INFRARED-ULTRAVIOLET DOUBLE RESONANCE SPECTROSCOPY OF ACETYLENE: DYNAMICAL SYMMETRY BREAKING IN THE $4\nu_{CH}$ ROVIBRATIONAL MANIFOLD AT 12700 cm$^{-1}$

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Time-resolved fluorescence-detected infrared-ultraviolet optical double resonance (IR-UV DR) experiments have been performed with a Raman-shifted dye laser preparing gas-phase C$_2$H$_2$ molecules in the $"4\nu_{CH}"$ region followed by laser-induced fluorescence (LIF) probing in the $S_1 \leftarrow S_0$ vibronic band system. Unusual symmetry-breaking energy transfer has been observed, induced (at least in part) by collisions.$^a$ This takes the form of odd-numbered changes of the rotational quantum number $J$, despite the fact that intramolecular transfer between the ortho and para nuclear-spin modifications of such a molecule is usually forbidden.

The selection rules for IR-UV DR spectra determine that the final vibronic levels should be of gerade symmetry. UV spectra are obtained by IR excitation of particular rotational levels of the (10300)$^0$ vibrational eigenstate that terminate in ungerade vibronic levels. Odd-numbered changes of $J$ are also observed in these spectra.

We have verified that the mechanism is an intramolecular process. One possibility is collision-induced dynamical symmetry breaking involving transitions between "$+"$ and "$-"$ local-mode states which spoil the $g/u$ symmetry. We also consider whether $a/s$ nuclear-spin interchange symmetry can be involved.$^a$