# Rovibronic states of $\mathrm{CO}^{++}$ Spin-orbit predissociation and tunneling 

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## I. INTRODUCTION

## Facts motivating the study:

- Two articles appeared in 2018, in $\mathrm{JCP}^{1}$ and $\mathrm{PRL}^{2}$, presenting experiments on threebody fragmentation of the $\mathrm{OCS}^{3+}$ ion and a novel method of their analysis which allows for a complete separation of three pathways of the fragmentation process. In one of the pathways, the process goes via formation of the $\mathrm{CO}^{2+}$ ions at the first step and auto-dissociation of these intermediate ions at the second step. The papers provide information on this sequential pathway in the form of kinetic-energy-release (KER) spectra, i.e. distributions of kinetic energy of relative motion among the $\mathrm{C}^{+}+\mathrm{O}^{+}$fragments arising at the second step. The spectra may have contributions of a multitude of different rovibronic states in which the $\mathrm{CO}^{2+}$ ions may be formed at the first step. Reliable explanation of the KER spectra seems hardly possible without prior knowledge of basic characteristics of the rovibronic states, such as energies and dissociative lifetimes.
- Calculations on the $\mathrm{CO}^{2+}$ ion reported thus far were concentrated on purely vibronic states. In two calculations only, rotation was also taken into account when characterizing predissociation of the ion. However, energies and predissociation lifetimes of as few as 45 rovibronic states were only determined in Ref. 3, and not much more, about 400 states of two isotopomers, ${ }^{12} \mathrm{C}^{16} \mathrm{O}$ and ${ }^{13} \mathrm{C}^{16} \mathrm{O}$, in total, were characterized in Ref. 4.


## Goals:

- Performing calculations necessary to determine all rovibronic states of the $\mathrm{CO}^{2+}$ ion supported by the available electronic energy potentials ${ }^{5,6}$ in the lifetime range limited only from below (to 0.5 ps ), accounting for spin-orbit predissociation and tunneling, and branching in the predissociation between different available $\mathrm{C}^{+}+\mathrm{O}^{+}$channels.
- Performing simulations of the kinetic-energy-release spectra from different sub-sets of the determined rovibronic states; comparing them with the experimental spectra mentioned above; possibly, identifying (group of) states which have a role in forming the most discernible features of these spectra.


## II. MODEL

The model of dynamics of the $\mathrm{CO}^{++}$ion exploited in the present calculations is, apart from some necessary extensions, the same as the JP04r-v model constructed in Ref. 4 for an introductory characterization of rovibronic states of this ion. The dynamics is described with the use of Hamiltonian matrices $\mathbf{H}^{J p}=\left\{H_{s_{\Omega}, \tilde{s}_{\Omega^{\prime}}}^{J p}\right\}$ for $J=0,1, \ldots$ and $p=+1,-1 \Leftrightarrow e, f$ in the form of differential operators with respect to the internuclear distance $r$,

$$
\mathbf{H}^{J p}(r)=\frac{1}{2 \mu} \mathbf{p}_{r}^{2}+\mathbf{V}^{J p}(r) \quad \text { with } \quad \mathbf{p}_{r}:=-\imath \mathbf{I} \frac{d}{d r}
$$

Of the indices enumerating the matrices, $J$ is the quantum number of the total angular momentum operator squared $\mathbf{J}^{2}$ and $p$ is the total parity label. $\mathbf{J}$ is the sum of the total electronic angular momentum, the total electronic spin, and the nuclear rotation operators, $\mathbf{L}, \mathbf{S}$, and $\mathbf{R}$, respectively. The index $s_{\Omega}$ enumerating the elements of the Hamiltonian matrices is composed of the quantum numbers $S, \Lambda$, and $\Omega$ which are associated with $\mathbf{S}^{2}$ and with projections on the internuclear axis of $\mathbf{L}$ and $\mathbf{J}$, respectively; $s:={ }^{2 S+1} \Lambda^{\epsilon}$ identifies the electronic state (spin multiplet), and $\Omega$ - the multiplet component. $\epsilon=+/-$ indicates the definite parity of the electronic part of the state when $\Lambda=0$. Seven lowest states of the ion, $s=X^{3} \Pi,{ }^{3} \Sigma^{-}, a^{1} \Sigma^{+}, b^{1} \Pi, A^{3} \Sigma^{+}, c^{1} \Delta$, and $d^{1} \Sigma^{+}$, are accounted for. The first term of the matrices $\mathbf{H}^{J p}(r)$, with $\mu$ being the reduced mass of the ion, represents the vibrational part of the nuclear kinetic energy operator. For the ${ }^{12} \mathrm{C}^{16} \mathrm{O}^{2+}$ isotopomer considered here, $\mu=12497.592 m_{e}$. The matrices $\mathbf{V}^{J p}(r)$ are formed of: the electronic energy potentials $V_{s}(r)$ of the included states which have been determined in Ref. 5, the spin-orbit couplings $V_{s, \tilde{s}}(r)$ between them determined in Ref. 6, the spin-orbit 'constant' for the state ${ }^{3} \Pi$ determined in Ref. 7, and some terms originating from the rotational part $\frac{1}{2 \mu r^{2}} \mathbf{R}^{2}$ of the nuclear kinetic energy operator. The latter are the rotational energies $E^{J}\left(s_{\Omega} ; r\right)$ and the intra-multiplet interactions $C_{\Omega, \Omega \pm 1}^{J p}(s ; r)$ known $^{8}$ as the $\mathbf{S}$ uncoupling perturbations. Full details can be found in Ref. 4 and in Supplementary Material.

