

EXPLORING THE DIFFERENCES IN *ORTHO*- AND *PARA*-H₂-FLUOROBENZALDEHYDE COMPLEXES USING FTMW METHODS

B. KEMPKEN, R. M. DOHMEN, D. A. OBENCHAIN, *Institute of Physical Chemistry, Tammannstrasse 6, Georg-August-Universität Göttingen, 37077 Göttingen*; **P. PINACHO, M. SCHNELL**, *Deutsches Elektronen-Synchrotron Notkestrasse 85, 22607 Hamburg*

Understanding the intermolecular binding of molecular hydrogen to other compounds is a basic requirement for the design of possible H₂ storage materials. Nevertheless, studies on H₂ van der Waals complexes with e.g. H₂O,¹ OCS², HCN³, and AgCl⁴ show that to date, there are still gaps in the comprehension especially concerning differences in the binding of *ortho*- and *para*-H₂ to a specific host molecule. Our group investigates the structure of bimolecular *ortho*- and *para*-H₂ complexes with 2-, 3-, and 4-fluorobenzaldehyde, applying chirped pulse and high-resolution cavity Fourier-transform microwave (FTMW) spectroscopy. Rotational and centrifugal distortion constants were determined, supported by DFT-based predictions. Furthermore, the cavity FTMW measurements, taken with a Fabry-Pérot spectrometer, enabled us to resolve the nuclear spin-spin interaction for complexed *ortho*-H₂. The measured rotational constants were used to fit the intermolecular distance. We found that the H₂'s center of mass distance to the aromatic plane is 0.36 – 0.37 nm for *ortho*-H₂ and 0.34 – 0.35 nm for *para*-H₂ complexes. This result is surprising since the mentioned studies encourage the conclusion that *ortho*-H₂ generally binds more strongly to a host molecule than *para*-H₂. A possible explanation could be a coupling distortion of the *ortho*-H₂'s rotational energy levels due to internal rotation of the H₂ group, which we investigate here. DFT-predicted rotational barriers are between 16 and 32 cm⁻¹.

¹[doi:10.1063/S0009-2614\(03\)00476-7](https://doi.org/10.1063/S0009-2614(03)00476-7), X.-G. Wang, T. Carrington, Theoretical study of the rovibrational spectrum of H₂O-H₂, J. Chem. Phys. 134, 044313 (2011).

²[doi:10.1080/00268970210138904](https://doi.org/10.1080/00268970210138904), Z. Yu, K. J. Higgins, W. Klemperer, M. C. McCarthy, P. Thaddeus, K. Liao, W. Jäger, Rotational spectra of the van der Waals complexes of molecular hydrogen and OCS, J. Chem. Phys. 127, 054305 (2007).

³[doi:10.1063/1.462117](https://doi.org/10.1063/1.462117), M. Ishiguro, T. Tanaka, K. Harada, C. J. Whitham, K. Tanaka, Rotational spectra of the H₂-HCN cluster observed by millimeter-wave spectroscopy combined with a pulsed supersonic jet technique, J. Chem. Phys. 115, 5155 (2001).

⁴[doi:10.1364/AO.36.008533](https://doi.org/10.1364/AO.36.008533), G. S. Grubbs II, D. A. Obenchain, H. M. Pickett, S. E. Novick, H₂-AgCl: A spectroscopic study of a dihydrogen complex, J. Chem. Phys. 141, 114306 (2014).