

Supplemental material

Electronic energy transfer ionization in naphthalene-CO₂ clusters reveals excited states of dry ice

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The supplemental material contains the details of experimental and theoretical methods, separate calculated excitation spectra and corresponding conformers, a full-scale plot with the photoionization efficiencies (PIE) of Naphthalene-(CO₂)_p (p=1-6) clusters, a full scale plot the PIEs of pure CO₂ clusters divided by that of the (CO₂)₂ and a mass spectra at 13.4 eV photon energy.

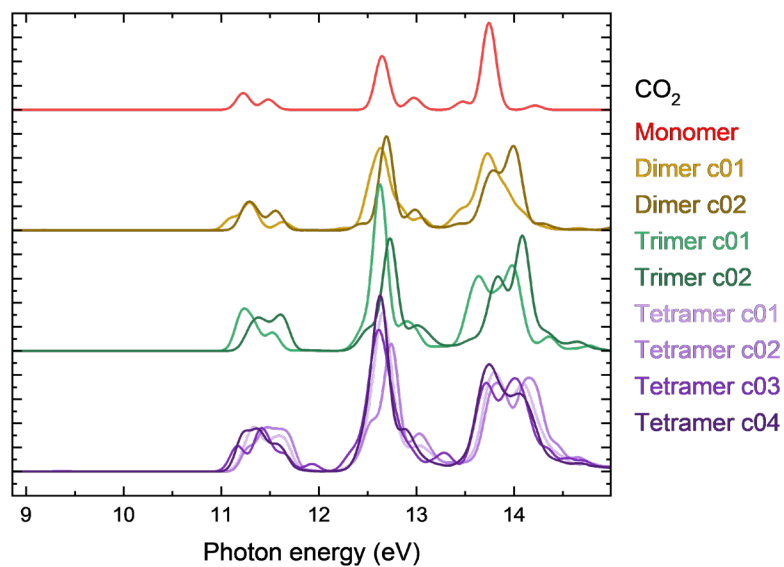
Methods

Experimental

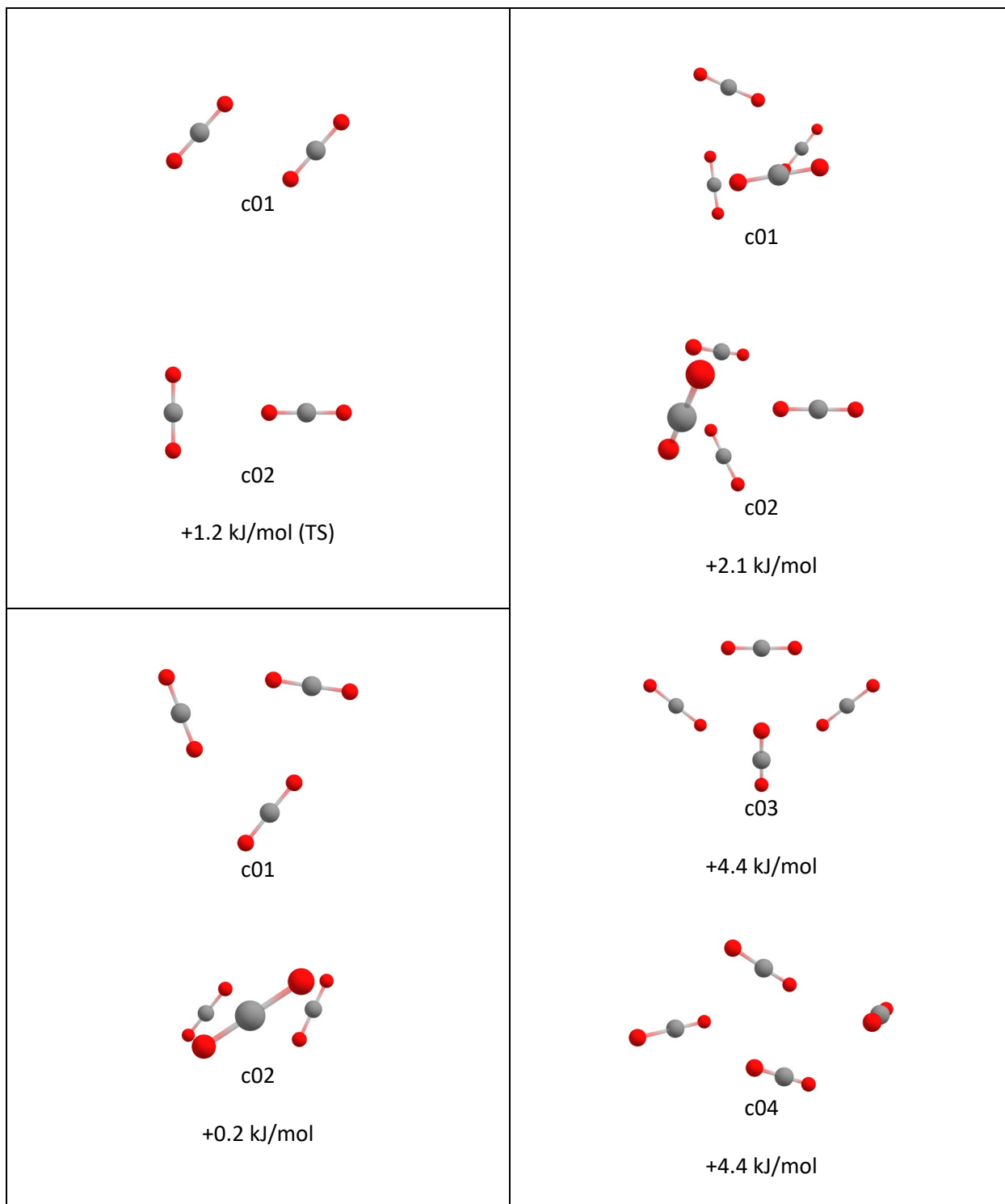
Experiments were performed at the Advanced Light Source beamline 9.0.2. in Berkeley.¹ Photoionization efficiency curves were measured using a molecular beam setup discussed in more detail previously.² Naphthalene (99% purity) was heated within the stainless steel tube connected to a 50 μm nozzle to about 40 °C, using glass wool to prevent clogging the orifice. A mixture of CO₂ (20%) and Ar is passed through the nozzle with a backing pressure 800 Torr and skimmed, creating a continuous molecular beam containing monomers and clusters. The molecules are probed using VUV synchrotron radiation with a spectral bandwidth of about 30 meV.³ The resulting ions are injected into a Jordan reflectron time-of-flight mass spectrometer by pulsing the repeller plate at 10 kHz. Photoionization efficiency curves (PIEs) are obtained by scanning the undulator in such manner as to create steps of 0.1 eV. The PIEs are divided by the photon flux to correct for power fluctuations.