The rovibronic states of the ion are treated as Siegert states ${ }^{9}$ of the Hamiltonians $\mathbf{H}^{J p}$ which correspond to resonances, i.e. to energies $\mathcal{E}_{n}^{J p}=E_{n}^{J p}-\frac{\imath}{2} \Gamma_{n}^{J p}$ with $E_{n}^{J p}>0, \Gamma_{n}^{J p}>0$, and $\Gamma_{n}^{J p} \ll E_{n}^{J p}$. Thus, the states are determined as solutions of the following eigenvalue problem

$$
\begin{align*}
& {\left[\mathcal{E} \mathbf{I}-\mathbf{H}^{J p}(r)\right] \boldsymbol{\Psi}^{J p}(r ; \mathcal{E})=0}  \tag{1}\\
& \boldsymbol{\Psi}^{J p}(0 ; \mathcal{E})=0  \tag{2}\\
& \left(\phi \mid \mathbf{B}^{+J p}\left(r_{\infty}, \mathcal{E}\right) \boldsymbol{\Psi}^{J p}(\mathcal{E})\right)=0 \tag{3}
\end{align*}
$$

The latter condition enforces on $\Psi^{J p}(r ; \mathcal{E})$ a purely outgoing-wave behavior in the asymptotic region by means of the Bloch operator ${ }^{10}$,

$$
\begin{equation*}
\mathbf{B}^{+J p}\left(r ; r_{\infty}, \mathcal{E}\right)=\delta\left(r-r_{\infty}\right)\left[\mathbf{p}_{r}+\imath \mathbf{L}_{O^{+}}^{J p}\left(r_{\infty} ; \mathcal{E}\right)\right], \tag{4}
\end{equation*}
$$

in which $\mathbf{L}_{O^{+}}^{J p}\left(r_{\infty} ; \mathcal{E}\right)$ is the log-derivative matrix on the out-going waves at $r=r_{\infty}$, where $r_{\infty}$ is a value large enough for $\mathbf{V}^{J p}(r) \approx \operatorname{diag} \mathbf{V}^{J p}(r)$ at $r \geq r_{\infty} . \phi$ is a vector of arbitrary functions and $(\phi \mid \psi)$ denotes the integral $\int_{0}^{\infty} \phi^{\dagger}(r) \psi(r) d r$. The matrix $\mathbf{L}_{O^{+}}^{J p}\left(r_{\infty} ; \mathcal{E}\right)$ is taken here in a WKB form,

$$
\begin{equation*}
\mathbf{L}_{O^{+}}^{J p}\left(r_{\infty} ; \mathcal{E}\right)=\imath \mathbf{k}^{J p}\left(r_{\infty} ; \mathcal{E}\right)-\frac{1}{2} \frac{d}{d r} \ln \mathbf{k}^{J p}\left(r_{\infty} ; \mathcal{E}\right) \tag{5}
\end{equation*}
$$

where $\mathbf{k}^{J p}\left(r_{\infty} ; \mathcal{E}\right)$ is a diagonal matrix built of the wave-number functions $k_{s_{\Omega}}^{J p}(r ; \mathcal{E})=\left[2 \mu \mathcal{E}-2 \mu V_{s_{\Omega}, s_{\Omega}}^{J p}(r)\right]^{1 / 2}$ with $\operatorname{Im} k_{s_{\Omega}}^{J p}<0(>0)$ for $\operatorname{Re}[\ldots]>0(<0)$.

