Photodissociation of carbon dioxide in singlet valence electronic states. I. Six multiply intersecting ab initio potential energy surfaces

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The global potential energy surfaces of the first six singlet electronic states of \( \text{CO}_2 \), \( 1—3^1A' \) and \( 1—3^1A'' \) are constructed using high level ab initio calculations. In linear molecule, they correspond to \( \tilde{X}^1\Sigma_g^+ \), \( 1^1\Delta_u \), \( 1^1\Sigma_u^- \), and \( 1^1\Pi_g \). The calculations accurately reproduce the known benchmarks for all states and establish missing benchmarks for future calculations. The calculated states strongly interact at avoided crossings and true intersections, both conical and glancing. Near degeneracies can be found for each pair of six states and many intersections involve more than two states. In particular, a fivefold intersection dominates the Franck-Condon zone for the ultraviolet excitation from the ground electronic state. The seam of this intersection traces out a closed loop. All states are diabatized, and a diabatic \( 5 \times 5 \) potential matrix is constructed, which can be used in quantum mechanical calculations of the absorption spectrum of the five excited singlet valence states.

I. INTRODUCTION

This and the subsequent^1 paper (termed ‘paper II’) describe the results of an ab initio quantum dynamical study of the absorption spectrum and the non-adiabatic dissociation mechanisms of carbon dioxide photoexcited with the ultraviolet (UV) light between 120 nm and 160 nm. A brief account of this work has already been published.\(^{2}\) Paper II gives the motivation behind the study and discusses its main result — the quantum mechanical absorption spectrum and its interpretation in terms of wave functions of metastable resonance states. The present paper sets the stage for paper II and describes the ab initio calculations

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and the topography of the potential energy surfaces (PESs) involved in photodissociation. This information, which is often stashed away in supplementary online sections, is a central and, indeed, an indispensable ingredient of a reliable dynamics calculation. The construction of ab initio PESs and their diabatization — which, without much exaggeration, amounts to learning the topography of PESs and their intersections by heart — is often more challenging than the subsequent quantum dynamical calculation.

Photoabsorption from the ground electronic state $\tilde{X}^1\Sigma_g^+$ of linear CO$_2$ at wavelengths 120 nm — 160 nm is due to the first five excited singlet valence states $1^1\Sigma_u^-$, $1^1\Pi_g$, and $1^1\Delta_u$. In the $C_s$ group notation, appropriate for bent molecule, these states are $2^3A'$ and $1, 2, 3^1A''$. UV light excites CO$_2$ into the region of multiple electronic degeneracies, nuclear motion through which induces strong non-adiabatic couplings between electronic states. These couplings directly affect the observed absorption spectrum of the valence states and control distributions of photofragments over the final states. Their indirect influence apparently extends to shorter wavelengths where Rydberg transitions dominate: The combined experimental and theoretical analysis indicates that the manifold of coupled valence states acts as a ‘sink’ for the optically bright Rydberg states and affects their dissociation lifetimes.

Electronic degeneracies in the Franck-Condon (FC) region, which have been the focus of several studies in the past, are of two types. Glancing intersections occur in the orbitally doubly degenerate $1^1\Pi_g$ and $1^1\Delta_u$ states which upon bending split into $A'$ and $A''$ components. Conical intersections (CIs) arise at the accidental $1^1\Pi_g/1^1\Delta_u$ crossing inside $A'$ and $A''$ symmetry blocks. In fact, CIs between valence states are ubiquitous and found far outside the near-linear FC region, at strongly bent geometries. Together with local minima and saddles, these crossings are the principal features shaping the topography of the singlet valence states.

The outline of the paper is the following. Section II sketches the technical details of ab initio calculations. Next, the constructed adiabatic PESs are presented for the ground (Sect. IIIA) and the excited (Sect. IIIB) electronic states. Their intersections are discussed for near linear (Sect. IIIC) and bent geometries (Sect. IIID), and put into perspective by a review of a network of closely spaced valence and Rydberg states (Sect. IIIE).

If the solution of the Schrödinger equation for nuclei is out of reach, the description of adiabatic surfaces in Sect. II would be the last step in theoretical ab initio analysis. If, on the other hand, one intends to treat nuclear dynamics quantum mechanically, ab initio PESs
featuring CIs have to be diabatized. This is especially desirable if — as in paper II — a discrete grid is used to represent the nuclear Hamiltonian, because the diabatized potential matrix is free from either divergent off-diagonal couplings or non-differentiable potential cusps. While general schemes for constructing approximate adiabatic-to-diabatic transformations are established (see, for instance, Ref. [12]), their application to the valence states of CO$_2$ is complicated by the number of CIs to be simultaneously treated. Simplifications are called for, as described in Sect. [IV], in which the diabatic representation is constructed separately for bent CIs (Sect. [IVA]) and linear CIs (Sect. [IVB]). Section [V] concludes.

II. ELECTRONIC STRUCTURE CALCULATIONS

All ab initio calculations are carried out with the MOLPRO package. The Gaussian atomic basis sets used in this work are due to Dunning. Previous studies indicate that diffuse functions should be added to the basis sets on oxygen and carbon atoms in order to account for the mixed valence-Rydberg character of the II state. A series of tests was conducted, in which $s$, $p$, $d$ etc. basis functions of triple and quadrupole zeta quality were selectively augmented by one or two diffuse functions. The pre-computed doubly augmented correlation consistent polarized valence quadrupole zeta (d-aug-cc-pVQZ) basis set, as implemented in MOLPRO, was found computationally most stable and selected for calculations of global PESs.

Three-dimensional (3D) PESs of states 1, 2, 3$^1A'$ and 1, 2, 3$^1A''$ are calculated at the internally-contracted multireference configuration interaction singles and doubles (MRD-CI) level, based on state-averaged full-valence complete active space self-consistent field (CASSCF) calculations with 16 electrons in 12 active orbitals and 6 electrons in three fully optimized closed-shell inner orbitals. The electronic configuration of the ground state $\tilde{X}^{1}\Sigma_g^+$ is ([core]$2\sigma_u^23\sigma_g^24\sigma_g^23\pi_u^21\pi_u^11\pi_g^1$). The dominant electronic excitations, leading to the lowest excited states, include $1\pi_u^4 \rightarrow 2p2\pi_u^1$ (giving states $1^1\Delta_u$ and $1^1\Sigma_u^-$) and $1\pi_g^4 \rightarrow 5s5\sigma_g^1$ (giving state $1^1\Pi_g$). Active orbitals in CASSCF comprised $2\sigma_u - 4\sigma_u$, $3\sigma_g - 5\sigma_g, 1\pi_u - 2\pi_u$, and $1\pi_g$. In $C_s$ symmetry, used in the calculations, these are $4\alpha' - 12\alpha'$ and $1\alpha'' - 3\alpha''$. In the MRD-CI step all 16 valence electrons were correlated. The maximum numbers of open shells allowed in the MRD-CI calculations were 8 in the reference space and 12 in the internal space. This lead to 38159928 contracted configurations. The Davidson correction was applied in order
to account for higher-level excitations and size-extensivity.\textsuperscript{15}

Adiabatic energies are calculated on a 3D grid of the two C–O bond lengths $R_{1,2}$ and the OCO bond angle $\alpha_{\text{OCO}}$: $R_2 \in [1.9 a_0, 3.0 a_0]$ (step size equals 0.1 $a_0$), $R_1 \in [R_2, 6.2 a_0]$ (step size varies between 0.1 $a_0$ and 0.4 $a_0$), $\alpha_{\text{OCO}} \in [70^\circ, 179.9^\circ]$ (step size varies between 2$^\circ$ and 10$^\circ$). Additionally, many cuts in the $(R_1, R_2)$ plane are computed for angles $\alpha_{\text{OCO}}$ between 60$^\circ$ and 0$^\circ$ within the continuing effort to construct a balanced description of both CO + O and C + O$_2$ arrangement channels. At present, the grid comprises 4800 symmetry distinguishable points. The resulting energies were scanned in one and two dimensions for obvious errors. The list of corrected adiabatic energies was subsequently interpolated using 3D cubic splines and also used for constructing the quasi-diabatic representation. Missing energies for $\alpha_{\text{OCO}} < 70^\circ$ in the dissociation channels were obtained from those for $\alpha_{\text{OCO}} > 70^\circ$ using trigonometric extrapolation.

Absolute intensity calculations of paper II require transition dipole moments (TDMs) with the ground state $\tilde{X}$. Components $(\mu_x, \mu_y, \mu_z)$ of the TDM vector are calculated, for each electronic state, on a 3D grid $R_{1,2} = [1.9 a_0, 2.4 a_0]$ and $\alpha = [165^\circ - 179^\circ]$ covering the spot over which the vibrational ground state in $\tilde{X}$ is delocalized. The molecular axes in these calculations are chosen such that $x'$ is orthogonal to the molecular plane, $z'$ runs along one of the CO bonds and $y' \perp z'$. For $A'$ states, the in-plane components are generally non-zero, while for $A''$ states, it is the $\mu_{x'}$ component which carries the transition.

III. PROPERTIES OF THE VALENCE PESs AND THEIR CROSSINGS

A. Ground electronic state

The $\sim 7.5$ eV deep adiabatic ground state PES supports three structural isomers: The familiar linear OCO molecule is the global equilibrium, while the carbene-like bent OCO and the linear COO are the two local ones. Table II summarizes the characteristic features of the $\tilde{X}^1\Sigma_g^+$ state at the three equilibria and compares them with the previous ab initio studies and with the available experimental data.

The vicinity of the global minimum is of capital importance for the environmental chemistry.\textsuperscript{16} The calculated equilibrium CO bond distance in linear OCO, $R_e = 2.1991 a_0$, agrees well with the experimental value of 2.1960 $a_0$. The accuracy of the vibrational zero-
point energy (ZPE) and the vibrational transitions frequencies is assessed in Table II which compares energies of the low lying vibrationally excited states in rotating \( \text{CO}_2 \) (the total angular momentum \( N_{\text{CO}_2} \geq 0 \)) with experiment\textsuperscript{17} and with recent electronic coupled cluster/vibrational configuration interaction calculations.\textsuperscript{18,19} Each eigenstate \((v_s, v_l^b, v_a)\) is labeled using the quantum numbers of the symmetric stretch \( v_s \), the bend \( v_l^b \) (with \( l \) indicating the vibrational angular momentum, \( N_{\text{CO}_2} \geq l \)), and the antisymmetric stretch \( v_a \).