Theoretical

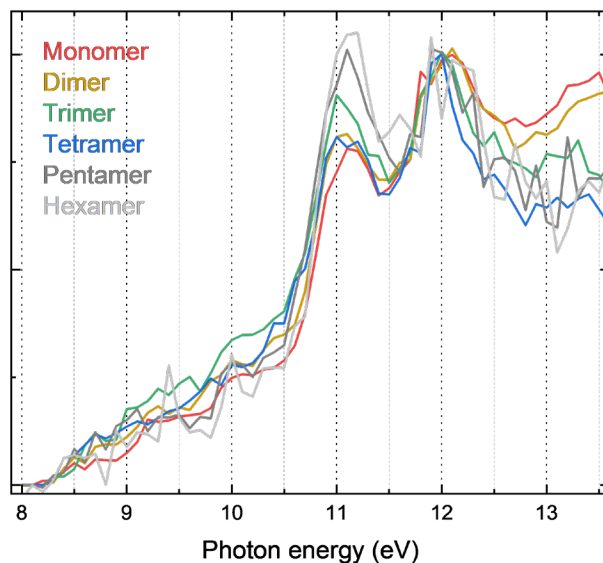
A conformational search was performed for pure (CO₂)_n (n=2-4) clusters using CREST at 10 K. Ground state geometries of pure (CO₂)_n (n=1-4) clusters are calculated using B3LYP/6-311+G** with GD3 empirical dispersion correction on a superfine grid using Gaussian16. The absorption spectra were calculated following the method described by Costa Cabral and coworkers⁴ using TDDFT on the LC-BLYP/daug-cc-pVTZ level of theory. Since long-range corrected BLYP (LC-BLYP)⁵ produces results that are consistent with equation-of-motion coupled-cluster with single and double excitations, considered to be the reference method⁶, LC-BLYP can be used in this study to scrutinize the observed electronic transitions.



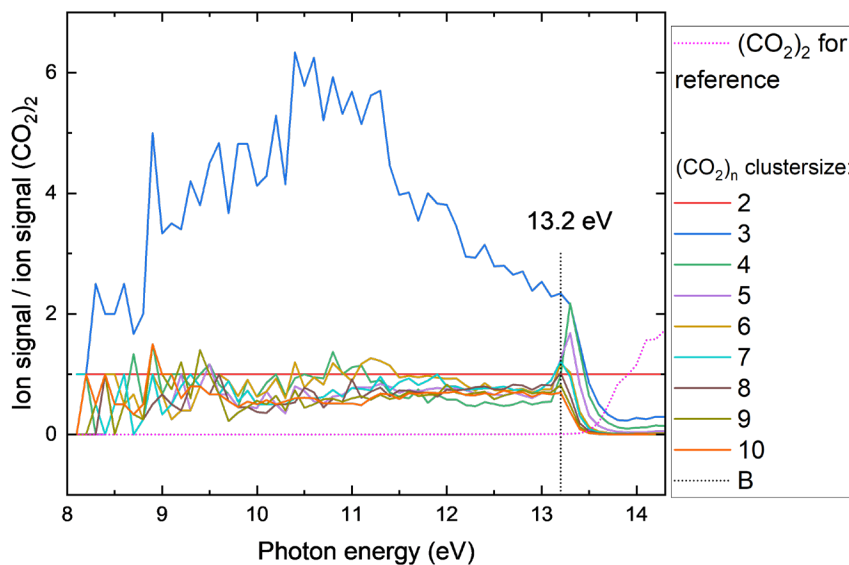
Supplemental figure 1: Calculated absorption spectra of pure CO₂ clusters (n=1-4) using TDDFT on the LC-BLYP/daug-cc-pVTZ level. Corresponding structures are displayed in supplemental figure 2.



