RECENT PROGRESS IN THE FULL-DIMENSIONAL CALCULATIONS OF INTRA- AND INTERMOLECULAR ROVIBRATIONAL STATES OF H_2O-HF AND H_2O-HCl FROM POTENTIAL ENERGY SURFACES

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Molecular complexes play an important role in the chemistry of planetary atmospheres. H_2O-HF and H_2O-HCl are of considerable interest because of two C_s equivalent minima separated by a very low inversion barrier (≈ 70 and ≈ 50 cm^{-1}, respectively). The recent methodological advances based on the full-dimensional calculations of intra - and intermolecular rovibrational states have significantly improved the understanding of molecular dynamics of Van der Waals complexes [1,2]. The rigid-monomer approximation is a good compromise when intramolecular frequencies are much higher than intermolecular frequencies but their application is often not sufficient for the high-resolution molecular spectroscopy. In particular, we show that for H_2O - HF dimer, the coupling between the intra- and intermolecular modes is not negligible (few cm^{-1} of difference between 5D and 9D calculations) and should be taken into account to predict accurately all the transition frequencies and tunneling splittings. All our calculations are based on a full dimensional *ab initio* potential energy surfaces[3,4]. The kinetic energy operator discussed initially by Brocks *et al.*[5] and written in terms of angular momentum operators defined in monomer- and dimer-fixed frames is used. A G_4 symmetry-adapted Lanczos algorithm and an uncoupled product basis are employed[1]. All computed results were confronted with available experimental data. The agreement between theory and experiment is clearly improved when 9D calculations are considered and confirms our suggestion of a possible reassignment for two bands of H_2O-HF. H_2O-HX dimers are excellent candidates for more experimental high-resolution studies.

[1] XG. Wang, T. Carrington, J. Chem. Phys., 2023, 158(8), 084107
[2] P.M. Felker, Z. Bacic, Phys.Chem. Chem. Phys., 2022, 24, 24655
[3] D. Viglaska, XG. Wang, T. Carrington, D.P. Tew, J.Mol. Spectrosc. 384 (2022), 111587
[4] Y.liu, J. Li, P.M. Felker, Z. Bacic, Phys. Chem. Chem. Phys., 2021, 23,7101
[5] G. Brocks et al., Mol. Phys. 50,1023 (1983)