Obviously, $E_{n}^{J p}, \Gamma_{n}^{J p}$, and $\boldsymbol{\Psi}^{J p}\left(r ; \mathcal{E}_{n}^{J p}\right):=\boldsymbol{\Psi}^{n J p}(r)$ are, respectively, the energy, the energy width, and the vector of radial functions of $2 J+1$ degenerate rovibronic states $n J M p$, with $M=-J, \ldots, J$ being the magnetic quantum number associated with $\mathbf{J}$. The formal index $n$ can be replaced with approximate quantum numbers $s_{\Omega}$ and $v$, the former being the label of dominating component of $\Psi^{n J p}(r)$ and the latter characterizing the oscillatory $r$ dependence of this component. Alternatively, the symbol $F_{i}$ with $i=1, \ldots, 2 S+1$ and the quantum number $N$ of the total angular momentum exclusive of spin are used to label the rotational levels of multiplet states. In cases of the triplet states of interest here the conversion to this labeling is: ${ }^{3} \Pi_{\Omega} J \rightarrow{ }^{3} \Pi F_{3-\Omega} N=J-\Omega+1$ and ${ }^{3} \Sigma_{\Omega}^{+} J p \rightarrow{ }^{3} \Sigma^{+} F_{3+(p-3) \Omega / 2} N=J+1+\frac{p-3}{2} \Omega$.

Of interest are all levels $n J p$ (states $n J M p$ ) obtainable from the model whose widths $\Gamma_{n}^{J p}$ are below $10.6 \mathrm{~cm}^{-1}$, i.e. lifetimes longer than 0.5 ps . In dissociation of the ion from these levels (states), three different fragmentation channels, more precisely, combinations of states of the $\mathrm{C}^{+}$and $\mathrm{O}^{+}$fragments, are possible. The thresholds of the channels, denoted here by $\varepsilon_{c}$ with $c=0,1$, and 2 , are the common asymptotes of the potentials $V_{s}$ of the states $s=X,{ }^{3} \Sigma^{-}, s=a, b, A$, and $s=d$, respectively. The lowest threshold lies ${ }^{11} 5.229 \mathrm{eV}$ below the bottom of the well in the potential $V_{X}$, where zero of energy is placed, and the two higher thresholds are ${ }^{12,13}: \varepsilon_{1}=\varepsilon_{0}+3.325 \mathrm{eV}$, and $\varepsilon_{2}=\varepsilon_{1}+1.7 \mathrm{eV}$. The kinetic energy released (in the centre-of-mass frame) upon dissociation of the ion being in state $n J M p$,

$$
\begin{equation*}
\operatorname{KER}(n J M p)=\sum_{c} p_{c}^{n J p}\left(E_{n}^{J p}-\varepsilon_{c}\right):=\sum_{c} p_{c}^{n J p} e_{c}^{n J p} \tag{6}
\end{equation*}
$$

depends on branching into the accessible fragmentation channels $c, \sum_{c} p_{c}^{n J p}=1$. The determination of the channel population probabilities $p_{c}^{n J p}$ or, equivalently, of the partial widths $\Gamma_{n, c}^{J p}=p_{c}^{n J p} \Gamma_{n}^{J p}$ within the Siegert-quantization formalism ${ }^{14}$ consists in exploitation of the continuity equation for the spatial probability density and probability flux associated with the function $\exp \left(-\imath \mathcal{E}_{n}^{J p} t\right) \Psi^{n J p}(r)$. The formula for $p_{c}^{n J p}$ is

$$
\begin{equation*}
p_{c}^{n J p}=\frac{\left(\mathbf{I}_{c} \boldsymbol{\Psi}^{n J p} \mid \mathbf{C}\left(r_{\infty}\right) \mathbf{I}_{c} \mathbf{\Psi}^{n J p}\right)}{\left(\boldsymbol{\Psi}^{n J p} \mid \mathbf{C}\left(r_{\infty}\right) \mathbf{\Psi}^{n J p}\right)} \tag{7}
\end{equation*}
$$

where $\mathbf{C}\left(r ; r_{\infty}\right)$ represents the flux operator ${ }^{15}$ through the surface $r=r_{\infty}$ (of sphere in the space of relative configurations of the nuclei),

$$
\begin{equation*}
\mathbf{C}\left(r ; r_{\infty}\right)=\frac{1}{2 \mu}\left[\delta\left(r-r_{\infty}\right) \mathbf{p}_{r}+\mathbf{p}_{r} \delta\left(r-r_{\infty}\right)\right] \tag{8}
\end{equation*}
$$

