Ultrafast probing of isotope-induced explicit symmetry breaking in ethylene

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Symmetry and symmetry breaking have been known to play a central role in contemporary physics and many of the natural phenomena occur due to the breakdown of symmetry [1,2]. Here, we show how isotope-induced inversion symmetry breaking influences ultrafast photoisomerization processes in ethylene. Extreme ultraviolet pump – near infrared probe time-of-flight mass spectrometry, performed replacing one of the carbon atoms in ethylene with a ^{13}C isotope leads to twice-faster structural relaxation in the photo-excited molecular cation. In particular, the ethylene to ethylidene conversion, *i.e.*, the relaxation channel involving the migration of one hydrogen atom from one carbon atom to the other, also identified in previous studies [3], was affected by the isotopic effect. We simulated the quantum-classical non-adiabatic molecular dynamics, using trajectory surface hopping method, and incorporating the nuclear symmetry. Our results suggest that this difference arises from the mixing of different normal modes in the isotope-substituted species, ^{13}C-ethylene, compared to the more symmetric unsubstituted or doubly substituted isotopologues. This facilitates efficient intra-molecular vibrational energy redistribution, thereby lowering the isomerization yield. These findings offer opportunities to use isotope-induced nuclear symmetry breaking to control the outcome of light-molecule interactions across ultrafast timescales.

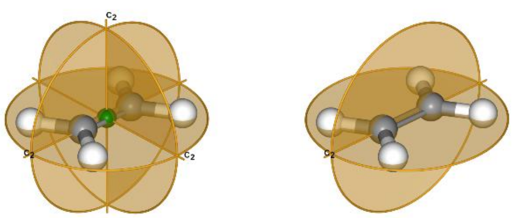

Figure 1. Point group symmetry elements in ethylene and ^{13}C^{13}C-ethylene (left) and ^{13}C-ethylene (right). From left to right the symmetry point group changes from D_{2h} to C_{2v}, with the corresponding lowering of the symmetry.

References:

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