonance widths are calculated from the Breit-Wigner line shape formula.

The stabilization method\textsuperscript{24–26} is based on the fact that the wave functions for resonance states closely resemble the wave functions for bound states. The energies of resonance states are stable when a basis set parameter, e.g., the dissociative coordinate $R$, is varying. In contrast, the energies associated with the nonresonant states increase monotonically as $R$ decreases. So the key idea of the boxing variant of the method is a repeated diagonalization of an appropriate Hamiltonian $\hat{H}$ in a series of enclosing boxes with their varying box size $R$: $R_0=R\leq R_0+\Delta R$. Plots of the eigenfunction of the Hamiltonian $E(R)$ as a function of $R$ are known as the stabilization diagram.

The primary result of this method is an average density of states $\rho(E)$, from which the resonance energies and widths can be determined by the Lorentzian fitting. The average density of states was evaluated as

$$\rho(E) = -\frac{1}{\Delta R} \sum_n \left( \frac{dE_n(R)/dR}{|E_{n}-E|} \right)^{-1}.$$  

The total phase shift $\phi(E)$ has been obtained from the stabilization diagram using the formula

$$\phi(E) = \sum_n \phi_n(E),$$

where $\phi_n$ is the contribution from the $n$th eigenvalue $E_n(R)$ defined by

$$\phi_n(E) = \begin{cases} 
0 & \text{for } E < E_n(R + \Delta R) \\
\pi \frac{R + \Delta R - R_n(E)}{\Delta R} & \text{for } E_n(R + \Delta R) < E < E_n(R) \\
1 & \text{for } E > E_n(R), 
\end{cases}$$

where $R$ is the current size of the coordinate box and $R_n(E)$ is a function obtained using the numerical inversion of $E_n(R)$. Using the Breit-Wigner formula, the resonance energies and widths have been obtained by fitting $\phi(E)$ near a resonance energy to

$$\phi(E) = \arctan \left( \frac{2(E - E_{\text{res}})}{\Gamma_{\text{res}}} \right) + \phi_b(E),$$

where $E_{\text{res}}$ and $\Gamma_{\text{res}}$ are the energy and the width of the resonance and $\phi_b(E)$ is the background term. The width of a metastable state is related to its lifetime through the uncertainty relationship $\tau = \hbar/\Gamma$. 

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In the complex-scaling method, the sought resonance characteristics are obtained from complex eigenvalues of a complex-scaled Hamiltonian. The advantage of this method is that the resonance solutions are square integrable, so the Schrödinger equation can be solved by bound-state techniques. The complex-scaled Hamiltonian \( \hat{H}_\theta(x) \) is obtained from the physical Hamiltonian \( \hat{H}(x) \) by complex scaling of the coordinate \( x \), such that \( \hat{H}_\theta(x) = \hat{H}(xe^{i\theta}) \), where \( \theta \) is a complex-scaling parameter \( 0 \leq \theta < \pi/4 \). The complex-scaled Hamiltonian for the \( \text{CO}_2^+ \) dissociation is obtained by the complex transformations of the kinetic energy operator, potential, and SO coupling, such that

\[
\hat{H}_\theta(x) = -e^{-2\mu} \frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + V(xe^{i\theta}),
\]

with approach that the potentials are coupled between each other by the SO operator. The complex transformations of SO coupling is straightforward also as \( \hat{C}_\theta(x) = C(xe^{i\theta}) \). Resonances are obtained as solutions of \( \hat{H}_\theta(x) \) and are characterized by \( \theta \)-independent complex eigenvalues. The complex resonance eigenvalues,

\[
\epsilon = E_{\text{res}} - \frac{i}{2} \Gamma_{\text{res}},
\]

define the resonance positions \( E_{\text{res}} \) and widths \( \Gamma_{\text{res}} \), respectively. Resonance states appear in the spectrum of \( \hat{H}_\theta(x) \) for \( \theta \) being larger than a critical value given by

\[
\theta_c = \frac{1}{2} \arctan \left( \frac{\Gamma_{\text{res}}}{2E_{\text{res}}} \right).
\]