the average of this operator standing in the denominator of Eq. (7) is the total flux through the surface, and the average in the nominator - the flux going into the channel $c$, as $\mathbf{I}_{c}$ sets to zero all components $\Psi_{s_{\Omega}}^{n J p}(r)$ with $s \notin c$. Evaluation of these averages requires only the values of the functions on the surface since their derivatives are specified there by the boundary condition (3), viz.,

$$
\begin{equation*}
\left(\boldsymbol{\Psi}^{n J p} \mid \mathbf{C}\left(r_{\infty}\right) \boldsymbol{\Psi}^{n J p}\right)=\frac{1}{2 \mu \imath} \boldsymbol{\Psi}^{n J p \dagger}\left(r_{\infty}\right) \mathbf{L}_{O+}^{J_{p}}\left(r_{\infty} ; \mathcal{E}_{n}^{J p}\right) \boldsymbol{\Psi}^{n J p}\left(r_{\infty}\right)+\text { h.c. } \tag{9}
\end{equation*}
$$

The problem (1)-(3) was solved numerically for energies and total widths of the rovibronic states with the procedure described in Ref. 4. The extension of the procedure needed for evaluation of the partial widths, consisting mainly in adaptation of some algorithms of the generalized log-derivative method ${ }^{16,17}$, is described in Supplementary Material.

## III. SOME GLOBAL CHARACTERISTICS of THE ROVIBRONIC STATES

The model supports about 22 thousands of resonance levels $n J p$ (above 2 millions of $n J M p$ states) which live longer than the assumed lower limit of 0.5 ps . The range of energy covered by these levels extents from 5.3 to about 13.5 eV above the lowest atomic limit. The maximum value of the number $J$ is 189 . The composite index $n=\left(s_{\Omega} v\right)$ runs over 93 different vibronic states with the maximal value of $v$ being $11,22,22,15,7$, and $(7,2)$ is the states $s=X^{3} \Pi, a^{1} \Sigma^{+}, b^{1} \Pi, A^{3} \Sigma^{+}, c^{1} \Delta$, and the double-well $d^{1} \Sigma^{+}$, respectively. Several histograms are defined here to characterize globally this resonance set

- The energy density of states having lifetimes in a range $\Delta \tau=\left[t_{\text {low }}, t_{\text {high }}\right]$

$$
\begin{equation*}
\rho(E ; \Delta \tau)=\frac{1}{\Delta E} \sum_{i} N_{i}(\Delta \tau) \Theta\left(E_{i}-E\right) \Theta\left(E-E_{i}-\Delta E\right) \tag{10}
\end{equation*}
$$

where $\Theta(x)$ is the Heaviside step function and $N_{i}(\Delta \tau)$ is the number of states with lifetimes in the $\Delta \tau$ and energy in the interval $\left[E_{i}-\Delta E, E_{i}\right]$,

$$
\begin{align*}
& N_{i}(\Delta \tau)=\sum_{J p} \sum_{M} \sum_{n} \mathcal{P}(n J M p) \Theta\left(E_{i}-E_{n}^{J p}\right) \Theta\left(E_{n}^{J p}-E_{i}-\Delta E\right) \\
& \times \Theta\left(\tau_{n}^{J p}-t_{\text {low }}\right) \Theta\left(t_{\text {high }}-\tau_{n}^{J p}\right) \tag{11}
\end{align*}
$$

$\mathcal{P}(n J M p)$ denotes a weight with which the indicated state is included. Two basic choices of $\mathcal{P}(n J M p)$ of are:

$$
\begin{equation*}
\mathcal{P}_{\mathrm{DOS}}(n J M p)=1 \quad \text { and } \quad \mathcal{P}_{\mathrm{DOL}}(n J M p)=\mathcal{P}(M ; J) \quad \text { with } \quad \sum_{M} \mathcal{P}(M ; J)=1 \tag{12}
\end{equation*}
$$

With the first choice, $\rho(E ; \Delta \tau)$ is the 'true' density of states and is therefore denoted as $\operatorname{DOS}(E ; \Delta \tau)$. The second choice gives $\rho(E ; \Delta \tau)$ the meaning of density of $n J p$ levels; so, the acronym DOL is used.

