INFRARED-ULTRAVIOLET DOUBLE RESONANCE SPECTROSCOPY OF ACETYLENE: UNRAVELLING THE MYSTERIES IN THE $\nu_{CC} + 3\nu_{CH}$ REGION AT 11 600 cm^{-1}USING THE CLUSTER/POLYAD MODEL

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Time-resolved fluorescence-detected infrared-ultraviolet optical double resonance (IR-UV DR) experiments have been used to obtain detailed measurements of spectroscopic and dynamical processes in the "$\nu_{CC} + 3\nu_{CH}$" region of acetylene (C_2H_2) at 11 600 cm^{-1}. The rotational energy transfer (RET) and vibrational energy transfer (V-V) kinetic data collected have already been well fit to a detailed rate-equation model that incorporates empirical exponential-gap fitting laws. [a]

In order to explain some of the unusual effects observed in this region we now use the cluster/polyad model that has already successfully interpreted the vibrational energy pattern in C_2H_2 up to 12 000 cm^{-1}. [b] Our work emphasises rotational perturbations, after including the rotational *l*-type resonance interaction. This enables us to identify the intramolecular couplings responsible for enhancement of rotationally-resolved V-V energy transfer between coupled rovibrational levels of the "$\nu_{CC} + 3\nu_{CH}$" manifold. The model also provides qualitative evidence that Coriolis-type perturbations are responsible for other unusual symmetry-breaking phenomena in this region.

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