MANIFESTATIONS OF VIBRONIC COUPLING EFFECTS IN MOLECULAR SPECTROSCOPY: FROM THE QUENCHING OF EXCITONIC ENERGY SPLITTINGS TO THE CLEMENTS BANDS OF SO2

HORST KÖPPEL, *Theoretical Chemistry, Institute of Physical Chemistry, University of Heidelberg, D-69120 Heidelberg, Germany*.

We investigate the excitation of vibrational modes and its impact on the excitonic energy splittings in doubly hydrogen-bonded molecular dimers. The experimental analysis, performed in collaboration by S. Leutwyler and coworkers (Univ. Bern), is based on high-resolution resonant two-photon ionization spectroscopy. The potential energy surfaces underlying the theoretical investigation are obtained at the RICC2/aug-cc-pVTZ level and are used for the dynamical analysis in the framework of a well-established vibronic coupling approach.
The vertical electronic Davydov splitting of the S_1 and S_2 excited states exceeds the observed excitonic splitting by a factor of 10–40. This discrepancy can be understood by considering the quenching of the excitonic splitting by the excitation of vibrational modes in the electronic transition. Two different approaches have been employed and found to reconcile theory and experiment.[a,b] The analysis of the vibronic structure of the $S_2 \leftarrow S_0$ excitation spectrum focusses on the *ortho*-cyanophenol dimer as a representative example. Most of the observed spectral features can be reproduced by the calculations, although some deviations remain.
In the second part, new results on the UV absorption spectrum of SO_2 will be presented. This is complementary to the excitonic systems in that higher vibrational energies are involved and a conical intersection is accessible to the nuclear motion. Using the concept of regularized diabatic states [c] in combination with high-accuracy MRCI potential energy surfaces, semi-quantitative agreement with the complex experimental (low-resolution) spectrum has been achieved for the first time. [d]

[a] P. Ottiger, S. Leutwyler and H. Köppel, *J. Chem. Phys.* **136**, 174308 (2012).
[b] S. Kopec, P. Ottiger, S. Leutwyler and H. Köppel, *J. Chem. Phys.* **137**, 184312 (2012).
[c] H. Köppel and B. Schubert, *Mol. Phys.* **104**, 1069 (2006).
[d] C. Leveque, A. Komainda, R. Taieb and H. Köppel, *J. Chem. Phys.* **138**, 044320 (2013).