- The spectra of kinetic energy released from decay of states in sets characterized by different choices of $\Delta \tau$ and $\mathcal{P}$,

$$
\begin{equation*}
\kappa(e ; \Delta \tau)=\frac{1}{\Delta e} \sum_{i} n_{i}(\Delta \tau) \Theta\left(e_{i}-e\right) \Theta\left(e-e_{i}-\Delta e\right) \tag{13}
\end{equation*}
$$

$n_{i}(\Delta \tau)$ denotes the number of states with lifetimes in the $\Delta \tau$ whose decay gives the kinetic energy $e \in\left[e_{i}-\Delta e, e_{i}\right]$,

$$
\begin{align*}
n_{i}(\Delta \tau)=\sum_{J p} \sum_{M} \sum_{n} \mathcal{P}(n J M p) \sum_{c} p_{c}^{n J p} \Theta\left(e_{i}-e_{c}^{n J p}\right) & \Theta\left(e_{c}^{n J p}-e_{i}-\Delta e\right) \\
& \times \Theta\left(\tau_{n}^{J p}-t_{\text {low }}\right) \Theta\left(t_{\text {high }}-\tau_{n}^{J p}\right) \tag{14}
\end{align*}
$$

$p_{c}^{n J p}$ and $e_{c}^{n J p}$ denote, as in Eq. (6), the probability of decay of state $n J M p$ into channel $c$ and the kinetic energy released in this decay, respectively. Insertion of $\mathcal{P}_{\mathrm{DOS}}$ or $\mathcal{P}_{\mathrm{DOL}}$ for the $\mathcal{P}(n J M p)$ in Eq. (14) gives the two main examples of the KER spectra, hereafter denoted by symbols KERS and KERL, respectively, which will be presented in this study. Analysis of these examples will provide information on how much particular groups of the rovibronic states can possibly contribute to intensity of the $\kappa(e ; \Delta)$ spectrum in different regions of $e$. This information will be next exploited in attempts to reproduce the shapes of the spectra recorded in the referred experiments.

## IV. RESULTS



Fig. 1
(a) $\mathrm{N}\left(\tau \in\left[t_{\min }, t\right]\right)$ - the number of rotation-vibration levels of the ${ }^{12} \mathrm{C}^{16} \mathrm{O}^{++}$ion in the $X^{3} \Pi, a^{1} \Sigma^{+}$, $b^{1} \Pi$, and $A^{3} \Sigma^{+}$electronic states with lifetimes in the $\left[t_{\min }, t\right]$ range, shown as function of $t$ increasing up to $t_{0}=91627 \mathrm{~s}$ which is the lifetime of the lowest level of the ion, $X v=0 F_{1} N=1^{f}$, at $E_{0}=0.08127 \mathrm{eV}$. The values of $\mathrm{N}\left(\tau \in\left[t_{\min }, t_{0}\right]\right)$ for $t_{\min }=0.5 \mathrm{ps}, 5 \mathrm{~ns}, 1 \mu \mathrm{~s}$, and 1 ms are $20121,2129,726$, and 279 , respectively. Not counted in the plot are the levels $X v=0-6 F_{3} N=1^{f}$ for which $\tau \gg t_{0}$, see Table BI in Supplementary Material. Thus, $\mathrm{N}(\tau \geq 0.5 \mathrm{ps})$ - the number of all levels in the four states of the ion with lifetimes longer than 0.5 ps is 20128. The highest level in this set, $A v=0 F_{1} N=163$, lies at $E_{\max }=8.282 \mathrm{eV}$. [Zero of $E$ is at the bottom of the $X$ state potential well, the lowest dissociation limit is $\varepsilon_{0}=-5.229 \mathrm{eV}$.] The colored histogram represents the related log-lifetime spectrum, i.e. $\mathrm{N}\left(\tau \in\left[t_{\min }, t\right]\right)=\int_{\log t_{\min }}^{\log t} d \mathrm{~N} / d \lambda d \lambda$. From position and shape of its peak one infers that about one half of the number $\mathrm{N}(\tau \geq 0.5 \mathrm{ps})$ are levels from the narrow lifetime range of $20-200 \mathrm{ps}$.
(b) The log-lifetime spectrum resolved into contributions of each of the four states included in the spectrum of panel (a) and supplemented with contributions of states $c^{1} \Delta$ and $d^{1} \Sigma^{+}$. The integrated value $\mathrm{N}(\tau \in[0.5 \mathrm{ps}, 50 \mathrm{~ns}])$ is enlarged by about $4.4 \%$ by these contributions.
(c) The number of levels as function of the rotational quantum number $J, \sum_{J=0}^{189} \mathrm{~N}(J ; \tau \geq 0.5 \mathrm{ps})=20128$. The strips show contributions of the particular electronic states assigned with colors as in panel (b).