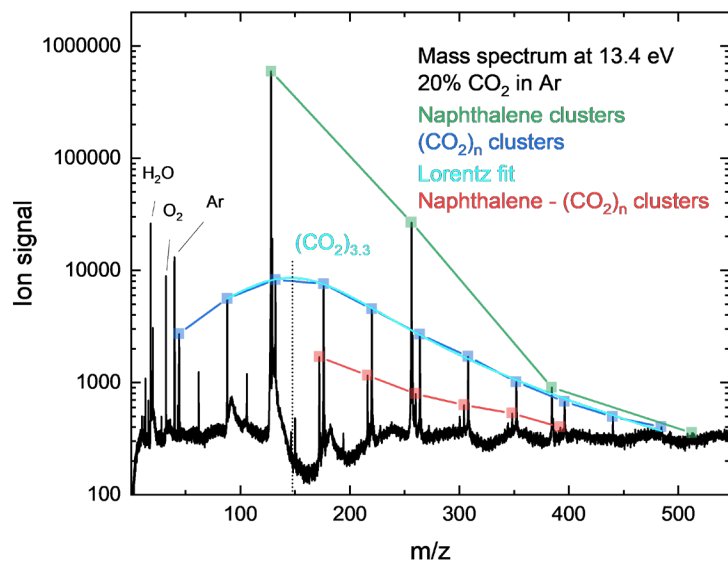
Supplemental figure 2: Molecular structures of CO₂ calculated at the B3LYP/6-311+G** level of theory (with GD3 empirical dispersion and a superfine grid). The binding energy of the c01 dimer is 5.5 kJ/mol (ZPE corrected) (0.057 eV)



Supplemental figure 3: full scale plot of figure 2 showing the PIEs of Naphthalene-(CO₂)_p (p=1-6) clusters



Supplemental figure 4: full scale plot of figure 3: PIEs of pure CO₂ clusters divided by (CO₂)₂ as function of photon energy showing the relative abundance of higher order clusters. As a reference, the (CO₂)₂ cluster PIE curve is plotted (pink, dotted line), showing that the cluster size peaks at around the appearance energy. (Note that the AE of (CO₂)_n n>1 are very similar).



Supplemental figure 5: Mass spectra at 13.4 eV photon energy (black) where more fragmentation is observed than at 13.2 eV (see figure 4). Indicated are the pure CO₂ clusters (dark blue), the naphthalene clusters (green) and the naphthalene-CO₂ clusters (red). A Lorentz fit of the pure CO₂ cluster size distribution (light blue), not including the monomer, indicates a mean cluster size of 3.3 CO₂ units.

References:

- (1) Suits, A. G.; Heimann, P.; Yang, X.; Evans, M.; Hsu, C. W.; Lu, K. T.; Lee, Y. T.; Kung, A. H. A Differentially Pumped Harmonic Filter on the Chemical Dynamics Beamline at the Advanced Light Source. *Review of Scientific Instruments* **1995**, *66* (10), 4841–4844. <https://doi.org/10.1063/1.1146161>.
- (2) Xu, B.; Stein, T.; Ablikim, U.; Jiang, L.; Hendrix, J.; Head-Gordon, M.; Ahmed, M. Probing Solvation and Reactivity in Ionized Polycyclic Aromatic Hydrocarbon-Water Clusters with Photoionization Mass Spectrometry and Electronic Structure Calculations. *Faraday Discuss* **2019**, *217*, 414–433. <https://doi.org/10.1039/c8fd00229k>.
- (3) Bandyopadhyay, B.; Kostko, O.; Fang, Y.; Ahmed, M. Probing Methanol Cluster Growth by Vacuum Ultraviolet Ionization. *Journal of Physical Chemistry A* **2015**, *119* (18), 4083–4092. <https://doi.org/10.1021/acs.jpca.5b00912>.
- (4) Costa Cabral, B. J.; Rivelino, R.; Coutinho, K.; Canuto, S. A First Principles Approach to the Electronic Properties of Liquid and Supercritical CO₂. *Journal of Chemical Physics* **2015**, *142* (024504), 1–9. <https://doi.org/10.1063/1.4905256>.
- (5) Iikura, H.; Tsuneda, T.; Yanai, T.; Hirao, K. A Long-Range Correction Scheme for Generalized-Gradient-Approximation Exchange Functionals. *Journal of Chemical Physics* **2001**, *115* (8), 3540–3544. <https://doi.org/10.1063/1.1383587>.
- (6) Triana, J. F.; Peláez, D.; Hochlaf, M.; Sanz-Vicario, J. L. Ultrafast CO₂ Photodissociation in the Energy Region of the Lowest Rydberg Series. *Physical Chemistry Chemical Physics* **2022**, *24* (22), 14072–14084. <https://doi.org/10.1039/d2cp01017h>.