The eigenfunctions and eigenvalues of \( \hat{H}_\theta(x) \) are obtained in a finite box using a Fourier basis set. Resonance eigenvalues are obtained in the finite basis set as the stationary points with respect to variation of the scaling parameter,

\[
\frac{\partial E_{\text{res}}}{\partial \theta} \bigg|_{\theta_{\text{stat}}} = \frac{\partial \Gamma_{\text{res}}}{\partial \theta} \bigg|_{\theta_{\text{stat}}} = 0.
\]

In order to enable the construction of the complex-scaled Hamiltonian [Eq. (5)], the potential energy \( V(x) \) and SO coupling \( C(x) \) are represented by analytical functions which allow for their analytical continuation to the complex plane \( x \rightarrow xe^{i\theta} \). The potential and SO coupling Hamiltonian matrices are calculated using a discrete variable representation.

### III. RESULTS AND DISCUSSION

The PEF’s of the ground and eight excited electronic states of \( \text{CO}_2^+ \), calculated at the icMRCI/cc-pV6Z/1AE level, are displayed in Fig. 1. Qualitatively, it is a very similar picture to that given in Ref. 20. Moreover, it includes the repulsive \( ^3\Delta \) and the quasibound \( ^1\Sigma^+ \) states. For most states considered, we have been able to calculate the PEF’s in the range \( 1.7 \leq R \leq 10.2 \) bohrs. The spectroscopic constants derived from these PEF’s are very similar to those of Eland et al., obtained by the same method with all valence electrons correlated. For all states, our equilibrium internuclear distances are slightly lower (by about 0.002–0.009 Å) than those in Ref. 20. It should be noted that Veseth deduced (using the many-body calculations) the equilibrium internuclear distance of 1.238 Å for the ground state \( ^3\Pi \) of \( \text{CO}_2^+ \) from photoionization cross sections of \( \text{CO}^+ \); this value is very close to the icMRCI/V6Z/1AE and RCCSD(T)/V6Z/1AE results, 1.2392 and 1.2377 Å, respectively. Our harmonic frequencies are by about 10–35 cm\(^{-1}\) higher than the previous theoretical values with an exception of the \( d^1\Sigma^+ \) state having the double-minimum potential with lower frequency for the outer potential well, \( \omega_{\text{co}} = 1099.3 \) cm\(^{-1}\), comparing with 1125.6 cm\(^{-1}\) of Eland et al. All the calculated spectroscopic constants are presented in Table A in the supplementary material.

The quality of the computational treatment can also be assessed by a comparison of the computed band origins for the vibrational progressions of several electronic states of \( \text{CO}_2^+ \) (excitation energies from the CO ground state) with the previously reported experimental and theoretical data (see Table I). The agreement of our icMRCI+Q values with the TOF-PEPECO data seems to be even slightly better than that obtained by Eland et al. for their unshifted theoretical values. Another important quantity which can be compared with the experiment and used to characterize the decay mechanism is the kinetic energy released upon unimolecular dissociation of \( \text{CO}_2^+ \). In this connection, it is noteworthy that only the ground state \( ^3\Pi \) and the purely repulsive \( ^3\Sigma^- \) state have the lowest common asymptotic atomic limit \( C^+(2P_u) + \text{O}^+(4S_a) \). Using the one-state calculation of the \( X^3\Pi \) state at the icMRCI+Q/V6Z/1AE level of theory, we have been able to obtain energies of up to \( R=250 \) bohrs. An extrapolation to infinity was performed using an assumed \( 1/R \) functional form. For the (\( X^3\Pi, v=2 \)) (\((a^1\Sigma^+, v=1),(b^3\Pi, v=1 \)) and \((a^3\Sigma^+, v=0 \)) states, we obtained \( E_2=5.654, 5.711, 5.829, \) and 7.802 eV, which are in very good agreement with the experimental data of Lundqvist et al., 5.655, 5.713, 5.841, and 7.833 eV, respectively. It should be mentioned that the experimental KER value \( E_2=5.713 \) eV, originally associated with the \( a^1\Sigma^+, v=0 \) state, was later reassigned by Hochlaf et al. to the \( v=1 \) state.
TABLE I. Band origins for vibrational progressions of the CO$^{2+}$ dication determined from experiment and ab initio calculations. The energy zero in the calculations is the X$^1\Sigma^+$, v=0, J=0 state of CO. The data are in eV.