The calculated fundamental frequencies of the infrared active bend \( (\omega_b = 668.6 \text{ cm}^{-1}) \) and antisymmetric stretch \( (\omega_a = 2350.6 \text{ cm}^{-1}) \) are accurate to within 1.5 \( \text{cm}^{-1} \). The zeroth order symmetric stretch frequency\textsuperscript{20} \( \omega_s^0 \approx 1333 \text{ cm}^{-1} \) is about twice as large as the bending frequency \( \omega_b \), and the two modes are involved in the accidental Fermi resonance.\textsuperscript{21} As a result, the vibrational spectrum is organized in polyads with the polyad quantum number \( P = 2v_s + v_l^b \); states with \( P = 2, 3 \) and \( 4 \) are given in Table II. In the original version of the PES, called ‘PES1’ in Table II, the energies of states \((1, 0^0, 0)\) and \((0, 2^0, 0)\), belonging to the lowest polyad \( P = 2 \), are underestimated by 20 \( \text{cm}^{-1} \) and the difference with the observed energies grows rapidly with \( P \). This systematic discrepancy is substantially diminished by slightly rescaling the symmetric stretch, \( R_+ = (R_1 + R_2)/\sqrt{2} \), and the bend \( \alpha_{\text{OCO}} \) via

\[
R_+ \rightarrow \sqrt{2}R_{1e} + (R_+ - \sqrt{2}R_{1e}) \cdot 1.023 \\
\alpha_{\text{OCO}} \rightarrow 180^\circ + (\alpha_{\text{OCO}} - 180^\circ) \cdot 1.0035.
\]

The vibrational energies in the scaled ‘PES2’ agree with their experimental counterparts to within 7 \( \text{cm}^{-1} \) and for the most states below 3000 \( \text{cm}^{-1} \) the accuracy is better than 3 \( \text{cm}^{-1} \). The results outperform even the highly accurate calculations of Refs.\textsuperscript{18} and \textsuperscript{19} shown in the second column of Table II, making ‘PES2’ one of the best available ab initio potentials of the \( \tilde{X}^1\Sigma_g^+ \) state. Since the coordinate dependent dipole moment \( \mu_X \) has also been calculated, the ab initio intensities of the infrared rovibrational transitions can be directly evaluated.\textsuperscript{22}

The other two isomers in Table I have never been detected in the gas phase, and the only reference data stem from the previous ab initio studies. For the bent OCO, discovered by Xantheas and Ruedenberg,\textsuperscript{23} the present calculations confirm the \( C_{2v} \) symmetric equilibrium with the CO bond lengths of 2.51 \( a_0 \) and the OCO bond angle of 73.2\textdegree. This minimum is located 6.03 eV above the global one, again in good agreement with the previous findings.\textsuperscript{23,24} The fundamental excitations in the OCO well, calculated for \( N_{\text{CO}_2} = 0 \), are \( \omega_a = 680 \text{ cm}^{-1}, \omega_l^b = 720 \text{ cm}^{-1}, \) and \( \omega_s = 1550 \text{ cm}^{-1} \). For the linear COO, the calculated CO and OO
bond lengths are identical to the ones given in Ref. [24]; both are elongated compared to free diatoms (2.14 $a_0$ for CO and 2.45 $a_0$ vs 2.28 $a_0$ for OO). The calculations place the COO minimum at 7.35 eV, about 0.1 eV below the lowest dissociation threshold.

The ground electronic state correlates adiabatically with two dissociation channels,

\[
\begin{align*}
\text{CO}_2 + h\omega (E_{ph} \geq 7.41 \text{ eV}) & \rightarrow \text{O} (^1D) + \text{CO} (X^1\Sigma^+) \quad (1) \\
\text{CO}_2 + h\omega (E_{ph} \geq 11.52 \text{ eV}) & \rightarrow \text{C} (^3P) + \text{O}_2 (X^3\Sigma^-) , \quad (2)
\end{align*}
\]

and the ZPE corrected dissociation energies $D_0$ are shown in Table I. In channel (1), the calculated $D_0$ is 0.13 eV less than the experimental value. The deviation might reflect a large basis set superposition error introduced by the diffuse functions and as such is the downside of the highly accurate vibrational spectrum in Table II. The error is independent of the arrangement channel, and $D_0$ in channel (2) [closed between 120 nm and 160 nm] is equally underestimated. The calculations of Hwang and Mebel [24], using a noticeably smaller basis set, perfectly agree with the experimental dissociation energy for this channel.

One-dimensional (1D) cuts through the ground state PES are given for several $\alpha_{OCO}$ angles in panels (a,c,e) of Figs. 1 and 2. Black solid circles are the raw adiabatic energies. The O + CO limit is reached smoothly and no barrier is detected towards the asymptote for any orientation of the CO diatom. The same is true for the C + O$_2$ channel, as illustrated in Fig. 2(e); the potential well in Fig. 2(e) is the COO isomer. Angular dependence of the $\tilde{X}^1A'$ state is shown in panels (a,c,e) of Figs. 3 and 4 for two sets of fixed CO bonds. In Fig. 3, $R_1$ is fixed at the FC value; in Fig. 4, it is fixed close to the equilibrium of the bent OCO. Consequently, although the carbene-type minimum is perceptible in all panels, it is best seen in Fig. 4. As CO$_2$ bends, the adiabatic $\tilde{X}^1A'$ state (black dots) forms a sharp narrowly avoided crossing with the state $2^1A'$ around $\alpha_{OCO} = 100^\circ$ (see, for example, Fig. 3). A dynamically meaningful representation for such nearly degenerate pairs is diabatic rather than adiabatic. In fact, the black line in Figs. 1–4 depicts the $\tilde{X}^1A'$ state locally diabatized at bent geometries as described in Sect. IV A. This is the reason why the black dots sometimes switch away from the black line and why lines of different colors cross. In this locally diabatic picture, the bent OCO minimum correlates with the state $2^1A'$ [purple line]. The transition state separating the bent and the linear minima, analyzed by Xantheas and Ruedenberg [23] and Hwang and Mebel [24] is thus the signature of this two-state intersection. The two-dimensional (2D) contour plots of the PES of the locally diabatic $\tilde{X}^1A'$ state, used
in the above calculations of vibrational states, are shown in Fig. 5.

**B. Overview of the excited electronic states**

Potentials of the excited electronic states are shown in Figs. 1 and 2 along one CO bond for $A'$ and $A''$ symmetries. As with the $\tilde{X}$ state, the solid circles indicate ab initio adiabatic energies. In the CO + O arrangement channel, which is the focus of the present investigation, all calculated states but one converge to the dissociation threshold (1). The state $2^1A''$, correlating with $1^1\Sigma_u^-$ at the FC point, reaches the higher lying threshold

$$CO_2 + h\omega(E_{ph.} \geq 11.46 \text{ eV}) \rightarrow O(^3P) + CO(a^3\Pi).$$

(3)

In the C + O$_2$ arrangement channel [Fig. 2(e,f)], three electronic states, the $\tilde{X}$ state and the two components of the $\Pi$ state, correlate with channel (2). Three other states ($\Sigma^-$ and $\Delta$) converge to the electronically excited fragments:

$$CO_2 + h\omega(E_{ph.} \geq 13.75 \text{ eV}) \rightarrow C(^1D) + O_2(^1\Delta).$$

(4)

Topographic hallmarks of the excited states can be exemplified using the states 2, 3$^1A'$. In the FC region near linearity [Fig. 1(a)], the states 2$^1A'$ and 3$^1A'$ form two sharp avoided crossings near $R_1 = 2.2a_0$ and $R_1 = 2.8a_0$. These crossings are in fact two CIs between states $1^1\Pi_g$ and $1^1\Delta_u\text{.}^{2,3,9,10}$ The CIs are not independent: They are connected into a whole line, called a ‘CI seam’, unusual properties of which$^3$ are discussed in Sect. III C. As the molecule bends, the gap between the adiabatic states grows. In the lower state 2$^1A'$, the intersection cone first turns into a broad barrier along the dissociation path [$\alpha_{OCO} > 170^\circ$, Fig. 1(c)]. As $\alpha_{OCO}$ decreases further, the local minimum near $2.3a_0$ deepens and the dissociation barrier disappears [Fig. 1(e) and Fig. 2(a)]. In linear COO [$\alpha_{OCO} = 0^\circ$, Fig. 2(e)], the sharp avoided crossing between states 2, 3$^1A'$ reappears again, this time at $R_1 = 3.5a_0$. Similar to $\tilde{X}$, the state 2$^1A'$ supports a COO intermediate, although the local minimum lies 0.7 eV above the C + O$_2$ threshold (2). The evolution of the uppermost state 3$^1A'$ with decreasing angle is different, because its topography is very much influenced by a pronounced barrier located outside the FC zone near $R_1 = 3.6a_0$ and separating the flat inner region from a steep decline towards the asymptotic limit. This barrier is distinct over a broad angular range and its sharpness suggests a CI with a higher lying state. The nature of this intersection becomes apparent in Sect. III E discussing valence/Rydberg crossings.
The $A''$ states are similar in many respects. Near linearity, both symmetries mirror the topography of the orbitally degenerate states $1^1\Pi_g$ and $1^1\Delta_u$, the states $1, 3^1A''$ are involved in the same CIs in the FC region [Fig. 1(b)], and their behavior in the bent molecule up to $\alpha_{OCO} = 120^\circ$ closely follows that of $2, 3^1A'$. The $1^1A''$ state stabilizes with decreasing $\alpha_{OCO}$, while the $3^1A''$ state features a pronounced barrier around $R_1 = 3.6 a_0$ [Fig. 1(d,f) and Fig. 2(b)]. Similarities persist to $\alpha_{OCO} = 0^\circ$ [Fig. 2(f)]: The states $1, 3^1A''$ form a CI at $R_1 = 3.5 a_0$, and the state $1^1A''$ supports a local COO minimum. Differences with the $A'$ symmetry are due to the state $2^1A''$, which in the FC region correlates with $1^1\Sigma_u^-$ and which has no counterpart among the calculated $A'$ states. This state, which at linearity is accidentally degenerate with $1^1\Delta_u$, has a single minimum near $2.4 a_0$ and approaches the dissociation limit $3$ without a barrier. This simple shape is preserved through most cuts in Figs. 1 and 2. The state $2^1A''$ also supports a COO minimum [Fig. 2(f)].

