PATTERN RECOGNITION IN HIGHLY RESOLVED UV-SPECTRA OF HYDROGEN BONDED CLUSTERS

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Highly resolved sub-Doppler spectra of clusters with rotational resolution have been measured with mass selection in a resonance-enhanced two-photon excitation process. The first photon originates from a nearly Fourier-transform limited laser pulse with a frequency width of typically 70 MHz in the UV. The pulses are produced by pulsed amplication of cw single mode dye laser light and frequency doubling. Recently we extended our investigations to hydrogen-bonded aromatic molecule-water systems[a,b]. To analyze the complex rotational structure in the vibronic bands of these systems we developed a new automated fitting procedure yielding accurate values for the rotational constants by optimization of the crosscorrelation of a theoretical spectrum with the experimental spectrum (Correlation Automated Rotational Fitting: CARF[c]). Fitting of the rotational constants is possible without a preceding analysis and assignment of the rotational transitions. We present results for the structures for benzonitrile-water and indole-water, and the intermolecular dynamics of hydrogen bonding in phenol-water. In benzonitrile-water ($C_6H_5CN{\cdot}H_2O$) the water is found with its oxygen nearly in the plane of benzonitrile, nested between the cyano group and the ortho hydrogen. In indole-water the water is in a hydrogen accepting position attached to the amino hydrogen with its oxygen oriented towards the NH hydrogen[d]. In phenol-water ($C_6H_5OH{\cdot}H_2O$) an autocorrelation procedure of the highly resolved vibronic bands yields directly the torsional splitting of the individual vibronic bands prior to a rotational analysis. In this way we were able to assign several intermolecular vibrational states and investigate the tunnel splittings caused by the hindered rotation of the water moiety.

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[c] R.M. Helm, H.-P. Vogel, H.J. Neusser, Chem. Phys. Lett. **270**, 285 (1997).
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