

Electronic Supplementary Information

Visible photodissociation of the CO₂ dimer cation: Fast and slow dissociation dynamics in the excited state

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15

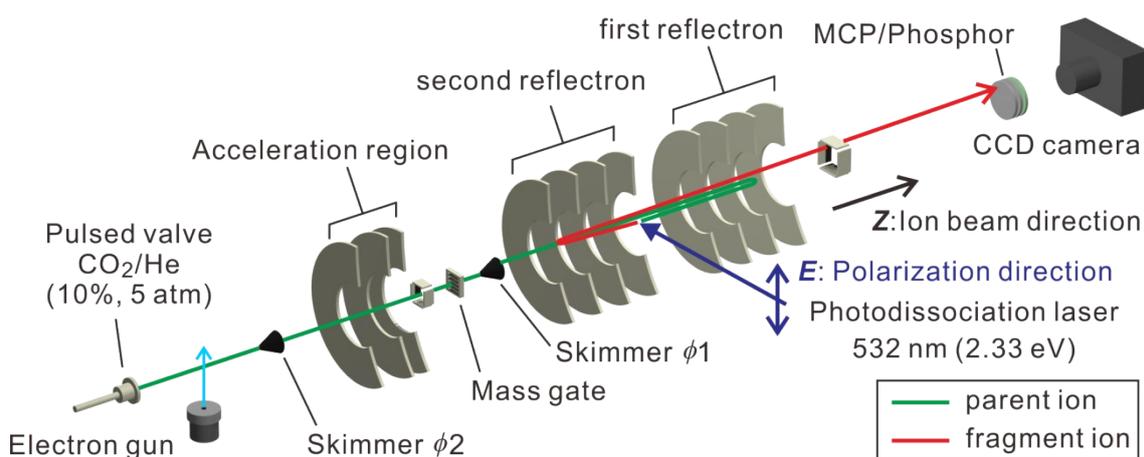


Fig. S1 A schematic image of the apparatus using a double linear reflectron with a position sensitive detector

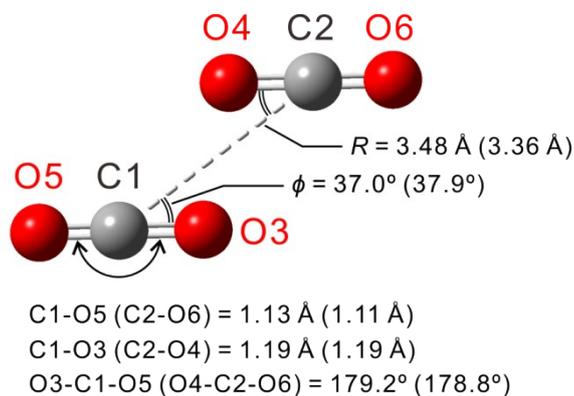


Fig. S2 The staggered structure of $(CO_2)_2^+$ optimized at UM06-2X/aug-cc-pVTZ and UHF/aug-cc-pVTZ level. Values from the HF calculations are in parenthesis. The point group is C_{2h} .

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Table S1 Summary of the electronic transitions of $(CO_2)_2^+$ with the staggered structure calculated at TD-UM06-2X/aug-cc-pVTZ level.

Transitions	Excitation wavelengths / nm	Excitation energies / eV	Oscillator strengths
$\tilde{A}^2B_g \leftarrow \tilde{X}^2B_u$	1960	0.63	0.000
$\tilde{B}^2A_u \leftarrow \tilde{X}^2B_u$	992	1.25	0.000
$\tilde{C}^2A_g \leftarrow \tilde{X}^2B_u$	500	2.48	0.262
$\tilde{D}^2B_u \leftarrow \tilde{X}^2B_u$	258	4.80	0.000
$\tilde{E}^2B_g \leftarrow \tilde{X}^2B_u$	243	5.09	0.023