<table>
<thead>
<tr>
<th></th>
<th>X$^1\Pi$</th>
<th>a$^1\Sigma^+$</th>
<th>b$^1\Pi$</th>
<th>A$^3\Sigma^+$</th>
<th>d$^1\Sigma^+$</th>
<th>e$^1\Delta$</th>
<th>e$^1\Sigma^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPE-DCO$^a$</td>
<td>41.294±0.01</td>
<td>41.500$^b$</td>
<td>41.814</td>
<td>43.826$^c$</td>
<td>45.480</td>
<td>45.480</td>
<td></td>
</tr>
<tr>
<td>DFKER$^d$</td>
<td>41.300$^e$</td>
<td>41.490$^f$</td>
<td>41.818</td>
<td>43.810</td>
<td>45.470</td>
<td>45.470</td>
<td></td>
</tr>
<tr>
<td>TPE-DCO$^g$</td>
<td>41.324±0.01$^h$</td>
<td>41.525±0.01</td>
<td>41.847±0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOF-PEPICO$^i$</td>
<td>41.275±0.03</td>
<td>41.438±0.02</td>
<td>(41.780)</td>
<td>43.799±0.03</td>
<td>45.461±0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DCT$^j$</td>
<td>41.52±0.05</td>
<td></td>
<td></td>
<td></td>
<td>45.51±0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eland et al.$^k$</td>
<td>41.064</td>
<td>41.252</td>
<td>41.585</td>
<td>43.622</td>
<td>45.434</td>
<td>43.581</td>
<td></td>
</tr>
<tr>
<td>icMRCI+Q/AE$^l$</td>
<td>42.229</td>
<td>41.370$^m$</td>
<td>41.749</td>
<td>43.722</td>
<td>45.343</td>
<td>43.590</td>
<td>46.899</td>
</tr>
</tbody>
</table>

$^a$Reference 12.
$^b$The reassignment suggested in Ref. 11 was used. (The vibration sequence begins one quantum lower than originally assigned in Ref. 12). The position of the v=0 level has been calculated using $\omega_v$ and $\omega_{vJ}$ of Ref. 11.
$^c$The reassignment suggested in Ref. 7 was used. The original value presented in Ref. 12 was 43.573 eV.
$^d$Reference 7.
$^e$The v=2 level was observed. E(v=0) has been calculated by subtracting the TPEsCO separation (Ref. 12) from E(v=2).
$^f$The value reassigned by Hochlaf et al. (Ref. 11). The position of the v=0 level has been calculated using $\omega_v$ and $\omega_{vJ}$ of Ref. 11.
$^g$Reference 11.
$^h$E(v=0) calculated from E$_v$ using the formula $E(0)=E_v+\omega_v/2-\omega_{vJ}/4$ with the data given in Table 2 of Ref. 11. See also Ref. 6.
$^i$Reference 13.
$^j$Reference 14.
$^k$Reference 20. Unshifted values.
$^l$All electrons correlated in the CASSCF/icMRCI+Q calculations. The energies of the X$^1\Pi$, b$^1\Pi$, and A$^3\Sigma^+$ states obtained using the one-state calculations.
$^m$The one-state icMRCI+Q calculation yields the value 41.394 eV.

The SO couplings among the six lowest dicationic states X$^1\Pi$, a$^1\Sigma^+$, b$^1\Pi$, X$^3\Sigma^-$, A$^3\Sigma^+$, and e$^1\Delta$ as a function of internuclear distance are displayed in Fig. 2 (some spin-orbit matrix elements are zero due to symmetry). The most striking feature of these interactions is the R dependence of the matrix element connecting the $^3\Sigma^-$ and $^1\Sigma^+$ states, which is by far the largest in the range 3.2< R < 4.6 bohrs. In the limited interval of the internuclear C–O separations, similar behavior has also been found by Andersen et al. By contrast, the SO a$^1\Sigma^+$–X$^3\Pi$ and X$^3\Sigma^-$–X$^3\Pi$ interactions calculated using the icMRCI method differ from those of Andersen et al., although the (global) minimum of the former SO curve lies at a similar internuclear distance (~3 bohrs).

