

Stability properties of CO₂²⁺

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LETTER TO THE EDITOR

Stability properties of CO_2^{2+}

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Abstract. The carbon dioxide molecular dication is investigated by multireference configuration interaction computations. Whereas the system is found to be unbound by $D_e = -5.12$ eV with respect to fragmentation into $\text{CO}^+(^2\Sigma^+) + \text{O}^+(^4S_u)$, the ground-state potential energy surface of CO_2^{2+} enjoys a local minimum for a collinear symmetric configuration where the carbon nucleus is centred between the outer two oxygen nuclei (with internuclear separation $R_{\text{C-O}} = 1.22$ Å). Potential barriers larger than 1 eV render the corresponding electronic ground state $^3\Sigma_g^-$ metastable against dissociative tunnelling. For the lowest seven excited states and system configurations restricted to linear symmetric geometries, potential energy curves are presented and compared with the experimental double ionization spectrum of CO_2 in the Franck–Condon region.

The doubly positively charged carbon dioxide molecular ion belongs to those dications most frequently studied in experiments [1–13]. The available information is based on a variety of experimental methods (double photon and electron impact ionization, charge transfer, single electron capture, Auger spectroscopy, charge separation mass spectrometry, in conjunction with various coincidence techniques), and includes data on appearance energies of numerous states, dissociation thresholds, ion branching ratios and lifetimes. In contrast, up till now the CO_2^{2+} system has only received surprisingly little theoretical consideration. Early treatments by Kelber *et al.*, Ågren and Laramore [14] use the one-electron approximation, SCF and restricted CI methods for the calculation of Auger transition intensities and energies. Millie *et al.* [6] computed the vertical Franck–Condon excitation spectrum $\text{CO}_2 \rightarrow \text{CO}_2^{2+} + 2e^-$ up to ≈ 12 eV above the lowest CO_2^{2+} energy, employing a variant (CIPSI) of polarization CI techniques. All these previous calculations, however, were performed for a fixed system geometry, i.e. the equilibrium configuration of CO_2 . None of these theoretical publications provides information on potential energy curves (PECs) or, in particular, on the experimentally observed metastability of CO_2^{2+} . This lack of data motivated the present study.

An inspection of the available experimental and theoretical energies shows that the lower part of the electronic spectrum of CO_2^{2+} is governed by a high density of closely spaced electronic states. Generation of potential energy surfaces (PESs) for all these states is an extended project [15] consuming an immense amount of computational resources. Here, we will restrict our attention to the ground-state PES and to some excited (but confined to linear symmetric geometries) states of CO_2^{2+} . Since from the outset numerous configurations are anticipated to enter the CO_2^{2+} wavefunctions, we chose the MRDCI (multireference single and double excitation configuration interaction) procedure [16] for our computations. Two different Gaussian basis sets were employed; basis I is of type (13s7p1d/8s4p1d) for both the

C and O atomic centres and contains the same orbitals as the basis set applied by Levasseur *et al* [17] in their investigation of CO^{2+} . Basis II is constructed by supplementing the orbitals for C and O given by Lie and Clementi [18] in their tables A5 and A7, respectively, by additional *s*-polarization functions (exponents $\zeta_{\text{C}} = 0.035$, $\zeta_{\text{O}} = 0.075$) and is of the form (14s8p2d/8s4p2d). In total, basis I includes 120 uncontracted or 84 contracted, and basis II 150 uncontracted or 96 contracted Gaussians. In the CI procedure, all electrons were considered and no core electrons frozen. As expected, a relatively large number of main reference configurations (30–60) was necessary to guarantee a satisfactory contribution $\sum_n c_n^2 \approx 0.9 \pm 0.02$ in the CI wavefunctions. Selection thresholds for the CI matrix were specified in the range between 4 and 8 $\mu\text{hartree}$. Contributions to the CI energies from higher than double excitations are estimated by the generalized Davidson procedure [19].

The lowest energies of CO_2^{2+} occur for a triplet state. As a result of our computations, in figure 1 part of the lowest triplet PES with C_{ov} symmetry (i.e. for collinear nuclear configurations) is depicted. In figure 1, the existence of a (local) minimum is obvious. This minimum is assumed for a geometry where the nuclei are arranged along a linear chain O–C–O with equal separations $R_{\text{C-O}} = R_e$ between O and C, corresponding to the electronic state ${}^3\Sigma_g^-$. Our computation predict $R_e = 2.28$ and $2.29 a_0$ (basis I and II, respectively) from the Davidson-uncorrected energies, or $R_e = 2.31 a_0$ (basis I and II) from the Davidson-corrected values. This critical point of the C_{ov} -PES at R_e also remains a (local) minimum (and does not turn into a saddle point) if the system geometry is no longer confined to a linear one, as illustrated in the case of bending deformations by the broken curve in the inset in figure 2.