Fig. 2.
Widths of rotational levels as functions of their energy in selected vibronic states:
(a) the $X^{3} \Pi v=0,3,10$ states. For each $v$, six curves are drawn by joining the energy-width values of $F_{i} N p$ levels with fixed number $F_{i}(i=1,2$, or 3$)$ and parity $p(=e$ or $f)$. The symbols on the curves represent selected individual levels; the colored numbers are their $N$ values.
(b) the $b^{1} \Pi v=0,6,11,21$ states. For each $v$, joined into one curve are the energy-width values of $J$ levels of given parity $p$. The colored numbers near the symbols are $J$ values of selected individual levels. In both panels, the straight line parts of the curves, on their high $N$ or $J$ ends, represent rapidly increasing participation of tunneling in the decay of the ion from these levels. Information on partial widths for this decay pathway is given in Supplementary Material (Fig. A3c, Table BIII).


Fig. 3
(a) Widths of rotational levels as functions of their energy in selected vibrational states of the electronic state $a^{1} \Sigma^{+}$. (b) The width function $\Gamma\left(E_{J}\right)$ for the state $a^{1} \Sigma^{+} v=0$ plotted together with three functions each of which accounts for only one decay pathway: (i) the tunneling through the barriers of the effective potentials $V_{a}^{J}(r)$, see Fig. A1b, or (ii)-(iii) the predissociation due to crossing and SO coupling of the $V_{a}^{J}$ curves with the curves $V_{s}^{J}$ of one state, $s={ }^{3} \Sigma^{-}$or $s=X^{3} \Pi$. The sum of the three functions nearly equals the $\Gamma\left(E_{J}\right)$ function in its high $J$ part. The large deviations occurring in the part for $J \in[0, \sim 100]$ are a manifestation of the fact that the a $v=0 J$ levels in this range decay indirectly, via the $a \rightarrow X \rightarrow{ }^{3} \Sigma^{-}$transitions. Of all other levels of the ion determined in this work, only the levels $a v=1 J<95$ and $a v=2 J<80$ appear to decay similarly, i.e. their widths cannot be approximated by sums of single-path contributions, see Figs. A3b and A3e.


Fig. 4

Widths of $A^{3} \Sigma^{+} v F_{i} N$ levels for $i=1,2,3$ in three selected $v$ states as functions of their energy: (a) total widths and (b) partial widths giving the probabilities $\Gamma_{1} / \Gamma$ for decay into the first excited fragmentation channel. In the $A$ state case, this channel is reached not only by tunneling from high $N$ levels through barriers of the effective potentials $V_{A}^{J}$ with $J=N, N \pm 1$, see Fig. A1, but also by predissociation to the state $b^{1} \Pi$ from all $v \geq 5 N$ levels and from majority of $v<5 \mathrm{~N}$ levels which lie close or well above the barrier-top of the respective potential $V_{b}^{J}$.


Fig. 5
(a) $\operatorname{DOS}(E)$ - the density of ${ }^{2 S+1} \Lambda_{\Omega} v J M p$ states having lifetimes in the range specified in the legend, represented by the shaded histogram, and $\operatorname{KERS}(e)$ - the kinetic energy release spectrum resulting from the DOS as defined in Eqs. (13)-(14) and (12), represented by the histogram drawn with the red line. The area encompassed by each histogram gives the total number of contributing states, $\sum_{i} N_{i}=\sum_{i} n_{i}$, multiplied by $\Delta E=\Delta e$. Above two millions of states ${ }^{2 S+1} \Lambda_{\Omega} v J M p$ contribute to the quantities. Basic information on them is given in the upper part of the panel: the labels of the electronic states and the lines with ticks showing energies ( $E$ or $E-\varepsilon_{0}$ if read on the bottom x axis) of the levels $v=0, \ldots, J=\Omega$ within these states.
(b) A partitioning of the $\operatorname{KERS}(e)$ according to magnitude of the number $J$ of the contributing states. In the inset: distribution of $J$ numbers among the states, $N_{\mathrm{S}}(J)$ where $N_{\mathrm{S}}:=\sum_{i} n_{i}$


Fig. 6

Resolutions of the distributions $\operatorname{DOS}(E)$ and $\operatorname{KERS}(e)$ shown in Fig. 5(a) into parts contributed by each of the included electronic states. In the inset: contributions of the particular vibronic states on the interval of $e$ indicated by the arrows around the maximum at $\sim 7.2 \mathrm{eV}$.