Potential cuts along bending angle are shown in Figs. 3 and 4. The doubly degenerate $1^1\Pi_g$ and $1^1\Delta_u$ states split into $A'$ and $A''$ components for $\alpha_{OCO} < 180^\circ$. Evolution of the electronic energies with decreasing $\alpha_{OCO}$ was analyzed by Spielfiedel et al. using Walsh rules. Based on this analysis, the adiabatic excited states are commonly classified as bent or linear. The energy of states $2^1A'$ and $1^1A''$ lowers as the molecule bends, while the energy of states $3^1A'$ and $3^1A''$ grows [see Fig. 3(a,b)]. The global minima of the ‘bent’ states lie near $120^\circ$ ($2^1A'$) and $130^\circ$ ($1^1A''$) and are located below the dissociation limit $1$ [Fig. 3(a,b) and Fig. 4(a,b)]. Bent equilibrium of the state $2^1A'$, which at $C_{2v}$ geometries becomes $1B_2$, was predicted by Dixon in his analysis of the CO flame emission bands. Finally, the state $2^1A''$, which together with $3^1A'$ and $3^1A''$ is ‘linear’, is the least anisotropic of all states in a broad vicinity of $\alpha_{OCO} \sim 180^\circ$.

Properties of various stationary points in the PESs of excited electronic states are given in Table III. The $C_s$ point group notation is used to label adiabatic states; $D_{\infty h}$ labels refer to the diabatic states at the FC point. Experimental reference data for the excited electronic states are scarce and fit into the footnote a. For the bent states, the experimental equilibrium CO distances and the bending angle are reproduced within $0.1 a_0$ and $3^\circ$, respectively; the bending frequencies are accurate to within $30 \text{ cm}^{-1}$ or better, and the calculated band origins lie within the experimental uncertainties. Results of the previous ab initio studies are also shown in Table III. Agreement in the equilibrium geometries is excellent, with the exception of the intersection-ridden uppermost states $3^1A'$ and $3^1A''$, for which
C\textsubscript{2v}-restricted calculations of Refs. [9] and [10] miss the local \( C\textsubscript{s} \) minima in the upper CI cones. Vertical excitation energies \( T\textsubscript{v} \) are close to those of Ref. [10]. Slight differences are not surprising for near degenerate states whose ordering is sensitive to the details of the ab initio set up. Peculiarity of the spectral region 120 nm — 160 nm is that \( T\textsubscript{v} \) values are poor approximations to the positions of the absorption maxima because all transitions are electronically forbidden and the TDMs at the FC point are strictly zero. Finally, the ab initio dissociation energies \( D\textsubscript{0} \) in channels [1], [2], [3], and [4], also given in Table III, agree with the experimental values\[12,28\] within \( \sim 0.15 \) eV irrespective of the particular arrangement or electronic channel.

C. Topography of state intersections in the FC zone

Intersections of electronic states in linear CO\textsubscript{2} follow simple ‘symmetry rules’\[29,30\] which severely restrict the intersection topography. Two types of intersections with regard to their symmetry properties are prominent in Figs. [1](a,b) and [3](a,b):

(1) Renner-Teller (RT) glancing intersections\[4,31\] involve the \( A' \) and \( A'' \) components of the \( 1\text{\,}1\Pi\text{\,}{g} \) or the \( 1\text{\,}1\Delta\text{\,}{u} \) state. In the rotating molecule, the \( A'/A'' \) interaction \( \sim \Lambda \Omega/\sin^2 \alpha_{OCO} \) is proportional to the projections \( \Lambda \) and \( \Omega \) of the electronic (\( \hat{L} \)) and the total angular momentum (\( \hat{J} = \hat{N}_{CO2} + \hat{L} \)) on the molecular axis and diverges for \( \alpha_{OCO} \rightarrow 180^\circ \)[4,31–33]. The \( 1\text{\,}1\Pi\text{\,}{g} \leftarrow \tilde{X}\text{\,}1\Sigma\text{\,}{g}^+ \) transition is best classified as linear-linear, and the \( 1\text{\,}1\Delta\text{\,}{u} \leftarrow \tilde{X}\text{\,}1\Sigma\text{\,}{g}^+ \) transition is linear-bent. The ‘degeneracy manifold’ for the intersecting states is the whole \(( R_1, R_2 \) plane defined by the condition \( \alpha_{OCO} = 180^\circ \).

(2) Two nested CIs involve the \( 2\text{\,}3\text{\,}\text{A}' \) and \( 1\text{\,}2\text{\,}\text{A}'' \) or \( 2\text{\,}3\text{\,}\text{A}'' \) states and stem from the accidental \( 1\text{\,}1\Pi\text{\,}{g}/1\text{\,}1\Delta\text{\,}{u} \) crossing. Both degeneracies are lifted linearly along the tuning and coupling modes spanning the common branching space\[25\] According to Fig. [1](a,b), the tuning mode is \( R\text{\,}{CO} \), i.e. a combination of the symmetric and antisymmetric stretch (their irreps are \( \sigma_+^{\pm} \) in the \( D_{\infty h} \) group); \( \alpha_{OCO} \) breaking the linear symmetry (irrep \( \pi \)) is the coupling mode. As a consequence of the ‘symmetry rules’, the CIs occur along a line \( F\text{\,}{CI}(R_1^*, R_2^*) = 0 \) in the \(( R_1, R_2 \) plane at \( \alpha_{OCO} = 180^\circ \): The ‘degeneracy manifold’ is a 1D seam\[4,25,34\].

The CI seam, constructed separately for the \( 2\text{,}3\text{\,}\text{A}' \) and \( 1\text{,}3\text{\,}\text{A}'' \) states on a fine \(( R_1, R_2 \) grid\[13\] is depicted in Fig. [6] It has two remarkable properties. First, the intersection along the seam is fivefold. Two CIs and two RT intersections imply four degenerate states. The
hitherto ignored state $^{1}\Sigma_{u}^{-}$ closely follows $^{1}\Delta_{u}$: The $\Delta/\Sigma$ energy gap falls consistently below 300 cm$^{-1}$ which is at the limit of the ab initio accuracy. Thus, the $^{1}\Pi_{g}/^{1}\Delta_{u}$ and the $^{1}\Delta_{u}/^{1}\Sigma_{u}^{-}$ pairs cross at the same CO bond distances and the total degeneracy is five. Second, the calculated seam traces out a closed loop. Closed CI seams are rarely encountered $^{34,35}$ although arguments have been devised to prove their ubiquity. $^{36,37}$ A technical implication of closed or strongly curved seams is that local diabatization schemes fail $^{38}$ and global or semiglobal diabatization $^{39}$ becomes necessary. The impact of closed seams on photodissociation dynamics has never been systematically investigated. $^{3}$ In CO$_{2}$, only a small portion of the loop is directly accessible to UV light. Nevertheless, paper II demonstrates that the seam topology deeply affects the observed absorption spectrum.

The curved intersection seam is responsible for a peculiar shape of the potentials in the FC region. The adiabatic PESs of the states $2,3^{1}A'$ in linear CO$_{2}$ are shown in Fig. $^{3}$ The lower adiabatic state $2^{1}A'$ has a $C_{2v}$ minimum at $R_1 = R_2 = 2.41 \, a_0$, and two $C_{s}$ symmetric saddles near $R_1 \approx 2.8 \, a_0$ or $R_2 \approx 2.8 \, a_0$, separating the $C_{2v}$ minimum from the dissociation asymptotics. Outside the area enclosed by the seam line, the $2^{1}A'$ state has the $\Pi$, inside the $\Delta$ character. The saddles hide portions of cusp lines, along which the states intersect and which are washed out by the spline interpolation. The topography of the upper adiabatic $3^{1}A'$ state is a literal mirror image of the lower state; one finds a $C_{2v}$ saddle at $R_1 = R_2 = 2.41 \, a_0$ and two $C_{s}$ symmetric minima near $(R_1, R_2) = (2.84 \, a_0, 2.27 \, a_0)$ and $(2.27 \, a_0, 2.84 \, a_0)$. The state character changes from $\Delta$ outside the seam line to $\Pi$ inside. The two minima are cusp-like and correspond to the upper cones of the CIs. The two other saddle points in the $3^{1}A'$ state, lying outside the FC zone near $(R_1, R_2) = (3.6 \, a_0, 2.2 \, a_0)$ and $(2.2 \, a_0, 3.6 \, a_0)$, result from an avoided crossing with a higher lying state.

Changes of the electronic character of $A''$ states across the intersection can be monitored using matrix elements of the electronic angular momentum $\hat{L}_z$. $^{39}$ The matrix elements $\left|\langle iA''|\hat{L}_z|jA'\rangle\right|$ along the line passing twice through the closed seam are depicted in Fig. $^{7}$ for $i = 1, 2, 3$ and $j = 2, 3$. The states $|2^{1}A'\rangle$ and $|3^{1}A'\rangle$ act as ‘probes’ whose assignment in terms of $\Pi$ or $\Delta$ is known. Outside the seam area, most matrix elements are close to integer values of 0, 1, and 2. For $R_1 \leq 2.2 \, a_0$ for example, $\left|\langle 1A''|\hat{L}_z|2A'\rangle\right| = 1$ and $\left|\langle 2A''|\hat{L}_z|2A'\rangle\right| = 0$ so that $|1A''\rangle$ is a $\Pi$ state, while $|2A''\rangle$ is a $\Sigma$ state. $\left|\langle 3A''|\hat{L}_z|2A'\rangle\right|$ vanishes too, but the state $|3A''\rangle$ is a $\Delta$ state, as confirmed by the matrix element $\left|\langle 3A''|\hat{L}_z|3A'\rangle\right| = 2$. As the CI seam is crossed at $R_1 = 2.25 \, a_0$ into the area interior to the seam loop, the three-state
intersection induces violent changes in the electronic labels of the adiabatic states. The state $|3A''\rangle$ becomes a $\Pi$ state ($\langle 3A''|\hat{L}_z|3A'\rangle = 1$); the state $|2A''\rangle$ acquires $\Delta$ character ($\langle 2A''|\hat{L}_z|2A'\rangle \approx 2$), while the state $|1A''\rangle$ acquires $\Sigma$ character ($\langle 1A''|\hat{L}_z|2A'\rangle \approx 0.5$), and the non-integer values of the latter two reflect strong mixing of the near degenerate $\Delta_u/\Sigma_u$ pair. The next reshuffling occurs as the seam loop is crossed outwards at $R_1 \approx 2.8 a_0$. The state $|1A''\rangle$ becomes $\Pi$ again, while the matrix elements involving $|2A''\rangle$ and $|3A''\rangle$ vary until $R_1 \approx 3.6 a_0$ is reached, where $\langle 3A''|\hat{L}_z|3A'\rangle$ finally vanishes indicating that $|3A''\rangle$ emerges from the crossing region as a $\Sigma$ state converging towards the upper threshold (3), while $|2A''\rangle$ becomes $\Delta$ state correlating with threshold (1). The positions of cusps, minima, and saddles in the PESs of the $A''$ states at linearity are identical to those in $A'$ states. Exception is the PES of the state $2^1A''$, correlating in the FC region with $1^1\Sigma_u^-$. Its appearance, illustrated in Fig. 8, is very much simplified by it being tightly linked with the diabatic $1^1\Delta_u$ state. The PES has a single $C_{2v}$ minimum at $R_1 = R_2 = 2.41 a_0$, is free from cusps seen in other adiabatic PESs, and provides a nature’s illustration of the shape of the diabatic $1^1\Delta_u$ PES.