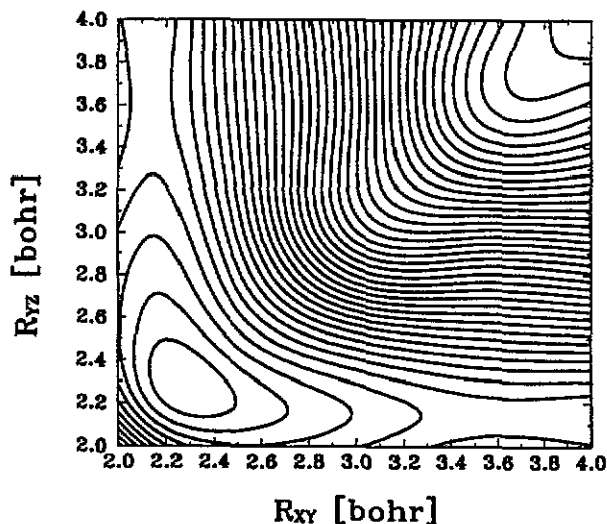


Figure 1. Contour lines $E(R_{XY}, R_{YZ}) = E_0 + n\Delta_E$, $n = 0, 1, 2, \dots, 40$, of the lowest triplet C_{ov} PES of CO_2^{2+} . Here $R_{ij} := |R_i - R_j|$ denotes the internuclear distance, with R_X, R_Z being the positions of the O nuclei, and R_Y representing the position of the C nucleus. The contour lines are constructed from the Davidson-corrected energies from basis I, starting at $E_0 = -186.965$ hartree (innermost contour) and increasing by $\Delta_E = 10$ mHartree.

Whereas the contours in figure 1 reveal a clearly visible dissociation channel for which one of the C–O distances increases while the other one shrinks to $R_{\text{C-O}} \approx 2.1 a_0$, the local character of the observed minimum cannot be inferred from the restricted range of figure 1. The metastability becomes fully evident from the cross section of the C_{ov} -PES plotted in figure 2 with one of the distances fixed at $R_{\text{C-O}} = 2.12 a_0$. In a complementary calculation on CO^+ , this distance $R_{\text{C-O}} = R_e(\text{CO}^+(X^2\Sigma^+))$ was obtained as the equilibrium position of the CO^+ ground state $X^2\Sigma^+$ (experimental value: $2.107 a_0$ [20]). Hence, this curve in figure 2 represents the energy behaviour when an O^+ ion approaches ground-state CO^+ .

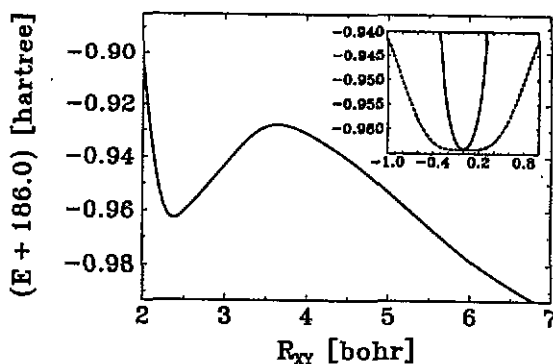


Figure 2. PECS (Davidson-corrected energies from basis I) for triplet CO_2^{2+} . The situation of $\text{C}_{\infty\infty v}$ geometry with subsystem CO fixed at $R_{YZ} = 2.12 a_0$ with the other O nucleus moving from $R_{XY} = 2.0$ to $7.0 a_0$ is shown. Inset, full curve: $\text{C}_{\infty\infty v}$ geometry, both outer O nuclei fixed at $R_{XZ} = 2R_e$, the C nucleus varying between $R := R_{XY} - R_e = -1.0$ and $+1.0 a_0$ (asymmetric stretching). Inset, broken curve: C_{2v} geometry, fixed distances $R_{XY} = R_{YZ} = R_e$, whereas $|R_{\perp}| := |R_Y - (R_X - R_Z)/2|$ (= distance from the C nucleus to the centre of the line between the O nuclei) varies from -1.0 to $+1.0 a_0$ (bending); this corresponds to a variation of the bond angle between -128° and $+128^\circ$.