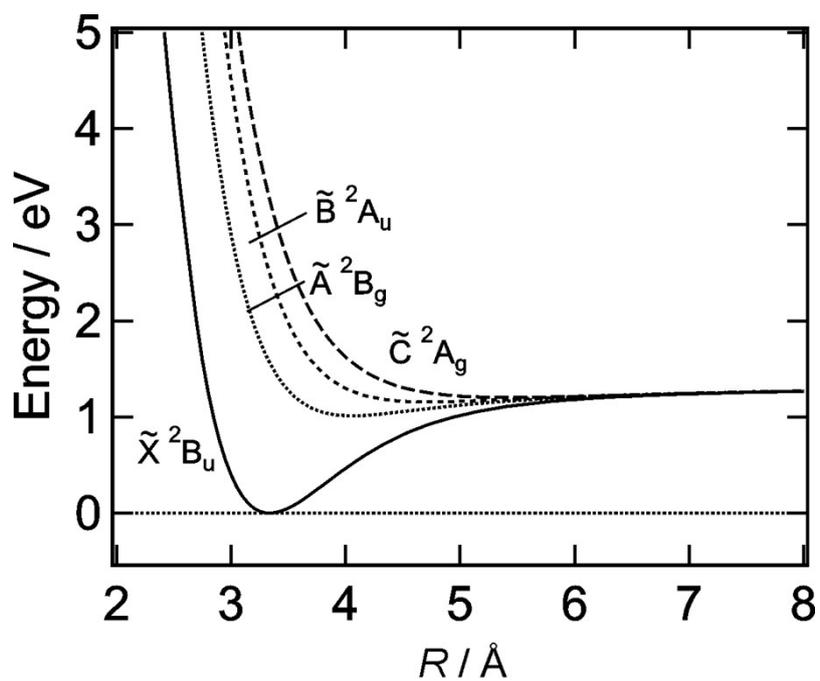


Fig. S3 Potential energy curves (PECs) of $(\text{CO}_2)_2^+$ with C_{2h} symmetry along the intermolecular C-C distance using a SA-CASSCF(7, 4)/ cc-pVTZ level. The horizontal axis R is the distance between the two carbon atoms as shown in Fig. 3(a).

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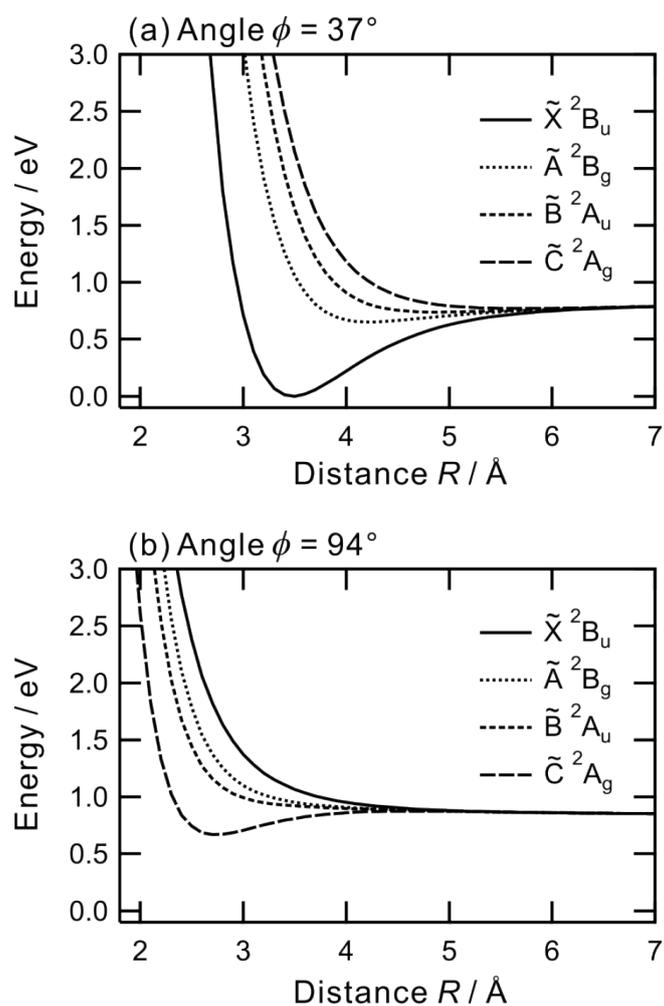


Fig. S4 Potential energy curves (PECs) of $(\text{CO}_2)_2^+$ along the R coordinate obtained from the potential energy surfaces (PESs) in Figure 5. SA-CASSCF(17,13)/cc-pVTZ level was used. (a) PECs at $\phi = 37^\circ$ and (b) PECs at $\phi = 94^\circ$ are shown.

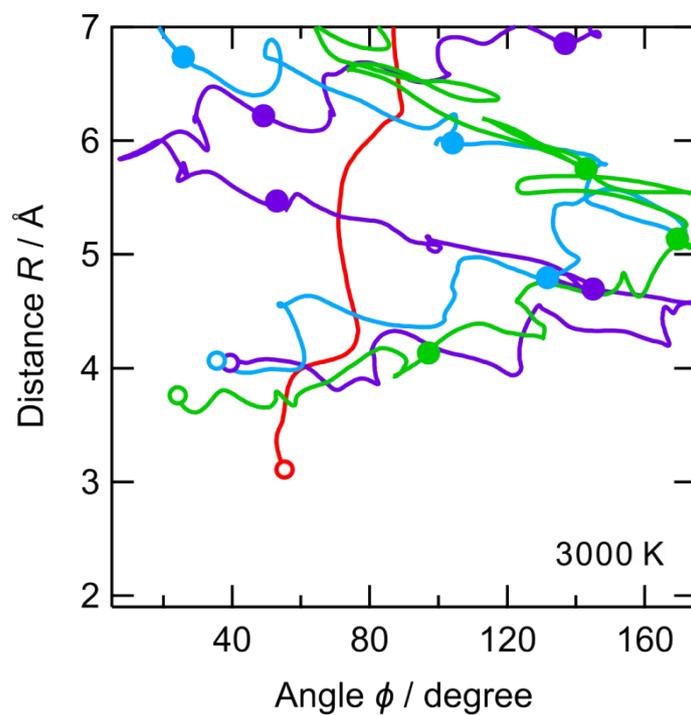
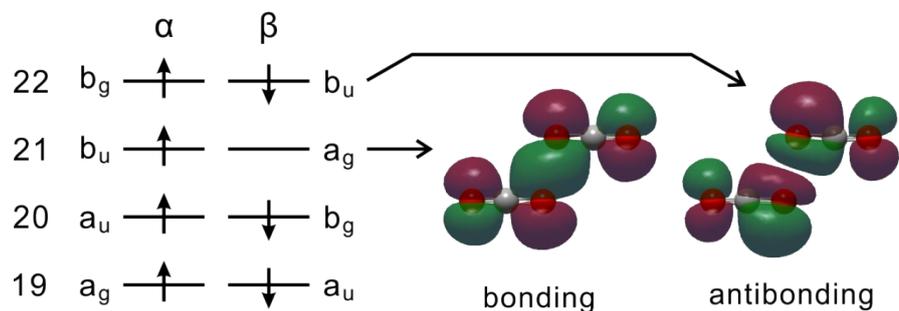