The tunneling (one dimensional) widths of the vibrational levels supported by the quasibound adiabatic potentials were calculated using the log-phase-amplitude method of Sidky and Ben-Itzhak. For the X$^1\Pi$, a$^1\Sigma^+$, b$^1\Pi$, and A$^3\Sigma^+$ states, these data are very close to the previously reported values of Eland et al. Our calculations show that both the extension of the basis set (V5Z→V6Z) and the inclusion of all electrons into correlation mostly decreases the width of the vibrational states. These results confirm the well-known fact that tunneling lifetimes are extremely sensitive to the basis set and the details of the potential. The tunneling lifetimes for some lower vibrational levels of the c$^1\Delta$, d$^1\Sigma^+$, and e$^1\Sigma^+$ states (cf. Table II) are long enough for tunneling through the potential barrier to be partly responsible for the dissociation of CO$^{2+}$ from these states. However, as noted by Larsson et al., it is difficult to populate the low-lying vibrational levels due to the long-range bonding nature of the c$^1\Delta$ state. For the d$^1\Sigma^+$ state, the tunneling lifetimes are supposed to be of the same order of magnitude as the electronic predissociation rates. However, it should be kept in mind that for quasibound electronic states, where the spin-orbit induced predissociation is possible, the tunneling widths represent lower bounds to real widths. For the e$^1\Sigma^+$ state, the tunneling mechanism could play a role in a predissociation dynamics, since the SOC

TABLE II. Tunneling widths (in cm$^{-1}$) for the vibrational levels of the c$^1\Delta$, d$^1\Sigma^+$, and e$^1\Sigma^+$ electronic states of CO$^{2+}$. Only widths greater than 10$^{-16}$ are shown.

<table>
<thead>
<tr>
<th>v</th>
<th>c$^1\Delta$</th>
<th>d$^1\Sigma^+$</th>
<th>e$^1\Sigma^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.779×10$^{-20}$</td>
<td>2.303×10$^{-16}$</td>
<td>3.380×10$^{-24}$</td>
</tr>
<tr>
<td>2</td>
<td>1.755×10$^{-15}$</td>
<td>1.309×10$^{-9}$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.161×10$^{-11}$</td>
<td>1.350×10$^{-16}$</td>
<td>8.349×10$^{-4}$</td>
</tr>
<tr>
<td>4</td>
<td>1.258×10$^{-7}$</td>
<td>1.020×10$^{-9}$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3.062×10$^{-4}$</td>
<td>1.481×10$^{-5}$</td>
<td>16.00</td>
</tr>
<tr>
<td>6</td>
<td>2.585×10$^{-1}$</td>
<td>2.644×10$^{-2}$</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>26.49</td>
<td>9.276</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Tunneling through the outer barrier is calculated.

FIG. 2. Spin-orbit couplings between the six lowest electronic states of CO$^{2+}$. dication.
integrals between the $e^1\Sigma^+$ and $3\Delta$ states are zero due to symmetry. As can be seen from Table II, the tunneling lifetimes for the $v = 2$ and $3$ vibrational states are of the order of milliseconds and nanoseconds, respectively.

The real (multichannel) linewidths were obtained by solving the system of the coupled channel Schrödinger equations,

$$\frac{d^2 y(R)}{dR^2} = [V(R) - E\mathbf{I}]y(R), \tag{9}$$

where the diagonal and off-diagonal elements of the potential energy matrix $V(R)$ consist of the adiabatic potential energy functions (Fig. 1) and the SO interactions (Fig. 2), respectively, $y(R)$ is a column vector, and $\mathbf{I}$ is the unity matrix. To get fully converged results for the observed states, the six lowest electronic states $X^1\Pi$, $a^1\Sigma^+$, $A^1\Sigma^-$, $b^1\Pi$, $c^1\Delta$, and $A^3\Sigma^+$ had to be involved.

In the actual stabilization calculations, $R_0$ was fixed at 1.7 bohr, $R$ was varied from 1.7 to 6.1 bohrs by the increment of 0.001 bohr, and Eq. (9) was solved using the renormalized Numerov method.\cite{12} The calculated positions and lifetimes of the probed states are collected in Tables III and IV. A typical detail of the global stabilization diagram and the corresponding density of states are illustrated in the supplementary material\cite{41} by Figs. A and B, respectively.