Its shape is characteristic for metastable molecular systems [21], with a well separated by a barrier from the energetically lower asymptotic configuration. The barrier height for the situation of figure 2 is given by 1.08 (Davidson-uncorrected) and 1.00 eV (Davidson-corrected), and, as a good approximation of the transition state, these values should also render the minimal barrier height that separates the minimum of figure 1 from the dissociated system. A schematic overview of the asymptotic fragmentation channels into diatomic plus atomic subsystems is assembled in figure 3. With respect to the lowest asymptotic state, i.e. $\text{CO}^+(\text{X}^2\Sigma^+) + \text{O}^+(\text{^4S}_u)$, the metastable ${}^3\Sigma_g^-$ minimum of CO_2^{2+} is unbound by $D_e = -5.65$ and -5.62 eV (basis I and II, respectively, Davidson-uncorrected) or by -5.12 eV (basis I or II, Davidson-corrected).

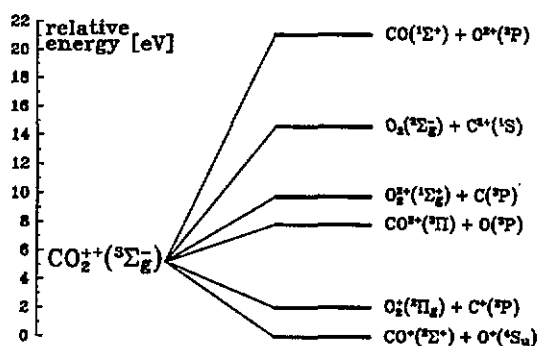


Figure 3. Possible fragmentation channels of CO_2^{2+} . Since neither CO^{2+} nor O_2^{2+} have true bound states, the asymptotic energies $\text{C}^+(\text{^2P}) + \text{O}^+(\text{^4S}_u)$ and $\text{O}^+(\text{^4S}_u) + \text{O}^+(\text{^4S}_u)$ fix the levels of CO_2^{2+} and O_2^{2+} , respectively. If the lowest metastable configuration of these systems is to be considered, the corresponding levels have to be lifted by 5.89 and 3.92 eV. Not shown are subchannels associated with excited states, as e.g. $\text{CO}^+(\text{^2Pi}) + \text{O}^+(\text{^4S}_u)$ at 2.57 eV.

The reported experimental dissociation thresholds (relative to the appearance energy of CO_2^{2+}) of 1.4 ± 0.5 eV [6] or 1.6 ± 0.3 eV [13] are somewhat larger than the minimal barrier resulting from our computations. For the tunnelling probability and thus for the lifetime of the system, more important than the barrier heights are the barrier widths. Figures 1 and 2 show that for energies not too much above the equilibrium $E(R_e)$ the

minimal barrier width is given by $\approx 2 a_0$. For its vibrational (and rotational) ground state, tunnelling dissociation of $^{16}\text{C}^{18}\text{O}_2^{2+}$ should be negligible, and a WKB estimate confirms that for the lowest vibronic level CO_2^{2+} is practically stable (lifetime $> 10^{10}$ s). However, similar to other metastable molecular dications [21], for vibrational motion above the zero-point energy the transmission coefficient through the barrier increases exponentially and the lifetime decreases correspondingly as the vibronic (resonance) levels converge to the barrier top. Experimental lifetimes vary from 0.9 to 21.6 μs [2, 5, 11], indicating that in these measurements probably CO_2^{2+} in excited vibronic (or electronic) states has been observed. The extremely broad range of possible lifetimes as a function of the vibronic excitation may also explain the conclusions drawn by Field and Eland [11], namely that CO_2^{2+} does not have a single characteristic lifetime, but instead at least three different mean lifetimes (in the 'stable', metastable and unstable range) would be necessary to model the measured data.

