

Femtosecond Symmetry Breaking and Coherent Relaxation of Methane Cations via X-ray Spectroscopy

Enrico Ridente^{1,2}, Diptarka Hait^{1,2}, Eric A. Haugen^{1,2}, Andrew D. Ross^{1,2},
Daniel M. Neumark^{1,2}, Martin Head-Gordon^{1,2}, and Stephen R. Leone^{1,2,3}

¹*Department of Chemistry, University of California, Berkeley, CA, 94720, USA*

²*Chemical Sciences Division, LBNL, Berkeley, CA 94720, USA*

³*Department of Physics, University of California, Berkeley, CA, 94720, USA*

Methane is the smallest molecule of the T_d symmetry group and its cation (CH_4^+) represents the simplest case of the Jahn-Teller (JT) $T_2 \otimes (e + t_2)$ problem. Here, we present a comprehensive picture of how JT distortions unfold in CH_4^+ by ionizing CH_4 using a 4 fs 800 nm pulse and probing the $1s(\text{C}) \rightarrow$ singly occupied molecular orbital (SOMO) via X-ray transient absorption spectroscopy. We measure the shift from T_d to C_{2v} to occur within 10 ± 2 fs, followed by a damped coherent vibrational oscillation with a lifetime of 58 ± 13 fs (**A**). X-ray absorption spectra calculated by OO-DFT (**B**) corroborated the experimental findings. Similar agreement between experimental measurements and theoretical calculations was obtained for CD_4^+ . The dynamics could be assigned to the asymmetric scissoring motion about the smallest H-C-H angle, which lead to a change in the character of the singly occupied molecular orbital (SOMO) (**C**). This research therefore provides direct observation of JT-induced coherent dynamics and relaxation pathways.

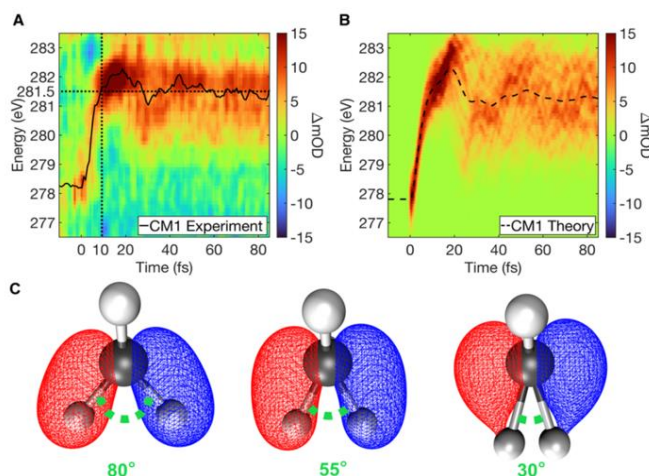


Figure caption: **(A)** XTAS measurements. The solid line indicates the first central moment (CM1) while the dotted line JT timescale and equilibrium energy. **(B)** OO-DFT calculations. **(C)** Change in SOMO associated with the scissoring motion of the molecule.