INTRAMOLECULAR FERMI RESONANCES SWITCHED ON IN SMALL (N= 3, 4) PYRAZOLE CLUSTERS

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Pyrazole species are favorable cases for the study of aggregation phenomena in different states (gas phase, liquid and solid state). Pyrazole has recently been investigated in a free jet expansion.[a] The IR spectrum shows a structured absorption band covering around $350\,\mathrm{cm}^{-1}$ in the NH stretching region. This band is assigned to pyrazole clusters beyond the dimer.
The origin of this broad band is analyzed in terms of the theoretical "Monomers–in–Clusters" (MIC) approach, already successfully applied to carboxylic acid dimers.[b] A pronounced intramolecular Fermi-type resonance between the NH stretching vibrations and overtones and combination bands of certain ring stretching vibrations is found to be responsible for the extended structure in the spectrum. MIC relies on distorted monomer potentials to describe the effect. Simulated spectra based on potential hypersurfaces of up to five dimensions calculated at different levels of electronic structure approaches (DFT and MP2) are presented. The agreement between simulated and experimental spectra suggests that the pyrazole cluster dynamics after NH stretching excitation are dominated by intramonomer redistribution of the vibrational energy. This validates the monomer-centred viewpoint of the MIC model.

[a] C. A. Rice, N. Borho, M. A. Suhm, Z. Phys. Chem. 219, 379 (2005)
[b] C. Emmeluth, M. A. Suhm, D. Luckhaus, J. Chem. Phys. 118, 2242 (2003)