By ionizing CO_2 , appearance energies E_a of CO_2^{2+} have been measured in a great number of experiments. Values for E_a determined via electron impact ionization vary between 36.4 and 38.6 eV [1, 2], while photoionization yields E_a from 36.2 to 37.7 eV [4, 6, 12, 13]. The appearance energies obtained by double charge transfer are almost identical, i.e. 37.7 eV [8, 10] and 37.8 eV [9]; a SEC (single electron capture) experiment leads to $E_a = 37.4$ eV [7] (the error bars of the experimental E_a range from ± 0.1 to ± 0.5 eV). The vertical transition energies $T_v(\text{CO}_2(^1\Sigma_g^+), \text{CO}_2^{2+}(^3\Sigma_g^-))$ at $R_e(\text{CO}_2(^1\Sigma_g^+))$ can be considered as a theoretical quantity relevant for comparison with E_a . Previous T_v values were computed by Millie *et al* [6], yielding the CIPSI result $T_v = 36.7$ eV, and by Langford *et al* [10] whose MP2 calculations produced 37.58 and 38.51 eV (depending on the basis set). To derive a MRDCI result for T_v , we employed basis I and II to compute the ground-state energy of CO_2 at its (approximate) equilibrium $R_e = 2.20 a_0$. The obtained (Davidson-corrected) values -186.3004 (basis I) and -186.3414 hartree (basis II) bracket the total energy -186.31141 hartree reported by Knowles *et al* [22] in their MRCI investigation of CO_2 with a (5s5p4d1f) basis set. The resulting vertical transition energies $T_v = 36.7$ (Davidson-uncorrected) and 36.9 eV (Davidson-corrected) from basis II are ≈ 0.3 eV higher than those from basis I, but, nonetheless, similarly to the CIPSI T_v , still lower than most of the experimental E_a . This discrepancy might indicate a lack of computational accuracy; however, one can also imagine other reasons. One possibility could be that in experiments CO_2^{2+} in excited vibronic states is predominantly detected; at least, this is very probable for those measurements that record only short-lived CO_2^{2+} , i.e. CO_2^{2+} with vibronic (resonance) levels close to the barrier top and thus ≈ 0.5 – 1.0 eV above the electronic $^3\Sigma_g^-$ energy at $R = 2.20 a_0$. In this direction also points the observation that—despite the comparable equilibrium bondlength—the Franck–Condon overlap between the vibronic ground states of CO_2 and CO_2^{2+} seems not to be substantial (e.g. the distance $R_{\text{C-O}} = 2.2 a_0$ lies slightly to the left of the inner turning point and thus already in the classically forbidden region of the lowest symmetric stretching mode of $\text{CO}_2^{2+}(^3\Sigma_g^-)$). On the other hand, adding to our computed $T_v = 36.9$ eV the difference 0.1–0.2 eV by which the vibrational zero-point energy of CO_2^{2+} exceeds that of CO_2 , we arrive at a result within the error bars of a recent apparently rather precise value $E_a = 37.2 \pm 0.1$ eV from photoionization experiments [12]. The adiabatic transition energies $T_e(\text{CO}_2(^1\Sigma_g^+), \text{CO}_2^{2+}(^3\Sigma_g^-))$ from our calculations are almost exactly 0.2 eV below the corresponding T_v (basis I, II) given above.

As already indicated for the zero-point energy, the vibrational normal modes in CO_2^{2+} are higher than in CO_2 , i.e. $\omega(A_{1g}) = 1400 \text{ cm}^{-1}$, $\omega(A_{1u}) = 3240 \text{ cm}^{-1}$, $\omega(E_{1u}) = 980 \text{ cm}^{-1}$, compared to the analogous frequencies 1388, 2349, and 667 cm^{-1} in CO_2 [23], thus reflecting the somewhat stiffer bond structure of the dication. This is in accordance

with the fact that in the neighbourhood of its equilibrium, the electronic configuration of $\text{CO}_2^{2+}({}^3\Sigma_g^-)$ is chiefly determined by two holes (formed by non-binding π_g electrons) in the $\text{CO}_2({}^1\Sigma_g^+)$ configuration. Table 1 summarizes some characteristic theoretical properties of the metastable CO_2^{2+} ground state. That the metastable equilibrium is assumed in linear geometry should come as no surprise. Even for systems with bent neutral parents (as e.g. He_3 , Be_3), the additional Coulomb repulsion proved strong enough to push the (local) minimum of the dicationic ground state PES to a collinear configuration [24–26]. Compared with the stability properties of other doubly positive trimers, CO_2^{2+} plays an intermediate role: its equilibrium bondlength is longer than the $R_e = 1.75 a_0$ of He_3^{2+} [24], not much different from the $R_e = 2.43 a_0$ of C_3^{2+} [26], but distinctly shorter than the $R_e = 4.09 a_0$ of Be_3^{2+} [25]. The barrier height D_b in CO_2^{2+} exceeds the $D_b = 0.5$ eV computed for He_3^{2+} , but is smaller than the values 1.4 eV for Be_3^{2+} and 4 eV for C_3^{2+} . The energy 'stored' behind the barrier, $-D_c$, also behaves along these lines, with the CO_2^{2+} D_c situated between $D_c = -6.4$ eV for He_3^{2+} and the dissociation energies $D_e = -1.4$ eV for Be_3^{2+} or $D_e = -1.5$ eV for C_3^{2+} .

