STRUCTURE OF THE BENZENE DIMER—GOVERNED BY DYNAMICS

MELANIE SCHNELL, *Center for Free-Electron Laser Science, 22761 Hamburg, Germany; Max-Planck-Institut für Kernphysik, 69117 Heidelberg, Germany*; UNDINE ERLEKAM, GERT VON HELDEN, GERARD MEIJER, *Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin, Germany*; PHILIP R. BUNKER, *National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada*; JENS-UWE GRABOW, *Institut für Physikalische Chemie und Elektrochemie, Gottfried-Wilhelm-Leibniz-Universtät, 30167 Hannover, Germany*; AD VAN DER AVOIRD, *Institute for Molecules and Materials, Radboud University, 6525 AJ Nijmegen, The Netherlands*.

The benzene dimer is the prototype system for Van der Waals interactions between aromatic molecules. Here, we report a joint experimental and theoretical study [a] regarding normal $(C_6H_6)_2$ and the partially deuterated $(C_6D_6)(C_6H_6)$ isotopologue. Interestingly, although its tilted T-shaped equilibrium structure corresponds to an asymmetric rotor, both isotopologues exhibit the rotational spectrum of a symmetric rotor, with a characteristic quartet splitting pattern due to internal tunneling motions: each transition exhibits a $-2:-1:+1:+2$ splitting ratio with respect to its center.

We unravel these splittings with the aid of the unrivalled resolution of the supersonic-jet FT-microwave experiment which provides accurate split-patterns, by means of a reduced-dimensionality model for the internal dynamics of the (rotating) dimer that reproduces them. They turn out to originate from a concerted tunneling mechanism involving both the hindered rotation of the stem in the T-shaped dimer around its sixfold axis and tilt tunneling. We also show that the observed intensities of the tunneling components are not solely determined by nuclear spin statistical weights. Rather, taking small differences in the dissociation energies of different dimer nuclear spin species into account, the kinetics of the dimer formation and equilibration can bias the populations of the tunneling symmetry species.

Using Stark shift measurements, we determine the dipole moment of $(C_6H_6)_2$ to be μ = 0.580(51) D, in agreement with the value of 0.63 D calculated with the assumption that the dipole moment is mainly determined by the dipoles induced in both monomers by the electric field of the quadrupole of the other monomer.

[a] M. Schnell, U. Erlekam, P. R. Bunker, G. v. Helden, J.-U. Grabow, G. Meijer, A. van der Avoird, Angew. Chem. Int. Ed., DOI: 10.1002/anie.201300653 and 10.1002/ange.201300653