Fig. 7
Same as Fig. 5 for the density of ${ }^{2 S+1} \Lambda_{\Omega} v J p$ levels, $\operatorname{DOL}(E)$, and for the KER spectrum resulting from it, $\operatorname{KERL}(e)$. In this spectrum, the position of maximum is shifted down, to $\sim 6.8 \mathrm{eV}$, and the feature around $e=8.5 \mathrm{eV}$ is more pronounced than in the KER spectrum resulting from the DOS. The histogram $J_{\mathrm{av}}(e)$ shown additionally in panel (b) is defined by the relation: $\operatorname{KERS}(e) / \operatorname{KERL}(e)=2 J_{\mathrm{av}}(e)+1$. In the inset: the distribution of $J$ numbers among the levels, $N(J)$, here $\sum_{i} n_{i}:=N$. Obviously, it is related to the $N_{\mathrm{S}}(J)$ shown in Fig. 5 b as $N(J)=N_{\mathrm{S}}(J) /(2 J+1)$.


Fig. 8
Same as Fig. 6 for the distribution $\operatorname{DOL}(E)$ and the related $\operatorname{KERL}(e)$.


Fig. 9
Examples of distributions $\kappa(e ; \Delta \tau)$ to compare with the experimental spectra: KER $\widetilde{S}(e)$ (blue) - with the spectrum of Ref. 1, $\operatorname{KER} \widehat{\mathrm{L}}(e)$ (red) and $\operatorname{KER} \overline{\mathrm{S}}(e)$ (pink) - with the spectrum of Ref. 2, obtained by using state-populations $\mathcal{P}_{\widetilde{\text { DOS }}}(n J M p)=\widetilde{\mathcal{P}}(n) \widetilde{\mathcal{P}}(J)$, $\mathcal{P}_{\widehat{\mathrm{DOL}}}(n J M p)=\widehat{\mathcal{P}}(n) \frac{1}{2 J+1} \widehat{\mathcal{P}}(J)$, and $\mathcal{P}_{\overline{\mathrm{DOS}}}(n J M p)=\widehat{\mathcal{P}}(n) \check{\mathcal{P}}(J)$, respectively, in which the factors $\mathcal{P}(n)$ eliminate some vibronic states $n=(s v)$ with high vibrational excitation and the factors $\mathcal{P}(J)$ modify (generally reduce) the participation of (high $J$ ) rotational states. Specifically, $\widetilde{\mathcal{P}}(n)=0$ for $X v>6, a v>18, b v>16, A v>11$, otherwise $\widetilde{\mathcal{P}}(n)=1$, and $\widehat{\mathcal{P}}(n)$ eliminates only two $X v$ states less, i.e. with $v>8$. In effect of these eliminations, the total number of states $N_{\mathrm{S}}$ listed in Fig. 5 decreases to values $\widetilde{N}_{\mathrm{S}}=2111538$ and $\widehat{N}_{\mathrm{S}}=2183613$, respectively. The corresponding populations of $J$ states, $\widetilde{N}_{\mathrm{S}}(J)$ and $\widehat{N}_{\mathrm{S}}(J)$, are shown by the gray, almost indistinguishable, curves in the inset. The blue, red, and pink $N(J)$ curves in the inset show the modified populations $\widetilde{N}_{\mathrm{S}}(J) \widetilde{\mathcal{P}}(J), \widehat{N}_{\mathrm{S}}(J) \frac{1}{2 J+1} \widehat{\mathcal{P}}(J)$, and $\widehat{N}_{\mathrm{S}}(J) \check{\mathcal{P}}(J)$, respectively. All the modifying factors have the form

$$
\mathcal{P}(J)=C \begin{cases}\exp \left[-a\left(J-J_{\mathrm{c}}\right)^{2}\right] & \text { with } a=\alpha_{1} \text { for } J<J_{\mathrm{c}} \text { and } a=\alpha_{2} \text { for } J \geq J_{\mathrm{c}} \\ \exp \left[-\alpha_{2}\left(J-J_{\mathrm{c}}\right)^{2}-\alpha_{3}\left(J-J_{\mathrm{a}}\right)\right] & \text { for } J \geq J_{\mathrm{a}}>J_{\mathrm{c}}\end{cases}
$$

but differ in the parameter values: $\left(\widetilde{\alpha}_{1}, \widetilde{\alpha}_{2}, \widetilde{\alpha}_{3}\right)=\left(2 \times 10^{4}, 10^{-4}, 0\right), \widetilde{J}_{\mathrm{c}}=70$, and $\widetilde{C}$ assures the normalization $\sum_{J=1}^{189} \widetilde{\mathcal{P}}(J)=1 ; \quad\left(\widehat{\alpha}_{1}, \widehat{\alpha}_{2}, \widehat{\alpha}_{3}\right)=\left(0,7.5 \times 10^{-2}, 0\right), \quad \widehat{J}_{\mathrm{c}}=82, \quad \widehat{C}=1$; $\left(\check{\alpha}_{1}=\check{\alpha}_{2}, \check{\alpha}_{3}\right)=\left(2.75 \times 10^{-4}, 0.1\right),\left(\check{J}_{\mathrm{c}}, \check{J}_{\mathrm{a}}\right)=(20,88)$ and $\check{C}$ assures equal areas under the red and pink curves. The areas are listed in the colored labels.