Table 1. Theoretically predicted properties of CO_2^{2+} (based on CI computations within non-relativistic Schrödinger theory, assuming the Born–Oppenheimer approximation).

Property	Theoretical prediction
Equilibrium	D_{oh} structure $\text{O}^+-\text{C}-\text{O}^+$
Ground state	${}^3\Sigma_g^-$, quasibound
$R_e = R_{\text{C-O}}$	$2.30 \pm 0.02 a_0$
Total energy $E(R_e)$	-186.9920 hartree
Barrier height	≥ 1.0 eV
Dissociation	Lowest channel: $\text{CO}^+({}^2\Sigma^+) + \text{O}^+({}^4S_u)$
Dissociation energy	-5.1 eV
Electronic configuration	$1\sigma_g^2 2\sigma_g^2 3\sigma_g^2 4\sigma_g^2 1\sigma_u^2 2\sigma_u^2 3\sigma_u^2 1\pi_u^4 1\pi_g^2$
$T_e(\text{CO}_2({}^1\Sigma_g^+), \text{CO}_2^{2+}({}^3\Sigma_g^-))$	36.7 eV

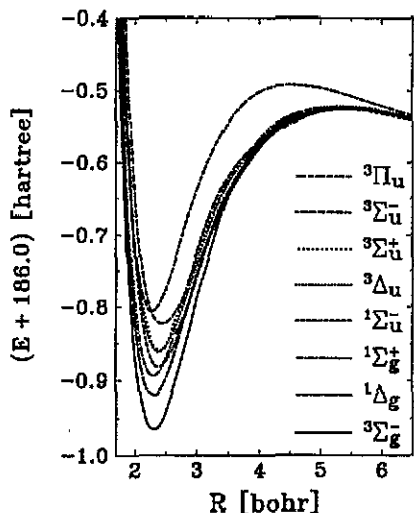


Figure 4. Potential energy curves for low-lying states of CO_2^{2+} in D_{ohh} geometry. The Davidson-corrected energies from basis I are plotted.

Turning now to an analysis of other electronic state of CO_2^{2+} , PECs for the eight lowest electronic states restricted to the D_{oh} geometry are displayed in figure 4. All these PECs converge rapidly to their common dissociation limit $\text{O}^+(^4\text{S}_u) + \text{C}(^3\text{P}) + \text{O}^+(^4\text{S}_u)$. What is remarkable about figure 4 is not only the high density of states already mentioned earlier, but also the striking similarity of all the shapes of the PECs, including the almost coincident positions of their minima. These similarities mirror the close relationship between the involved electronic configurations. In the vicinity of the minima, the states $^3\Sigma_g^-, ^1\Delta_g, ^1\Sigma_g^+$ are dominated by the π_g^{-2} holes, the states $^1\Sigma_u^-, ^3\Delta_u, ^3\Sigma_u^+, ^3\Sigma_u^-$ by $\pi_u^{-1}\pi_g^{-1}$, and the state $^3\Pi_u$ by $\sigma_u^{-1}\pi_g^{-1}$. Further properties of these states are collected in table 2. It may be appropriate to emphasize that the tabulated minima (except for the ground state) are valid only for the system in D_{oh} geometry. The role played by these points if the PESs are extended to asymmetrical linear or bent nuclear geometries is *a priori* not clear and needs to be examined in more detail [15]. Moreover, the $^3\Delta_u$ and $^3\Sigma_u^+$ states are energetically not much separated and their PECs hardly discernible on the scale of figure 4. In particular, their small T_e difference (cf table 2) renders a definite ordering between both states difficult and an improved resolution by more accurate computations would be required for a final decision.

Table 2. Low-lying states of CO_2^{2+} in D_{oh} geometry: Equilibrium distance $R_e = R_{\text{C-O}}$, excitation energy T_e , and vertical energy at the reference distance $R_{\text{ref}} = 2.2 a_0$. The Davidson-uncorrected and Davidson-corrected values are given in the upper and lower rows, respectively. All results are from basis I, unless otherwise indicated.