The complex-scaling calculations were performed using polynomially smoothed potential and SO coupling functions (see Eqs. A and B and Tables B and C in the supplementary material).

### Table III. Energy positions in cm$^{-1}$ of the lowest vibronic resonances of CO$_2^+$.\(^\text{11,12}\)

<table>
<thead>
<tr>
<th>State</th>
<th>$v$</th>
<th>Reference 11(^a)</th>
<th>Reference 12(^b)</th>
<th>Stabilization method</th>
<th>Complex scaling</th>
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</thead>
<tbody>
<tr>
<td>$X^1\Pi$</td>
<td>0</td>
<td>677.1</td>
<td>806.7</td>
<td>732.7</td>
<td>732.5</td>
</tr>
<tr>
<td></td>
<td>1</td>
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<td>2258.3</td>
<td>2138.8</td>
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<td></td>
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<td>3484.3</td>
<td>3550.2</td>
<td>3549.5</td>
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<tr>
<td></td>
<td>3</td>
<td>4553.4</td>
<td>...</td>
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<td>4884.5</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>5774.5</td>
<td>...</td>
<td>6168.9</td>
<td>6168.9</td>
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<tr>
<td></td>
<td>5</td>
<td>6960.2</td>
<td>...</td>
<td>7401.5</td>
<td>7401.6</td>
</tr>
<tr>
<td>$a^1\Sigma^+$</td>
<td>0</td>
<td>2298.7</td>
<td>...(^d)</td>
<td>2175.0</td>
<td>2169.6</td>
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<tr>
<td></td>
<td>1</td>
<td>3911.9</td>
<td>4081.1</td>
<td>4062.5</td>
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<td></td>
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<td>5524.9</td>
<td>6000.7</td>
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<td></td>
<td>3</td>
<td>7138.0</td>
<td>7670.3</td>
<td>7784.6</td>
<td>7759.0</td>
</tr>
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<td>4891.8</td>
<td>5000.6</td>
<td>5030.6</td>
<td>5030.8</td>
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<td>6512.6</td>
<td>6511.4</td>
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<tr>
<td></td>
<td>2</td>
<td>7617.9</td>
<td>8009.1</td>
<td>7960.8</td>
<td>7959.0</td>
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</table>

\(^a\)Obtained from the values in Table 2 of Ref. 11 using the formula $E(v) = E_0 + \omega_v(v + 1/2) - \omega_x(v + 1/2)^2$.
\(^b\)The energy zero is $E_0 \left(X^1\Pi\right)$.
\(^c\)Calculated from the values in Table 3 and $E_0$ (Table 4) of Ref. 12.
\(^d\)Experimental data reassigned by Hochlaf et al. (Ref. 11).

### Table IV. Lifetimes $\tau$ (\(\mu\)s) of the lowest vibronic resonances of CO$_2^+$.\(^\text{11,12}\)

<table>
<thead>
<tr>
<th>$v$</th>
<th>DFKER (Ref. 7)</th>
<th>SR (Ref. 8)</th>
<th>DP(^a) (Ref. 6)</th>
<th>TDFI (Ref. 9)</th>
<th>Theory (Ref. 8)</th>
<th>Theory (Ref. 9)</th>
<th>Stabilization method</th>
<th>Complex scaling</th>
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<tr>
<td>$3\Pi$ state</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>$\geq 3$</td>
<td>$&gt;3.8 \times 10^6$</td>
<td>$\geq 10$</td>
<td>$2 \times 10^6$</td>
<td>$0.77 \times 10^4$</td>
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<td>$&gt;10$</td>
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<td>1</td>
<td>$&gt;3$</td>
<td>$8 \times 10^{18}$</td>
<td>$&gt;10$</td>
<td>0.3</td>
<td>0.17</td>
<td>$&gt;10$</td>
<td>$&gt;10$</td>
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<tr>
<td>2</td>
<td>$&lt;0.1$</td>
<td>0.2 $\pm$ 0.1</td>
<td>(0.32 $\pm$ 0.22)</td>
<td>0.29 $\times$ 10$^{-3}$</td>
<td>0.61</td>
<td>3.9</td>
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<tr>
<td>4</td>
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<td>0.72$^{0.02}_{0.01}$</td>
<td>0.67 $\pm$ 0.05</td>
<td>1.3 $\times$ 10$^{-3}$</td>
<td>8.8 $\times$ 10$^{-3}$</td>
<td>0.67</td>
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<td>15 $\times$ 10$^{-2}$</td>
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<tr>
<td>5</td>
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<tr>
<td>$a^1\Sigma^+$ state</td>
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<td>1.3 $\times$ 10$^{-3}$</td>
<td>8.8 $\times$ 10$^{-3}$</td>
<td>0.67</td>
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<td>15 $\times$ 10$^{-2}$</td>
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<tr>
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<td>8.7 $\times$ 10$^{-4}$</td>
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<tr>
<td>$b^1\Pi$ state</td>
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</tr>
<tr>
<td>0</td>
<td>&lt;0.1</td>
<td>0.2$^{0.15}_{0.2}$</td>
<td>0.026 $\pm$ 0.005</td>
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<td>&lt;0.1</td>
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<td></td>
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<tr>
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<td>&lt;0.1</td>
<td>&lt;0.1</td>
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</tbody>
</table>