Fig. S5 The plot of the four trajectories against the distance R and the angle ϕ . Each colored trajectory corresponds to the trajectory with the same color in Fig. 6. Open circles are placed at the initial positions and closed circle at every 100 fs on the trajectories. The trajectories are shown up to each of their dissociation lifetime.

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(a) staggered structure



(b) side-by-side structure

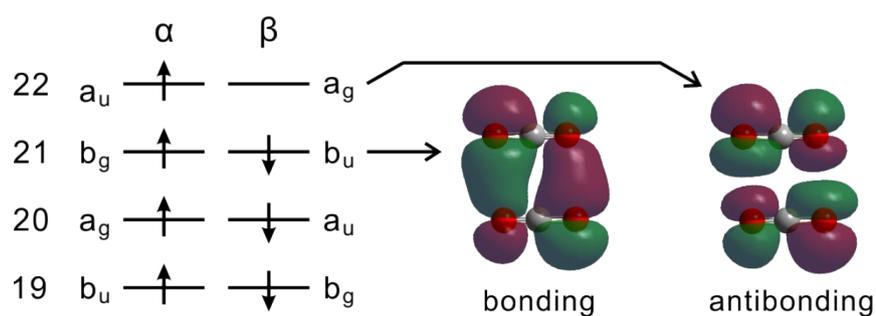


Fig. S6 Electronic configurations of $(CO_2)_2^+$ in the \tilde{C} excited state calculated at UHF/aug-cc-pVTZ level. The four highest alpha and beta orbitals are shown for each $(CO_2)_2^+$ structure. (a) Electronic configuration and molecular orbitals of the staggered structure, (b) those of the side-by-side structure.

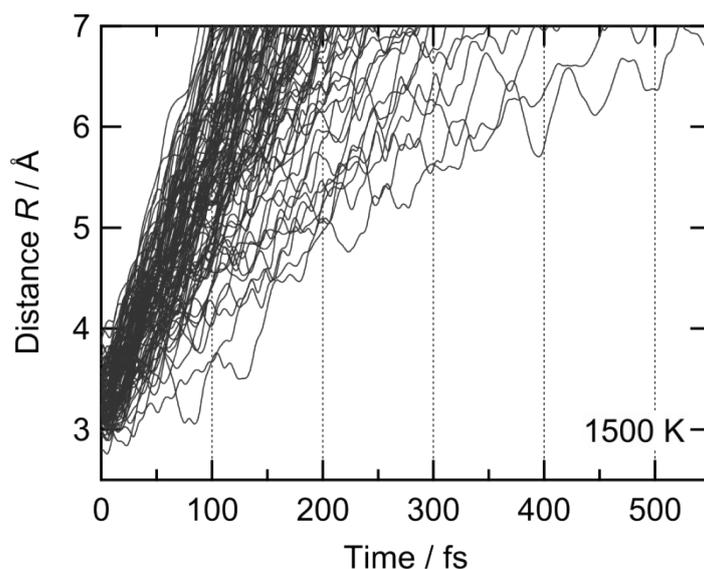


Fig. S7 The plot of the distance R against time obtained by nonadiabatic MD simulations at SA-CASSCF(7,4)/cc-pVTZ level with the initial condition sampled from the Boltzmann distribution at 1500 K in \tilde{X} . Nonadiabatic transitions from \tilde{C} to other electronic states were taken into account by the surface hopping method with a newly developed robust global switching algorithm [S1]. We implemented the algorithm in the Newton-X program [S2] and interfaced the modified Newton-X with MOLPRO. 105 trajectories are shown. Most of the trajectories hop onto the lower states and eventually $(\text{CO}_2)_2^+$ dissociates in \tilde{X} and \tilde{A} .

10

References

- [S1] K. Hanasaki, M. Kanno, T. A. Niehaus and H. Kono, *J. Chem. Phys.* **149**, 244117 (2018).
 [S2] M. Barbatti, G. Granucci, M. Ruckebauer, F. Plasser, R. Crespo-Otero, J. Pittner, M. Persico and H. Lischka, NEWTON-X: a package for Newtonian dynamics close to the crossing seam, version 1.4, 2013, www.newtonx.org.