CI s at linearity can also be recognized in the potentials plotted in the $(R_1, \alpha_{\text{OCO}})$ plane. An example including four electronic states at $R_2 = 2.2 a_0$ is shown in Fig. 9. Although the characteristic features are no longer $C_{2v}$ symmetric, a maximum in the $2^1A'$ state at $\alpha_{\text{OCO}} = 180^\circ$ and $R_1 = 2.8 a_0$ and two minima in the $3^1A'$ state at $\alpha_{\text{OCO}} = 180^\circ$ and $R_1 = 2.3 a_0$ and $R_1 = 2.8 a_0$ are recognizable in panels (a) and (b). Close to linearity, the $A''$ states [panels (c) and (d)] maintain the same contour maps as $A'$ states.

**D. Intersections and avoided crossings in bent CO$_2$**

As CO$_2$ bends and all above degeneracies are removed, the primary topographic features (cusps, minima, and saddles) remain clearly visible up to $\alpha_{\text{OCO}} \sim 160^\circ$. This is demonstrated in the $(R_1, \alpha_{\text{OCO}})$ plane in Fig. 9 and in the $(R_1, R_2)$ plane in Fig. 10. Further decrease of $\alpha_{\text{OCO}}$ spawns new avoided crossings, a detailed map of which is given in the angular cuts in Figs. 3 and 4. All pairs of calculated states become near degenerate at various geometries. For example, the $\tilde{X}$ state forms avoided crossings successively with states $2^1A'$ at $\alpha_{\text{OCO}} = 100^\circ$ and $3^1A'$ at $\alpha_{\text{OCO}} = 80^\circ$ (Fig. 4). The state $3^1A''$ approaches closely $2^1A''$ at $\alpha_{\text{OCO}} \sim 120^\circ - 130^\circ$ and $1^1A''$ at $\alpha_{\text{OCO}} = 90^\circ$, and the states $1^1A''$ and $2^1A''$ cross between $70^\circ$
and 80°. Solid lines in Figs. 3 and 4 cross because they refer to the states locally diabatized through the ‘bent’ avoided crossings (see Sect. IV A). Potential curves of the states $3^1A'$ and $3^1A''$ bear evidence of strong interactions with the next higher states. Especially pronounced in Fig. 3(d,f) and Fig. 3(b,d) are the sharp near-intersections in $3^1A''$ around 155°.

As a result of multiple avoided crossings, local bent equilibria are found in all calculated states. The diabatic origin of a particular local minimum is invariably different from the adiabatic one. Consider the carbene-like bent OCO with $\alpha_{OCO} \sim 70°$ in Fig. 4(a). Purely adiabatically (solid dots), this minimum belongs to the ground electronic state. In the locally diabatic picture, bent OCO belongs the state $2^1A'$ (purple line). An avoided crossing between states $2^1A'$ and $3^1A'$, recognizable in panel (a) around $\alpha_{OCO} \sim 95°$, implies that another diabatization might re-assign the bent OCO minimum to the $3^1A'$ state (brown line). Furthermore, the broad barrier in $3^1A'$ near $\alpha_{OCO} \approx 140°$ indicates another avoided crossing with the next higher $A'$ state which thus would be the true owner of the bent OCO minimum. Similar analysis applies to the bent OCO in the $A''$ states in Fig. 4(b). Depending on the chosen representation, it can be ascribed to the fully adiabatic state $1^1A''$ (dots), to the locally diabatic state $3^1A'$ (brown line), or — via the sharp near-intersection around 155° — to the next higher $A''$ state. Other bent conformations in the excited states result from state interactions, too. One such isomer with the valence angle of 100° is created via an avoided crossing in $3^1A'$ [Fig. 3(c,e)]. Crossing of the same $3^1A'$ state with the next higher state between 60° and 70° leads to another high-energy bent minimum [Fig. 4(a,e)].

E. Beyond the first six states: Valence/Rydberg crossings

Many local barriers and minima in the states $3^1A'$ and $3^1A''$ are due to intersections with ‘invisible’ higher lying electronic states. Previous detailed ab initio studies exposed these ‘invisible’ intersection partners as mainly Rydberg states. The aim of this section is to illustrate how the Rydberg/valence interaction affects the potential profiles along the dissociation path and to outline the geometries at which valence states can effectively drain population from the Rydberg manifold. To this end, CASSCF calculations of the first 10 states, 1—5$^1A'$ and 1—5$^1A''$, have been performed with the d-aug-cc-pVQZ basis set for the CO bond distances $R_2 \in [1.7 \, a_0, 5.0 \, a_0]$ and the OCO bond angles $\alpha_{OCO} \in [100°, 179°]$. One CO bond is kept fixed at $R_1 = 2.4 \, a_0$, so that only CO + O arrangement channel is covered.
The CASSCF potentials along $R_2$ are shown in Fig. 11. All five $A''$ states and four $A'$ states converge to thresholds (1) or (3). The states correlating with the lowest threshold (1) are of $\Sigma^+$, $\Delta$, and $\Pi$ symmetry. The states correlating with the highest threshold (3) are $\Sigma^\pm$, $\Delta$, and $\Pi$. One $A'$ state converges towards the asymptote

$$\text{CO}_2 + h\omega(E_{\text{ph}} \geq 9.64 \text{ eV}) \rightarrow \text{O}^1(S) + \text{CO}(X^1\Sigma^+) \ .$$

(5)

At linearity, this state is the Rydberg state $1^1\Sigma_u^+(3\pi_u)\ [33]$ Compared to Fig. 1, many new avoided crossings are found in Fig. 11(a,b). The $D_{\infty h}$ notation of a state $|i\rangle$ in these panels is related to the expectation value $\langle i|L^2_z|i\rangle$ which a diabatic state preserves across the intersections. Potential curves in Fig. 11(a,b) are color coded according to the $\langle L^2_z \rangle$ values: $\Sigma$ states ($\langle L^2_z \rangle = 0$) are shown in green; $\Pi$ states ($\langle L^2_z \rangle = 1$) are blue, and $\Delta$ states ($\langle L^2_z \rangle = 4$) are red/orange. Clearly, most adiabatic curves change color more than once as the CO bond stretches: They are tailored out of several diabatic states.

Familiar from the discussion in Sect. III C are the fivefold crossings involving $1^1\Sigma_y^+(5\sigma_y)$ and the accidentally degenerate pair $1^1\Delta_u(2\pi_u)/1^1\Sigma_u^-(2\pi_u)$. These crossings are marked with arrows in Fig. 11(b). As in the MRD-CI calculations, the $\Delta_u/\Sigma_u^-$ pair is easily recognizable using matrix elements of $L_z$. At linearity, $\langle L^2_z \rangle$ for these two states is either 0 or 4, but already a tiny deviation of 2° causes $\langle L^2_z \rangle$ to collapse towards an average value of $\sim 2$. This state mixing is stressed in Fig. 11(a,b) with the $\Delta_u/\Sigma_u^-$ label and with the red/green color. The second edition of the mixed $\Delta_u/\Sigma_u^-$ pair is found around 11.5 eV. The Rydberg state $2^1\Delta_u(3\pi_u)$, shown with an orange line in Fig. 11(a,b), carries as a satellite the state $2^1\Sigma_u^-(3\pi_u)$ [green line in Fig. 11(b)]. Again, $\langle L^2_z \rangle$ for these states assumes a non-integer value between 1.5 and 2.5 in even slightly bent molecule.

The valence pair $1\Delta_u/1\Sigma_u^-$ converges towards the uppermost threshold (3) and successively traverses the higher lying states. The prominent dissociation barrier in the $3^1A'$ and $3^1A''$ states near $R_2 = 3.6 a_0$ is a clear signature of the sixfold valence/Rydberg crossing involving $1\Delta_u/1\Sigma_u^-$, the $1^1\Sigma_u^+$ state [green line in Fig. 11(a)] and a repulsive $R^1\Delta_u$ state [orange line in Fig. 11(a,b)]. $1^1\Sigma_u^+$ is the optically bright Rydberg state responsible for the strong absorption band around 11.1 eV (111.7 nm)\ [2] The state $R^1\Delta_u$ corresponds to a pair of strongly repulsive $^1A'/^1A''$ states descending towards threshold (1) from very high energies. Two sections of this repulsive potential curve are seen in Fig. 11(a,b) in the intervals $[3.2 a_0, 3.7 a_0]$ and $[3.7 a_0, 5.0 a_0]$. Thus, the asymptotic repulsive portions of the $3^1A'$ and
$3^1A''$ states diabatically belong to $R^1\Delta_u$. The sixfold crossing $1\Sigma_u^+/R^1\Delta_u/1\Delta_u/1\Sigma_u^-$ near $R_2 = 3.6 a_0$ is not the only one involving $R^1\Delta_u$ state. At higher energies and shorter CO bonds, $R^1\Delta_u$ intersects the Rydberg pair $2\Delta_u/2\Sigma_u^-$ (cf. Fig. 11(a,b) near $R_2 \approx 3.0 a_0$). The diabatic $R^1\Delta_u$ state distinctly stands out because it strictly preserves the projection $\langle L^2 \rangle \approx 4$ even for $\alpha_{OCO} = 165^\circ$, while $\langle L^2 \rangle$ values for the other states become non-integer.

The above discussion is valid for both $A'$ and $A''$ states. The $A''$ symmetry block in Fig. 11(b) contains one more state, namely the Rydberg state $2^1\Pi_g(6\sigma_g)$ missing among the $A'$ states where it would have been $6A'$. This state, materializing out of nowhere at $R_2 = 3.0 a_0$, is involved in the $R^1\Delta_u/2\Delta_u/2\Sigma_u^-$ crossing — making it a sevenfold intersection.

