VRT-SPECTROSCOPY IN THE TRANSLATIONAL AND LIBRATIONAL BAND REGION OF LIQUID WATER: HYDROGEN BOND TUNNELING DYNAMICS IN WATER CLUSTERS

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We report the observation of a new vibration-rotation-tunneling (VRT) band of $(D_2O)_3$ at 142.8 cm^{-1} and a set of four bands of $(H_2O)_3$ around 520 cm^{-1}. These new bands represent the first observation of a translational and librational vibration for a water cluster.
The observed VRT spectrum of $(D_2O)_3$ at 142.8 cm^{-1}, in the translational band of the liquid, is assigned to a combination band or mixed level of the asymmetric hydrogen bond stretch and a torsional vibration. The predicted frequencies of the hydrogen bond stretching modes are too high, presumably because calculations fail to include the necessary coupling between stretching and torsional motions [a].
The bands of $(H_2O)_3$ around 520 cm^{-1} lie in the librational band region of liquid water and are tentatively assigned to the out of plane librational vibration. The observation of at least four bands within 8 cm^{-1} is explained by a dramatically increased splitting of the excited state rovibrational levels by bifurcation-tunneling. The experimental results presented should therefore allow for the first exact determination of the height of the bifurcation tunneling barrier. The tunneling time scale is estimated at 2-4ps, similar to those of several important dynamical processes in bulk water [b].

[a] W. Klopper, M. Schutz, H. P. Luthi, S. Leutwyler, J. Chem. Phys. 103, 1085 (1995).
[b] A. Luzar, D. Chandler, Nature 379, 55 (1996).