State	R_e (a_0)	T_e (eV)	$T_v(R_{\text{ref}})$ (eV)		
			Basis I	Basis II	[6]
$^3\Sigma_g^-$	2.28	0	0	0	0
	2.31	0	0	0	0
$^1\Delta_g$	2.29	1.24	1.23	1.24	1.21
	2.32	1.21	1.23	1.24	
$^1\Sigma_g^+$	2.29	2.01	2.04	1.90	1.83
	2.31	1.92	1.95	1.88	
$^1\Sigma_u^-$	2.36	2.30	2.79	2.53	2.87
	2.38	2.25	2.81	2.61	
$^3\Delta_u$	2.36	2.84	3.30	3.01	3.25
	2.38	2.82	3.33	3.07	
$^3\Sigma_u^+$	2.35	2.87	3.48	3.50	3.44
	2.37	2.87	3.60	3.40	
$^3\Sigma_u^-$	2.42	3.94	4.66	4.64	4.85
	2.45	3.83	4.62	4.62	
$^3\Pi_u$	2.26	4.44	4.41	4.40	4.17
	2.27	4.29	4.27	4.25	

Table 2 contains also the relative vertical excitation spectra from basis I and II at $R_{\text{ref}} \approx R_e(\text{CO}_2(^1\Sigma_g^+))$, together with the T_v values computed by Millie *et al.* A corresponding schematic comparison of the experimental and theoretical vertical excitation energies is presented in figure 5. For the three lowest states $^3\Sigma_g^-, ^1\Delta_g, ^1\Sigma_g^+$, inspection of figure 5 shows a satisfactory—yet not perfect—agreement between all the experimental and theoretical data. Although for the next higher level, $^1\Sigma_u^-$, our result is somewhat below the CIPSI value, there still exists a unique correspondence between the energies from theory and experiment. For the more excited states, $^3\Delta_u, ^3\Sigma_u^+, ^3\Sigma_u^-$ and $^3\Pi_u$, the theoretical

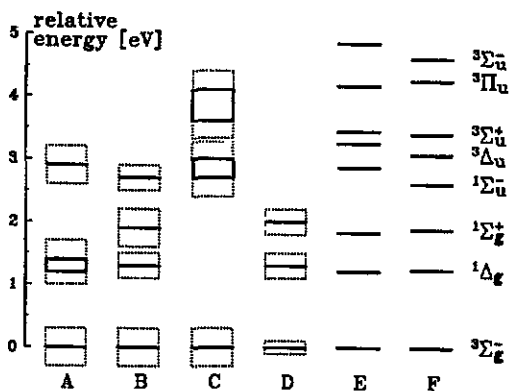


Figure 5. Lower part of the vertical excitation spectrum of CO_2^+ in $D_{\infty h}$ geometry at $R_{\text{ref}} = 2.2 a_0$. Levels relative to the appearance (experiment) or ground-state (theory) energy of CO_2^+ are shown. The experimental error bars are indicated by dotted boxes. Full boxes mark energy intervals observed in experiment for the same state: A, PI (photoionization) and DCT (double charge transfer) [6]; B, SEC (single electron capture) [7]; C, DCT [10]; D, PI [12]; E, CIPSI computation [6]; F, MRDCI computation (basis II), this work.

values agree within $^{+0.2}_{-0.1}$ eV. This may be acceptable, but also leaves room for improvement. From the available experimental levels within the considered energy interval, the window around 2.8 eV observed in the double charge transfer experiment by Langford *et al* [10] can be assigned to the ${}^3\Delta_u$ state. In contrast, the window around 3.9 eV falls between the theoretical ${}^3\Sigma_u^+$ and ${}^3\Pi_u$ levels, and a unique assignment seems difficult. Let us mention that the ordering of states according to increasing T_e or T_v energies produces identical sequences, except for the ${}^3\Pi_u$ and ${}^3\Sigma_u^-$ states with PECs that cross between $R_e(\text{CO}_2({}^1\Sigma_g^+))$ and $R_e(\text{CO}_2^+({}^3\Sigma_u^-))$.

In conclusion, our computations provide theoretical evidence for metastability in CO_2^+ . However, an experimental preparation and observation of those long-living low-lying vibrational states trapped behind the potential barriers of the electronic ground state seems not to be an easy task. Most of the ground-state ions produced and recorded in experiments can be expected to decay by dissociative tunnelling from their highly excited vibronic motion. Although the agreement within the theoretical levels and with the relative experimental energies of the lower part of the vertical excitation spectrum seems acceptable, further calculations with improved accuracy would be helpful. More generally, a detailed investigation of the structure of the low-lying PESS should not only be of interest for the experiments on CO_2^+ , but may also lead to deeper insight into the binding and stability properties of heteronuclear polyatomic dications.

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