While the adiabatic gaps in the valence/valence intersection $1\Pi_g/1\Delta_u/1\Sigma_u^-$ grow as $\alpha_{OCO}$ deviates from $180^\circ$, all Rydberg/Rydberg and Rydberg/valence intersections not only remain recognizable in bent CO$_2$, but clearly sharpen up. This is illustrated in panels (c) — (f) of Fig. 11 drawn for $\alpha_{OCO} = 175^\circ$ and $160^\circ$. As a side result, the repulsive $R^1A'$ and $R^1A''$ states, deriving from $R^1\Delta_u$, remain distinct at all angles, despite new ‘bent’ intersections in the $3,4,5^1A'$ and $3,4,5^1A''$ states [see, for example, Fig. 11(e,f)]. Via these intersections, carbon dioxide excited with vacuum UV light can — at bent geometries — reach any of the shown dissociation channels. Although a detailed analysis of these multiple pathways is beyond the scope of the present work, a brief description of intersections involving the optically bright $^1\Sigma_u^+$ state is added at the end of this section.

Potential curves along $\alpha_{OCO}$ are shown in Fig. 12. The crossing patterns, especially numerous among $A''$ states, explain intricate topography of states $3^1A'$ and $3^1A''$ in Fig. 3. For example, the sharp barrier in the state $3^1A''$ at angles between $150^\circ$ and $170^\circ$ [Fig. 3(d,f) and Fig. 3(b,d)] originates from a complicated three state crossing around $165^\circ$ involving states $3,4,5^1A''$ [Fig. 12(b)]. Diabatically, the decreasing branch of the $3^1A''$ state at $\alpha_{OCO} < 160^\circ$ belongs to $4^1A''$ — the state which at linearity merges into the Rydberg pair $2\Delta_u/2\Sigma_u^-$. This diabatic state can be followed to even smaller angles through another intersection, this time with $2^1A''$ near $130^\circ$. Ultimately, as indicated with an arrow in Fig. 12(b), it is this diabatic state which the carbene-like OCO minimum belongs to. The avoided crossings in the $A'$ symmetry block are similar and simpler. The three state crossing of $3,4,5^1A''$ is a mere ghost because the adiabatic gap is almost 2 eV wide and the barrier in the $3^1A'$ state is broad and low. The state $4^1A'$, originating from $2^1\Delta_u$, stabilizes upon bending and is easily traced to smaller angles through the intersection with $3^1A'$ near $\alpha_{OCO} = 150^\circ$. Again, the
carbene-like OCO correlates diabatically with the state originating from $2^1\Delta_u$ at linearity.

The analysis of broadening and splittings in the strong absorption band of the Rydberg state $1^1\Sigma_u^+$ focused on the interactions of $1^1\Sigma_u^+$ with valence states.\cite{7,41,42} Present calculations reveal numerous avoided crossings with both valence and Rydberg states inside and outside the FC zone. At linearity, the $1^1\Sigma_u^+$ state cuts twice through the Rydberg state $2^1\Delta_u$ [Fig. 11(a)], and both crossings persist to smaller angles [Fig. 11(c,e)]. Another crossing occurs near $R_2 = 3.7\, a_0$ (for all calculated angles) and mixes $1^1\Sigma_u^+$ with $R^1\Delta_u$. This interaction strongly perturbs the ab initio $\langle L_z^2 \rangle$ values but vanishes beyond $R_1 = 4.0\, a_0$. The potential cut along $\alpha_{OCO}$ in Fig. 12(a) exposes another avoided crossing at $\sim 120^\circ$ which involves the states $4, 5^1A'$ and leads to a local minimum in $5^1A'$ (the state, correlating with $1^1\Sigma_u^+$ at these $R_{CO}$). Finally, the barrier in $5^1A'$ near $150^\circ$ implies interaction with the next higher state, which according to the analysis of Ref. 42 correlates with $2^1\Sigma_u^+$ at linearity. While all these crossings can redirect population from the optically bright $1^1\Sigma_u^+$ state along various linear and bent routes, Fig. 11 clearly demonstrates that the diabatic $1^1\Sigma_u^+$ state, calculated at the CASSCF level, is repulsive at all geometries and thus can dissociate directly.

**IV. QUASI-DIABATIZATION OF THE VALENCE STATES**

As explained in the Introduction, the diabatic representation\cite{45} although not generally indispensable, is best suited for the particular implementation of nuclear quantum dynamics used in paper II. Rigorously speaking, diabatization has to be performed simultaneously on all six calculated valence states, because each pair of states intersects either in the FC zone or at bent geometries. Simplifications to this ‘Herculean task’\cite{46} stem from the expectation that the two groups of intersections influence photodissociation in different ways: While the ‘bent’ CIs affect later stages of the product formation, the electronic branching ratios, and/or the rovibrational photofragment distributions,\cite{47} the ‘FC’ CIs are directly responsible for the shape of the observed absorption spectrum. This distinction guides the practical construction of the diabatic states: The ‘bent’ CIs and the ‘FC’ CIs are analyzed at two different levels of detail, commensurate with their expected impact on the absorption spectrum. As a result, the complete multistate problem splits into several steps and the need for a global diabatization of six multiply intersecting states is obviated.
A. Intersections at bent geometries: Local diabatization

The vicinity of ‘bent’ CIs is diabatized locally, using the energy-based scheme as described, for example, by Köppel. All considered CIs are shown in Figs. 3 and 4 and include

(a) the $\tilde{X}^1A'/2^1A'$ pair at $\alpha_{\text{OCO}} = 90^\circ - 110^\circ$;

(b) the $2^1A''/3^1A''$ pair at $\alpha_{\text{OCO}} = 120^\circ - 150^\circ$;

(c) the $1^1A''/3^1A''$ pair, with $3^1A''$ state diabatized in step (b), at $\alpha_{\text{OCO}} = 70^\circ - 100^\circ$.

The $\tilde{X}^1A'/2^1A'$ pair is considered as an example. At $C_{2v}$ geometries, these states belong to $A_1$ and $B_2$ irreps, so that their CI is ‘symmetry allowed’. Its branching space includes $\alpha_{\text{OCO}}$ as the tuning mode (irrep $A_1$) and the antisymmetric stretch $R_-$ as the symmetry breaking coupling mode (irrep $B_2$). The $2 \times 2$ diabatic potential matrix $V^d$ is constructed on the ab initio grid of bond distances ($R_1, R_2$) from the diagonal adiabatic potential matrix $V^a$ using the orthogonal adiabatic-to-diabatic transformation (ADT)

$$V^d = S^T V^a S,$$

with the transformation matrix $S$ parameterized by the mixing angle $\Theta$,

$$\Theta(R_1, R_2, \alpha_{\text{OCO}}) = -\frac{1}{2} \arctan \left( \frac{\alpha_{\text{OCO}} - \alpha^*_{\text{OCO}}(R_1, R_2)}{W_0(R_1, R_2)} \right),$$

which varies between 0 and $\pi/2$; $\alpha^*_{\text{OCO}}(R_1, R_2)$ denotes the crossing point of the diabatic potentials ($\Theta = \pi/4$); the width $W_0$ of the function $\Theta(\alpha_{\text{OCO}})$ is evaluated from the adiabatic energy gaps $\Delta V^a/2$ and the average slope of the diabatic potentials $\bar{F}$,

$$W_0 = \left. \frac{\Delta V^a}{2\bar{F}} \right|_{\alpha^*_{\text{OCO}}},$$

at each grid point $(R_1, R_2)$ for $\alpha^*_{\text{OCO}} = 100^\circ$. With the off-diagonal coupling in Eq. (6) neglected, the ground state $\tilde{X}^1A'$ becomes completely decoupled from other $A'$ states. The remaining diagonal matrix element in $V^d$ is the potential waiting to be further diabatized at linearity. The diabatization is kept local by restricting the interval, over which $\Theta(\alpha_{\text{OCO}})$ varies from 0 to $\pi/2$, to the vicinity of $\alpha^*_{\text{OCO}}$:

$$\tilde{\Theta}(R_1, R_2, \alpha_{\text{OCO}}) = g_1 \left[ g_2 \Theta(R_1, R_2, \alpha_{\text{OCO}}) + \frac{\pi}{2}(1 - g_2) \right],$$
The two switching functions \( g_{1,2}(\alpha_{\text{OCO}}) \):

\[
g_{1,2}(\alpha_{\text{OCO}}) = \left[ 1 + \exp\left( -(\alpha_{\text{OCO}} - \alpha_{1,2})/\lambda_{1,2} \right) \right]^{-1},
\]

with \( \alpha_1 = 95^\circ, \alpha_2 = 105^\circ, \) and \( \lambda_1 = -\lambda_2 = 5^\circ, \) are adjusted to restrict the diabatization to angles \( 90^\circ - 110^\circ. \) If \( (\alpha_1 - \alpha_2) \to 0 \) in \( g_{1,2}, \) the so-called ‘diabatization by eye’ is recovered, which corresponds to a relabeling of ab initio energies at the crossing angle \( \alpha_{\text{OCO}}^\star. \)

The main advantage of local diabatization, the results of which are shown in 1D in Figs. 3 and 4, is that smooth potentials are created for strongly bent geometries at relatively low cost. The quality of the resulting PESs in 2D, either in the \((R_1, R_2)\) or in the \((R_1, \alpha_{\text{OCO}})\) plane is illustrated for all states in Figs. 5, 8, 9, 10, and 13. For the lowest excited states in each symmetry block, \( 2^1A' \) and \( 1^1A'' \), the global bent equilibrium at 120° or 130° [Fig. 9(a,c)] is not affected by the local diabatization. In contrast, the carbene-like bent OCO minima change the owner: They appear in the state \( 2^1A' \) [local minimum near 70° barely visible in Fig. 9(a) but pronounced in Fig. 13(a)] and in the state \( 3^1A'' \) [Fig. 13(d)]. Barriers and local minima arising in the avoided crossings with Rydberg states are not diabatized within this scheme. Examples are the sharp barrier in \( 3^1A'' \) near 150° [Fig. 9(d) and Fig. 13(d)] and the deep local minimum in \( 3^1A' \) near 100° [Fig. 9(b) and Fig. 13(b)].