\(^a\)The data were taken with $^{13}$C$^{16}$O$_2^+$.\(^b\)Tentatively assigned by Hochlaf et al. (Ref. 11).
The calculated vibrational energies of the probed ($X^3\Pi$, $a^1\Sigma^+$, and $b^1\Pi$) electronic states are not compared with the experimental values of Hochlaf et al.\textsuperscript{11} and Dawber et al.\textsuperscript{12} It can be seen that for the majority of states the calculated vibrational energies obtained by both theoretical methods differ very slightly and lie between the respective experimental data.

The main result of this study, i.e., the lifetimes of the vibrational states of the lowest electronic states, is reported and compared with the experimental and other theoretical data in Table IV. It should be noted that both the stabilization and complex-scaling methods can provide accurate estimates only for lifetimes shorter than 10 $\mu$s. Yet, it is still possible to deduce from the calculations that the $X^3\Pi$, $v=0$ and $v =1$ levels are the only quasistable levels with lifetimes of much longer than 10 $\mu$s. This qualitative result is in good agreement with the limit $\tau>3.8$ s, determined by means of a heavy ion storage ring\textsuperscript{8} and with $\tau=0.8$ ms measured by Andersen et al.\textsuperscript{8} and reassigned by Hochlaf et al.\textsuperscript{11} respectively. The lifetime $\tau(X^3\Pi, v=2)=0.61$ $\mu$s obtained using the more accurate stabilization method compares favorably with $\tau=0.2\pm0.1$ ms which relied upon double photoionization using synchrotron radiation\textsuperscript{9} and $0.32\pm0.22$ $\mu$s determined using the 3D-image imaging technique.\textsuperscript{9} For this vibrational state, the complex scaling yields a somewhat higher value (3.9 $\mu$s). The lifetime of higher vibrational levels decreases dramatically as their energy increases. The computed values for $v=3$ and 4 states are consistent with the experimental upper bounds determined by the DFKEER spectroscopy\textsuperscript{7} and the double photoionization.\textsuperscript{8} On the contrary, the theoretical estimates obtained by Larsson et al.\textsuperscript{15} Andersen et al.\textsuperscript{8} and Bouhnik et al.\textsuperscript{9} are in a profound disharmony with experiment.

For the $a^1\Sigma^+$, $v=0$ state, our computed lifetimes are again much longer than 10 $\mu$s, being in accord with $\tau =6$ ms measured by Andersen et al.\textsuperscript{8} and reassigned by Hochlaf et al.\textsuperscript{11} Among all studied vibronic states of CO$^2+$, the most information is reported for the $v=1$ ($a^1\Sigma^+$) vibrational state. The experimental values range from 0.6 to 0.7 $\mu$s. The stabilization method gives a lifetime of 0.67 $\mu$s, which is, fortuitously, the same as that based on the simultaneous measurement of kinetic energy release and lifetime by Bouhnik et al.\textsuperscript{9} The complex-scaling procedure again leads to a higher value (5 $\mu$s) than the stabilization method.