## V. DISCUSSION

All the distributions DOS, DOL, KERS, and KERL presented in Fig. 5-8 were constructed to account for states of the ion which have lifetimes in the range $\Delta \tau=[100 \mathrm{ps} / J, 5 \mathrm{~ns}]$. This range was chosen to adjust to the limitations mentioned in the experimental papers ${ }^{1,2}$. Still, the two KER distributions remain idealizations because of the used state-populations. However, even with the unrealistic $\mathcal{P}$, the distributions $\operatorname{KERL}(e)$ and $\operatorname{KERS}(e)$ capture some likeness to the two experimental spectra presented in Ref. 2 and in Refs. 1, hereafter referred to as PRL18 and JCP18 spectrum, respectively. Namely, the maximum position in the $\operatorname{KERL}(e)$, at $e=6.8 \mathrm{eV}$, is not far from the position in the PRL18 spectrum, at 6.5 eV , the shoulders in the right and left wings appear at $e \approx 8 \mathrm{eV}$ and $e \approx 4.5 \mathrm{eV}$, respectively, i.e. at the same positions as in the experimental spectrum. Inconsistent with the experiment are mainly the relative heights of the three features in the KERL. In turn, the distribution KERS(e) resembles rather the JCP18 spectrum, mostly in that its maximum position is shifted to a larger $e$ value (to 7.2 eV versus observed 7.5 eV ) and also in that it is much broader than the PRL08 spectrum.

The analysis of contributions to the $\operatorname{KERL}(e)$ and $\operatorname{KERS}(e)$ of the particular electronic, vibronic and rotational states of the ion in Figs. 5-8 and A5-A8 reveals several facts relevant to the explanation of the spectra obtained in the referred experiments. The most interesting finding concerns the origin of the feature occurring in the low $e$ wing of the PRL18 spectrum. In contrast to what seemed likely in the preliminary explanations ${ }^{2}$, the states $X(v=0-2)$ and $a(v=0-1)$ do not participate in forming this feature. The low $J$ levels of the states, though close in energy, live much longer than the allowed upper limit of a few nanoseconds. Tunneling from some levels of the states $c^{1} \Delta$ and $d^{1} \Sigma^{+}$appears a more likely origin of the feature.
Rather unexpected was also the present finding that levels of the state $A^{3} \Sigma^{+}$contribute so significantly to the peaks in the PRL18 and the JCP18 spectra, especially to their lower $e$ sides. Significant predissociation to the first excited fragmentation channel, $\mathrm{C}^{+}\left({ }^{2} \mathrm{P}\right)+$ $\mathrm{O}^{+}\left({ }^{2} \mathrm{D}\right)$, is responsible for this fact. As expected, in turn, the feature in the PRL18 spectrum with a clear edge at $e \approx 8 \mathrm{eV}$ and the part of the broad peak between 8 and 9 eV in the JCP18 spectrum have indeed significant contributions from the states $A v=1-4$, but not from the state $A v=0$. Rotational levels of the latter state with $J$ values up to $\sim 80$ are outside the allowed lifetime range, cf. Fig. A3d. The edge occurring also clearly in the theoretical KERL $(e)$ coincides with the energy $E$ of $J=0,1$ levels in the $A v=1$ state, cf. Fig. A6.
These observations suggests some modifications of the populations factors $\mathcal{P}_{\text {DOL }}$ and $\mathcal{P}_{\text {DOS }}$ (though not any sound justification for them) which can make the distributions $\operatorname{KERL}(e)$ and $\operatorname{KERS}(e)$ more similar to the experimental spectra. Three such ways are demonstrated in Fig. 9. Positive effects are achieved, particularly in the case of the distribution KER $\widehat{L}(e)$. Considering the modification made in this case, one may conjecture that highly excited rovibrational levels of the four lowest electronic states of the $\mathrm{CO}^{2}$ ion are unlikely to contribute to the PRL18 spectrum.

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