**B. Intersections at linear geometries: Regularized diabatic states**

In the second step, the CIs in the FC region are diabatized; kinematic singularities due to glancing intersections between \( A' \) and \( A'' \) states are not considered. Accurate diabatization schemes rely on direct numerical differentiation of the electronic wave functions with respect to nuclear coordinates or on the orbital rotation method as implemented in MOLPRO. Both types of calculations become prohibitively expensive with the d-aug-cc-pVQZ basis set, and further approximations are needed in order to find the diabatic potential matrix, consisting of a \( 2 \times 2 \) block of \( A' \) and a \( 3 \times 3 \) block of \( A'' \) states:

\[
V^d = \begin{pmatrix}
V_{\Delta'} & V_{\Pi',\Delta'} \\
V_{\Pi',\Delta'} & V_{\Pi'} \\
V_{\Sigma''} & V_{\Sigma''\Pi''} & V_{\Sigma''\Delta''} \\
V_{\Sigma''\Pi''} & V_{\Pi''} & V_{\Pi''\Delta''} \\
V_{\Sigma''\Delta''} & V_{\Pi''\Delta''} & V_\Delta''
\end{pmatrix}
\]
The five diagonal matrix elements are the five diabatic states $\Sigma''$, $\Pi'$, $\Pi''$, $\Delta'$, and $\Delta''$, with the smooth intersecting potentials in the $(R_1, R_2)\alpha_{\text{OCO}} = 180^\circ$ plane constructed to coincide at $\alpha_{\text{OCO}} = 180^\circ$ with the ab initio PESs for $1^1\Sigma^-$, $1^1\Pi_g$, and $1^1\Delta_u$, respectively. The semi-global diabatization scheme, akin to the vibronic coupling models and adjusted to the topography of the closed fivefold CI seam, has already been introduced in Ref. 3. Diabatization proceeds in two steps. First, a model diabatic matrix of the form Eq. (11) with elements $V_{ij}^{(0)}$ is constructed. Due to orbital degeneracy, $V_{\Pi'}^{(0)}(R_1, R_2) = V_{\Pi''}^{(0)}(R_1, R_2)$ and $V_{\Delta'}^{(0)}(R_1, R_2) = V_{\Delta''}^{(0)}(R_1, R_2)$. Moreover, the accidental near-degeneracy of states $1^1\Sigma_u^-$ and $1^1\Delta_u$ implies $V_{\Sigma u}^{(0)}(R_1, R_2) \approx V_{\Delta u}^{(0)}(R_1, R_2)$ in a broad vicinity of the closed CI seam — the property which substantially simplifies diabatization of $A''$ states. Deviations from linearity, measured by the coordinate $Q_u \sim \sin \alpha_{\text{OCO}}$, are included in the model via off-diagonal matrix elements represented as symmetry adapted expansions in $Q_u$:

$$V_{\Pi'\Delta'}^{(0)} = \sum_{k=0}^{N'} \alpha_k(R_1, R_2)Q_u^{2k+1}$$

$$V_{\Sigma'\Pi''}^{(0)} = V_{\Pi'\Delta''}^{(0)} = \sum_{k=0}^{N''} \beta_k(R_1, R_2)Q_u^{2k+1}.$$  

Couplings of the accidentally degenerate $\Sigma''$ and $\Delta''$ states to $\Pi''$ are set equal, while the matrix element $V_{\Sigma'\Delta''}^{(0)}$ for the RT-like $\Sigma''/\Delta''$ interaction is neglected. The model is complete after the expansion coefficients in $V_{ij}^{(0)}$ are calculated from a non-linear least-squares fit to ab initio energies. In the second step, the regularized diabatic states approach is invoked and the matrix elements $V_{ij}^{(0)}$ are used to define the orthogonal ADT matrix, which is applied to the adiabatic matrix $V^a$ via Eq. (6) giving the desired diabatic matrix elements of Eq. (11) on the full ab initio grid. Final interpolation is performed using 3D splines.

The diabatization is localized to the vicinity of the CI seam by modifying matrix elements $V_{ij}^{(0)}$ ($i \neq j$) in Eq. (12),

$$\tilde{V}_{ij}^{(0)} = \frac{V_{ij}^{(0)}}{1 + \exp\left(\frac{(\rho - \rho_0)/\lambda_0}{\lambda_0}\right)},$$

with $\rho = [(R_1 - 2.605 a_0)^2 + (R_2 - 2.605 a_0)^2]^{1/2}$ being a radial distance from the center of a circle enclosing the seam; $\rho_0 = 1.0 a_0$ and $\lambda_0 = 0.1$. Adiabatic and diabatic states are forced to coincide if either bond becomes longer than $\sim 3.8 a_0$, so that diabatization regions for linear and bent CIs are cleanly kept apart.
The constructed representation describes best the vicinity of linearity in which non-adiabatic transitions occur. The exact range of validity is determined by the length of the expansion in Eq. (12). The choice \( N' = N'' = 1 \) gives a model which fits ab initio data with a root mean square error of \( \sim 180 \text{ cm}^{-1} \) for angles \( \alpha_{\text{OCO}} \geq 150^\circ \). The ADT, constructed using this model, is guaranteed to remove kinematic singularities at the CIs, but leaves the strength of residual non-adiabatic couplings unspecified. The ultimate test of the scheme is the quantum mechanical absorption spectrum described in paper II. In order to assess the accuracy of the truncated \( Q_u \) expansion, three diabatic representations are constructed, based on the expansion coefficients obtained from fitting in three different angular ranges \( 180^\circ - 170^\circ \), \( 180^\circ - 160^\circ \), and \( 180^\circ - 150^\circ \). The corresponding absorption spectra are virtually identical. The spectra are also insensitive to small variations in \( \rho_0 \) and \( \lambda_0 \) in Eq. (14) — the modifications take place too far away from the crossing seam to affect nuclear dynamics.

Another test of the constructed ADT is given in Fig. 14, in which the model mixing angle \( \tilde{\Theta} \) for states \( 2, 3^{1}A' \) is compared with the ab initio one calculated using MOLPRO with a smaller cc-pVQZ atomic basis set. The dependence \( \tilde{\Theta}(R_1) \) on the CO bond length has a characteristic bell shape: The closed CI seam is intersected twice giving rise to the ascending and the descending branch. The curve \( \tilde{\Theta}(R_1) \) flattens out as \( \alpha_{\text{OCO}} \) decreases and CO\(_2\) leaves the degeneracy plane at \( 180^\circ \). Agreement between the model and the ab initio results is satisfying for all angles. A constant shift of \( 25^\circ \) applied to the ab initio mixing angle has no effect on the strength of non-adiabatic coupling proportional to \( \partial \tilde{\Theta}/\partial R_1 \).

One-dimensional cuts through the diabatic PESs (diagonal matrix elements corresponding to states \( 1^{1}\Pi_g \) and \( 1^{1}\Delta_u \)) are shown in Fig. 15. They cross at all geometries and can be directly compared with adiabatic states in Fig. 1. The off-diagonal coupling matrix elements are large in the intersection region vanishing off towards the asymptotic channels. Diabatic matrix elements are further illustrated in Fig. 16 in the \( (R_1, R_2) \) plane and in Fig. 17 in the \( (R_1, \alpha_{\text{OCO}}) \) plane. In all cuts, the diabatic PESs smoothly depend on internal coordinates. In the \( (R_1, R_2) \) plane, the off-diagonal diabatic coupling stays localized in the inner region. In contrast, the coupling along bending coordinate is delocalized across a substantial \( \alpha_{\text{OCO}} \) range in the \( (R_1, \alpha_{\text{OCO}}) \) plane. As a result, the angular shape of the diabatic potentials is distorted compared to the adiabatic case: Diabatic potentials along the coupling mode \( \alpha_{\text{OCO}} \) are close to the average adiabatic potential \( \frac{1}{2}(V_i^a + V_j^a) \).
V. CONCLUSIONS

This paper describes properties of global PESs of the first six singlet electronic states of CO$_2$ constructed from about 5000 symmetry unique ab initio points calculated with the d-aug-cc-pVQZ basis set using the MRD-CI method. The main results can be summarized as follows:

1. Calculations accurately reproduce the known benchmarks for all states and establish missing benchmarks for the future calculations: Bond distances and bond angles are accurate to within 0.1%, known fundamental frequencies (mainly ground state $\tilde{X}^1A'$) are accurate to within 1.5 cm$^{-1}$, the accuracy of the vertical excitation energies is expected to be better than 0.05 eV; dissociation energies agree with experimental thresholds within 0.15 eV for four covered arrangement channels.

2. Local equilibria are abundant in the calculated states. Bent OCO isomer is found in the adiabatic states $1, 3^1A'$ and $1, 3^1A''$. Linear COO is found in $1, 2^1A'$ and $1, 2^1A''$. Their diabatic electronic origin is clarified, and the properties, including equilibrium geometries, excitation energies, and vibrational frequencies, are established.

3. Near degeneracies can be found for each pair of six valence states, at linear or bent geometries, or at both. Avoided crossings and conical and glancing intersections literally shape the observed topography of the excited electronic states. Detected intersections are not limited to the valence manifold and the search for electronic origins of local minima and barriers involves valence/Rydberg and Rydberg/Rydberg intersections.

4. Characteristic for state intersections in CO$_2$, both conical and glancing, is that they include several states. In the FC region, a fivefold intersection between $1^1\Sigma_u^-$, $1^1\Pi_y$, and $1^1\Delta_u$ states is found. The seam of this intersection forms a closed loop, spectroscopic manifestations of which are discussed in paper II. Outside the FC region at linearity, six- and sevenfold intersections are predicted, some of which persist over extended angular range in the bent molecule.

5. Diabatic $6 \times 6$ potential matrix, with all elements smoothly depending on internal coordinates, is constructed using two-step local diabatizations of linear and bent conical intersections.
It is tempting to try to infer the course of photodissociation and the principal features of
the absorption spectrum — the outcome of a complicated quantum mechanical calculation
— from the constructed PESs alone. Two issues have to be resolved if one deals with five
interacting states. The first is the strength of diabatic (intra-symmetry) and RT (inter-
symmetry) coupling. If the off-diagonal vibronic coupling is weak, the diabatic potentials
should be chosen as ‘zeroth order guides’. If the vibronic coupling is strong, it is the adiabatic
description which becomes relevant — and the difference between the two pictures is striking,
especially along the bending angle as Figs. 9 and 17 demonstrate. As discussed in paper
II, the vibronic coupling is strong, the RT interaction between \( A' \) and \( A'' \) states is to a
large extent quenched, and the adiabatic potentials can be used for qualitative analysis.
The global minima of states \( 2^1A' \) or \( 1^1A'' \) are bent and lie \(~2.0\text{ eV} \) below the dissociation
threshold \([1]\) or \(~4.5\text{ eV} \) below the FC point. The route connecting the FC region with these
bent equilibria is barrierless. In contrast, there is a barrier to dissociation near linearity —
the leftover of the lower cone of the \( \Pi/\Delta \) CI. Thus, one expects the low energy bands in the
absorption spectrum, associated with \( 2^1A' \) and \( 1^1A'' \) states, to reflect highly excited bending
motion. This interpretation is commonly given in the literature.[5] Instead of dissociating
directly, the molecule bends first. With growing photon energy, the contribution of direct
dissociation through linear geometries will certainly grow, because the barrier is only about
0.2 eV high and is located \(~0.4\text{ eV} \) below the FC point. Above \(~9\text{ eV} \), the valence states \( 3^1A' \)
and \( 3^1A'' \) will contribute to the observed spectrum. These ‘linear’ states are separated from
the dissociation asymptote by a \(~1\text{ eV} \) high and broad barrier, with the implication that
\text{CO}_2 in these states can decay only through non-adiabatic interactions with the dissociation
continuum of the lower states. In other words, one expects to see a resonance-dominated
absorption spectrum. The next qualitative change in the absorption spectrum within the
valence manifold can be expected after the photon energy reaches the top of the dissociation
barrier in the upper valence states and allows direct dissociation from linearity.