In the case of the $b^1\Pi$, $v=0$ state the precise value of 0.026$\pm$0.005 $\mu$s is provided by Bouhnik et al.\textsuperscript{9} The double photoionization method yields a much higher value, 0.20$\pm$0.15 $\mu$s. However, the corresponding error bars are rather high. As a matter of fact, our theoretical estimates are even larger (8.3 and 23 $\mu$s), being thus the only data of this study which are in a factual disharmony with experiment. Similarly to the $X^3\Pi$ and $a^1\Sigma^+$ states, the lifetimes for higher vibrational levels rapidly decrease as their energy increases.

The most striking feature governing the decay and dynamics of the low-lying vibrational states is the crossing of the PEC’s of the respective quasibound states by that of the purely repulsive $3\Sigma^-$ state. For the three lowest electronic states $X^3\Pi$, $b^1\Pi$, and $a^1\Sigma^+$, the crossing points lie at $R \approx 2.8, 2.6$, and 2.7 bohrs, respectively. In this region, at about $R \approx 2.7$ bohrs, the values of the spin-orbit coupling integrals $\langle X^3\Pi, m_s=1|L_sS_s|3\Sigma^-, m_s=0\rangle$, $\langle b^1\Sigma^+, m_s=0|L_sS_s|3\Sigma^-, m_s=1\rangle$ are similar; they range between 22 and 28 cm$^{-1}$. However, the second integral begins to rise sharply with increasing $R$ and at about 3.6 bohrs it reaches its highest value of 136 cm$^{-1}$. Whereas the $X^3\Pi$, $b^1\Pi$, and also $A^1\Sigma^+$ and $d^1\Sigma^+$ states predissociate directly by the spin-orbit coupling with the $3\Sigma^-$ state, the excited $a^1\Sigma^+$ state decays mainly by indirect predissociation\textsuperscript{45} because of mixing between the $X^3\Pi$ and $a^1\Sigma^+$ states.\textsuperscript{8,9} This is supported by the fact that the $a^1\Sigma^+$, $v=0$ and $X^3\Pi$, $v=1$ states, located near the crossing point, are almost degenerate and also by the relatively large value of the SO matrix element $\langle X^3\Pi, m_s=1|L_sS_s|a^1\Sigma^+, m_s=0\rangle$ ($\approx 33$ cm$^{-1}$) in the crossing region. It is high enough to allow such predissociation.

Summarizing, we have obtained the first complete consistent sets of the theoretical lifetimes for 13 low-lying vibronic states of the CO$^2+$ dication. The spin-orbit induced lifetimes calculated by the stabilization method are in reasonable agreement with the experimental data in contrast to the theoretical lifetimes reported earlier.

IV. CONCLUSIONS

The CASSCF/icMRCI wave functions were used to calculate the potential energy curves and spin-orbit couplings of the CO$^2+$ dication. These results were employed in calculating the positions and lifetimes of the vibrational states of the $X^3\Pi$, $a^1\Sigma^+$, and $b^1\Pi$ electronic states using the stabilization, complex-scaling, and log-amplitude-phase methods. The first two approaches taking into account spin-orbit interaction yielded lifetimes in qualitative accord with the experimental data, the stabilization method even in a semi-quantitative agreement. While the lowest vibrational levels ($v=0$) of the $X^3\Pi$, $a^1\Sigma^+$, $b^1\Pi$, and $A^1\Sigma^+$ states are practically stable against tunneling dissociation, the tunneling lifetimes for some of the lower vibrational levels ($3 \leq v \leq 7$) of the $c^1\Delta$, $d^1\Sigma^+$, and $e^1\Sigma^+$ states have the tunneling lifetimes ranging between seconds and nanoseconds. However, the calculated lifetimes confirm that the spin-orbit induced predissociation is a dominant decay mechanism for CO$^2+$.
ACKNOWLEDGMENTS

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33 H.-J. Werner, P. J. Knowles, R. Lindh et al., MOLPRO Version 2002.6, a package of ab initio programs, 2003; see http://www.molpro.net.
41 See EPAPS Document No. E-JCPA6-124-008618 for the results comprising a complete set of the spectroscopic constants of the probed electronic states and details illustrating the stabilization and complex-scaling procedures used in the present study. This document can be reached via a direct link in the online article’s HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).