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

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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 $C_2H_2$ 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] M. A. Payne, A. P. Milce, M. J. Frost and B. J. Orr, *Chem. Phys. Lett.* **265**, 244 (1997).