The above discussion is based on 1D and 2D potential cuts and the data in Table [II]—
given the adiabatic representation is the adequate one. However, there is another important
piece of information still missing, namely the TDMs with the ground state. As has already
been mentioned in Sect. [III B], the electronic transitions in the wavelength range of 160 nm
— 120 nm are forbidden. The bands are observed only because the TDMs are not constant
but strongly change with molecular coordinates as one moves away from the high-symmetry
FC point. This dependence is a manifestation of the Herzberg-Teller effect[1] which plays the leading role in shaping the absorption bands, is at least as important as the potential profiles discussed above, and has to be considered on equal footing with the state intersections. The discussion of the coordinate dependence of the TDMs is deferred to paper II.

Acknowledgments

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43 CASSCF energies at $R_1 = 2.4\ a_0$, $R_2 = 5.0\ a_0$, and $\alpha_{\text{OCO}} = 179^\circ$, relative to the minimum of the $\tilde{X}^1A'$ curve, are $E_e \approx 7.1\ eV$, $8.9\ eV$, and $11.2\ eV$ for channels (3), (4), and (7), respectively.
Note that the avoided Rydberg/valence crossings between $1, 2^1\Delta_u$ and $1, 2^1\Sigma_u^-$ states, investigated in Ref. [41] lie outside the cuts shown in Fig. 11.

Whenever ‘diabatic representation’ is mentioned, a quasi-diabatic representation\cite{42} in which the kinematic singularities and the potential cusps at the intersections are removed, is meant.

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TABLE I: Properties of the adiabatic ground electronic state $\tilde{X}^1\Sigma_g^+$: The OCO bond angle ($\alpha_{OCO}$, in $^\circ$), CO and OO bond distances (in $a_0$), and the energy $\Delta E$ relative to the global minimum (in eV, including the vibrational ZPE corrections), calculated for three equilibrium geometries and the two arrangement channels.

| Geometry       | $\alpha_{OCO}$ | $R_{CO,1}$ | $R_{CO,2}$ | $R_{OO}$ | $\Delta E^a$ | Reference |
|----------------|----------------|------------|------------|----------|--------------|-----------|
| OCO linear     | 180.0          | 2.1991     | 2.1991     | 4.3982   | 0.0          | this work |
|                | 180.0          | 2.2050     | 2.2050     | 4.4100   | 0.0          | 24        |
|                | 180.0          | 2.1924     | 2.1924     | 2.3848   | 0.0          | [9,10]    |
|                | 180.0          | 2.1960     | 2.1960     | 4.3920   | 0.0          | 20        |
| OCO bent       | 73.2           | 2.51       | 2.51       | 2.99     | 5.90         | this work |
|                | 72.9           | 2.52       | 2.52       | 2.99     | 6.04         | 24        |
|                | 73.1           | 2.53       | 2.53       | 3.01     | 5.97$^c$     | 23        |
| COO linear     | 0.0            | 2.20       | 4.65       | 2.45     | 7.35$^c$     | this work |
|                | 0.0            | 2.20       | 4.65       | 2.45     | 7.14         | 24        |
|                | 0.0            | 2.17       | 5.37       | 3.20     | 6.86         | 23        |
| O($^1D$)+CO($\tilde{X}^1\Sigma^+$) | —            | 2.14       | $\infty$  | $\infty$ | 7.28         | this work |
|                | 2.175          | $\infty$  | $\infty$  | 7.64     | 24        |
|                | 2.132          | $\infty$  | $\infty$  | 7.41     | [4,28]$^b$ |
| C($^3P$)+O$_2$($\tilde{X}^3\Sigma_g^-$) | —            | $\infty$  | $\infty$  | 2.30     | 11.35       | this work |
|                | $\infty$       | $\infty$  | 2.356      | 11.49    | 24        |
|                | $\infty$       | $\infty$  | 2.283      | 11.52    | 4$^b$      |

$^a$The ab initio ZPEs are: ZPE(CO$_2$) = 0.314 eV, ZPE(CO) = 0.130 eV, and ZPE(O$_2$) = 0.095 eV.
$^b$Experimental values.
$^c$Energy without ZPE correction.
TABLE II: Energies (in cm$^{-1}$) of the low lying vibrational states in the ground electronic state $\tilde{X}^1\Sigma_g^+$, measured relative to the ground level (0,0,0). The states calculated with the original ab initio potential (‘PES1’) and with the potential rescaled along the symmetric stretch and the bend (‘PES2’) are compared with the best theoretical estimates of Refs. [18, 19] and with the experimental values of Ref. [17] (denoted ‘Exp’). The energy difference $E_{\text{observed}} - E_{\text{calculated}}$ (in cm$^{-1}$) is shown in parenthesis. The quantum numbers $(v_s, v_b, v_a)$ are defined in text.

| State     | Refs. [18, 19] | PES1     | PES2     | Exp  |
|-----------|----------------|----------|----------|------|
| (0, 0, 0)$^a$ | 0.0            | 0.0      | 0.0      | 0.0  |
| (0, 1, 0)   | 669.1 (-1.7)   | 668.6 (-1.2) | 670.3 (-2.9) | 667.4 |
| (1, 0, 0)   | 1288.9 (-3.5)  | 1265.3 (20.1) | 1284.1 (1.3) | 1285.4 |
| (0, 2, 0)   | 1339.6 (-4.5)  | 1336.6 (-1.5) | 1336.8 (-1.7) | 1335.1 |
| (0, 2, 0)   | 1389.3 (-1.1)  | 1373.5 (14.7) | 1389.2 (-1.0) | 1388.2 |
| (1, 1, 0)   | 1938.0 (-5.5)  | 1913.2 (19.3) | 1933.4 (-0.9) | 1932.5 |
| (0, 3, 0)   | 2011.4 (-8.2)  | 2005.9 (-2.7) | 2006.1 (-2.9) | 2003.2 |
| (0, 3, 0)   | 2080.0 (-3.1)  | 2061.7 (15.2) | 2079.6 (-2.7) | 2076.9 |
| (0, 0, 1)   | 2349.2 (0.0)   | 2350.6 (-1.4) | 2351.4 (-2.2) | 2349.2 |
| (1, 2, 0)   | 2552.0 (-8.6)  | 2516.4 (27.0) | 2549.5 (-6.1) | 2543.4 |
| (2, 0, 0)   | 2676.3 (-5.2)  | 2626.0 (45.1) | 2668.3 (2.8) | 2671.1 |
| (0, 4, 0)   | 2809.1 (-12.0) | 2761.8 (35.3) | 2790.2 (6.9) | 2797.1 |
| (1, 2, 0)   | 2589.8 (-4.7)  | 2581.6 (3.5) | 2585.1 |

$^a$The energy difference between the ground vibrational level and the potential minimum is 2516 cm$^{-1}$ for PES1 and 2533 cm$^{-1}$ for PES2. The ZPE = 2508.5 cm$^{-1}$, given in the NIST database [20] is evaluated from the fundamental frequencies via $\omega_b + \frac{1}{2}(\omega_a + \omega_s)$. For PES1 and PES2, this value is 2503.6 cm$^{-1}$ and 2512.5 cm$^{-1}$, respectively.
TABLE III: Properties of the PESs of the first five excited singlet states of CO$_2$; Vertical excitation energy $T_v$ (in eV); band origin $T_0$ (in eV), which includes ZPEs of the ground and the excited electronic states; equilibrium CO bond lengths $R_{1,e}$ and $R_{2,e}$ (in $a_0$); equilibrium OCO bond angle $\alpha_e$ (in $^\circ$); quantum mechanical vibrational frequencies $\omega_s$, $\omega_a$, and $\omega_b$ near equilibrium (in cm$^{-1}$); quantum mechanical dissociation thresholds $D_0$(O/CO) and $D_0$(C/O2) in the O+CO and C+O$_2$ arrangement channels, respectively (in eV).

| Property | $1^1A''^a$ | $2^1A'^a$ | $2^1A''$ | $3^1A'^b$ | $3^1A''b$ |
|----------|-------------|------------|-----------|------------|------------|
| $C_s$    | $1^1\Pi_g$  | $1^1\Pi_g$ | $^1\Sigma_{-u}$ | $^1\Delta_u$ | $^1\Delta_u$ |
| $D_{acch}$ | $1^1\Pi_g$  | $1^1\Pi_g$ | $^1\Sigma_{-u}$ | $^1\Delta_u$ | $^1\Delta_u$ |
| O+CO channel$^c$ | $^1D/1\Sigma$ | $^1D/1\Sigma$ | $^3P/3\Pi$ | $^1D/1\Sigma$ | $^1D/1\Sigma$ |
| C+O$_2$ channel$^c$ | $^1D/1\Delta$ | $^1D/1\Delta$ | $^1D/1\Delta$ | $^3P/3\Sigma$ | $^3P/3\Sigma$ |
| $T_0$    | 5.36        | 5.39       | 7.95      | 8.67       | 8.67       |
| $T_v$    | 8.92        | 8.92       | 8.79      | 9.16       | 9.17       |
| $T_v$, Refs. $^{[10]}$ | 9.00        | 9.00       | 9.19      | 9.28       | 9.28       |
| $R_{1,e}$ | 2.37        | 2.36       | 2.41      | 2.25       | 2.25       |
| $R_{2,e}$ | 2.37        | 2.36       | 2.41      | 2.80       | 2.80       |
| $R_e$, Ref.$^{[9,10]}$ | 2.38        | 2.38       | 2.40      | 2.29       | 2.29       |
| $\alpha_e$ | 127.3     | 117.9      | 176.0     | 180.0      | 180.0      |
| $\alpha_e$, Ref.$^{[10]}$ | 127.0       | 117.8      | 180.0     | 180.0      | 180.0      |
| $\omega_s$ | 1283        | 1340       | 1015      | 520        | 550        |
| $\omega_a$ | 905         | 865        | 1118      | 1560       | 1550       |
| $\omega_b$ | 670         | 580        | 577       | 2290       | 3100       |
| $D_0$(O/CO)$^d$ | 7.27        | 7.27       | 11.31     | 7.27       | 7.27       |
| $D_0$(C/O2)$^d$ | 11.34       | 11.34      | 13.59     | 13.59      | 13.59      |

$^a$Experimental data from Ref.$^{[10]}$ are: For $^1^1A''$ $R_e = 2.28 \pm 0.02\ a_0$, $\alpha_e = 129 \pm 1^\circ$, $T_0 \leq 6.2\ eV$, $\nu_b \approx 632\ cm^{-1}$; for $^2^1A'$ $R_e = 2.35 \pm 0.015\ a_0$, $\alpha_e = 122 \pm 2^\circ$, $T_0 \approx 5.7\ eV$, $\nu_b \approx 600\ cm^{-1}$.

$^b$For the $^3^1A'$ and $^3^1A''$ states, the geometries refer to the local minimum in the FC region. The vibrational frequencies are strongly perturbed by CI cusps, and the corresponding ZPEs are omitted in $T_0$.

$^c$Dissociation thresholds, labeled with electronic states of atomic/diatomic fragment, are correlated with the diabatic states of CO$_2$.

$^d$Experimental dissociation thresholds are given in Eqs.$^{[1]}$, $^{[2]}$, $^{[3]}$, and $^{[4]}$. Ab initio ZPEs are: ZPE[CO$_2$(\tilde{X}^1\Sigma_g^+)] = 0.314\ eV; ZPE[CO(\tilde{X}^1\Sigma_g^+)] = 0.130\ eV; ZPE[CO(a^3\Pi)] = 0.099\ eV; ZPE[O$_2$(\tilde{X}^3\Sigma_g^-)] = 0.095\ eV; ZPE[O$_2$(\tilde{1}\Delta_g)] = 0.080\ eV.
FIG. 1: Cuts through the PESs of the states 1, 2, 3;1$A'$ (a,c,e) and 1, 2, 3;1$A''$ (b,d,f) along one CO bond distance $R_{CO}$. The second CO bond is fixed at 2.2$a_0$; the fixed bond angle is indicated in each panel. Dots are the ab initio adiabatic energies. Solid lines are states diabatized at bent CIs as described in Sect. [IV.A] For $A''$ states, the ground electronic state $\tilde{X}1A'$, shown with gray dots, sets the vertical energy scale. At linearity, components of the same orbitally degenerate state $\Pi_g$ or $\Delta_u$ have the same color in panels (a) and (b).

FIG. 2: Cuts through the PESs of the states 1, 2, 3;1$A'$ (a,c,e) and 1, 2, 3;1$A''$ (b,d,f) along one CO bond distance $R_{CO}$. The fixed bond angle is indicated in each panel. The second CO bond is fixed at 2.2$a_0$ in (a-d). In (e) and (f), the OO bond is kept fixed at 2.3$a_0$. Dots are the ab initio adiabatic energies. Solid lines are states diabatized at bent CIs as described in Sect. [IV.A] For $A''$ states, the ground electronic state $\tilde{X}1A'$, shown with gray dots, sets the vertical energy scale.

FIG. 3: Cuts through the PESs of the states 1, 2, 3;1$A'$ (a,c,e) and 1, 2, 3;1$A''$ (b,d,f) along bond angle $\alpha_{OCO}$. The two CO bonds are fixed, one at 2.2$a_0$ and the other as indicated in each panel. Dots are the ab initio adiabatic energies. Solid lines are states diabatized at bent CIs as described in Sect. [IV.A]

FIG. 4: Cuts through the PESs of the states 1, 2, 3;1$A'$ (a,c,e) and 1, 2, 3;1$A''$ (b,d,f) along bond angle $\alpha_{OCO}$. The difference with Fig. 3 is that one CO bond is fixed at 2.5$a_0$.

FIG. 5: Contour maps of the ground electronic state $\tilde{X}1A'$: $(R_1, R_2)$ plane, with $\alpha_{OCO}$ fixed at 179° (a) and 70° (b), and $(R_1, \alpha_{OCO})$ plane with $R_{CO}$ fixed at 2.2$a_0$ (c) and 2.6$a_0$ (d). Energy of the dotted contour in (a), (c), and (d) is 2.1 eV, in (b) it is 8.4 eV. Contour spacing is 0.35 eV.

FIG. 6: Contour maps in the $(R_1, R_2)$ plane of the adiabatic states 2;1$A'$ (a) and 3;1$A'$ (b) for $\alpha_{OCO} = 179^\circ$. The states are components of 1;1$\Pi_g$ and 1;1$\Delta_u$, respectively. Black solid line in each panel indicates the closed CI seam for $A'$ (a) and $A''$ (b) symmetry states. Black dashed line in (a) shows the path along which the matrix elements $\left|iA''|\hat{L}_z|jA'\right|$ in Fig. 7 are calculated. Energy of the dotted contour is 7.5 eV, and the contour spacing is 0.25 eV.
FIG. 7: MRD-CI matrix elements of $\hat{L}_z$, $|iA''|\hat{L}_z|jA'|$, for electronic state pairs $(i = 1, j = 2)$ (black), $(i = 2, j = 2)$ (purple), $(i = 3, j = 2)$ (brown), and $(i = 3, j = 3)$ (red) calculated as functions of the CO bond distance $R_1$ for $R_2 = 2.2 a_0$ and $\alpha_{OCO} = 179^\circ$ along the dashed line shown in Fig. [6].

FIG. 8: Contour maps of the adiabatic state $2^1 A''$: $(R_1, R_2)$ plane, with $\alpha_{OCO}$ fixed at $179^\circ$ (a) and $70^\circ$ (b), and $(R_1, \alpha_{OCO})$ plane with $R_{CO}$ fixed at $2.2 a_0$ (c) and $2.6 a_0$ (d). Energy of the dotted contour in (a), (c), and (d) is 9.0 eV, in (b) it is 12.5 eV. Contour spacing is 0.25 eV.

FIG. 9: Contour maps in the $(R_1, \alpha_{OCO})$ plane of the adiabatic states $2^1 A'$ (a), $3^1 A'$ (b), $1^1 A''$ (c), and $3^1 A''$ (d). The second CO bond is fixed at $2.2 a_0$. Energy of the dotted contour is 7.6 eV, and the contour spacing is 0.20 eV.

FIG. 10: Contour maps in the $(R_1, R_2)$ plane of the adiabatic states $2^1 A'$ (a), $3^1 A'$ (b), $1^1 A''$ (c), and $3^1 A''$ (d). The angle $\alpha_{OCO}$ is fixed at $160^\circ$. Energy of the dotted contour is 8.0 eV, and the contour spacing is 0.25 eV.

FIG. 11: CASSCF energies of the electronic states 1—5$^1 A'$ (a,c,e) and 1—5$^1 A''$ (b,d,f) along one CO bond distance $R_{CO}$. The second CO bond is fixed at $2.4 a_0$: the fixed bond angle is indicated in each panel. In all panels, dots and solid lines denote adiabatic energies. In panels (a) and (b), lines are color coded according to the ab initio $\langle L_z^2 \rangle$ values as explained in text. Following a particular color, one follows a diabatic state. Diabatic assignments using spectroscopic symbols are given. Arrows in panel (b) indicate the $\Delta/\Pi$ CIs discussed in Sect. III.C. For $A''$ states, the ground electronic state $\tilde{X}^1 A'$, shown with gray dotted line, sets the vertical energy scale.

FIG. 12: Adiabatic CASSCF energies of states 1—5$^1 A'$ (a) and 1—5$^1 A''$ (b) along the bond angle. Fixed CO bond distances are $2.4 a_0$ and $2.5 a_0$. The two uppermost states in each symmetry block are drawn gray. Arrow indicates direction towards the carbene-like OCO minimum in the given state. Correlation with the diabatic states at linearity is marked to the right of each panel.

FIG. 13: Contour maps in the $(R_1, \alpha_{OCO})$ plane of the adiabatic states $2^1 A'$ (a), $3^1 A'$ (b), $1^1 A''$ (c), and $3^1 A''$ (d). The second CO bond is fixed at $2.6 a_0$. Energy of the dotted contour is 9.0 eV, and the contour spacing is 0.20 eV.
FIG. 14: The mixing angle $\tilde{\Theta}$ for the states $2,3^1A'$ calculated as a function of one CO bond distance. Solid lines and open circles denote $\tilde{\Theta}$ from the regularized diabatic states model of Eqs. (12)–(14). Solid squares are the values obtained using quasi-diabatization procedure in MOLPRO. The second CO bond is fixed at $R_1 = 2.2 a_0$; the bond angle $\alpha_{\text{OCO}}$ is indicated in each panel. The ab initio mixing angle, obtained with the cc-pVQZ basis set, is lifted by $25^\circ$.

FIG. 15: Diabatic potentials (diagonal matrix elements) for the $\Sigma$ (green), $\Pi$ (blue), and $\Delta$ (red) states and the off-diagonal couplings (black solid line) as functions of one CO bond distance. $A'$ ($A''$) states are shown in the left (right) panels. The second CO bond is fixed at $2.2 a_0$; the fixed bond angle is indicated in each panel. Black dashed line indicates the ground electronic state.

FIG. 16: The diabatic potentials $V_{\Pi'}$ (a), $V_{\Pi''}$ (b), and $V_{\Delta''}$ (d), and the off-diagonal coupling elements $V_{\Pi'\Delta'}$ (e) and $V_{\Pi''\Delta''}$ (f) in the $(R_1, R_2)$ plane with the bond angle fixed at $175^\circ$. Energy of the dotted contour in (a), (b), (c), and (d) is 7.5 eV, and the contour spacing is 0.25 eV. In (e) and (f), the respective numbers are -0.3 eV and 0.05 eV.

FIG. 17: The diabatic potentials $V_{\Pi'}$ (a), $V_{\Pi''}$ (b), and $V_{\Delta''}$ (d), and the off-diagonal coupling elements $V_{\Pi'\Delta'}$ (e) and $V_{\Pi''\Delta''}$ (f) in the $(R_1, \alpha_{\text{OCO}})$ plane with the CO bond fixed at $2.2 a_0$. Energy of the dotted contour in (a), (b), (c), and (d) is 8.6 eV, and the contour spacing is 0.20 eV. In (e) and (f), the respective numbers are -1.20 eV and 0.20 eV.
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 6
Fig. 7
Fig. 9
Fig. 10
Fig. 12
Fig. 13
Fig. 15
Fig. 16
Fig. 17