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Benchmarking *ortho/ para* structures in H_2 and D_2 complexes with COF mimics

Abstract

Given the vast range of gas-phase molecular complexes with their structures determined by rotational spectroscopy, there are surprisingly few molecular complexes formed with hydrogen studied by this technique, especially given the uptick in research on hydrogen storage materials. This article highlights our recent efforts to observe the structures of molecular hydrogen in complexes with simple aromatic rings, moving from the known small, simple complexes, to larger benzaldehyde complexes, and continuing to sub-units of covalent organic frameworks as analogs for understanding the interactions of hydrogen with storage materials.

Introduction

Molecular rotational spectroscopy has a long history of molecular structure determination in the gas phase. It has a rich diversity in chemical structures studied, including confirming the polarizability of rare gases when making simple complexes, identification of Criegee intermediates, and the structures of small clusters of water including the water hexamer. [1-3] Given the simplicity of hydrogen as a gas-phase complex partner, there is a relative scarcity of hydrogen complexes studied in the gas-phase. The few known complexes are only with simple molecules, such as H_2-OCS. [4] Given the demand for increased hydrogen technologies in the energy sector, there was an obvious opportunity for microwave spectroscopy to improve our descriptions of how hydrogen binds into different motifs, specifically to molecules that mimic energy storage materials. The known data on simple molecules is not sufficient to benchmark the interactions of hydrogen storage materials.

Before our studies, a series of metal organic frameworks (MOF) mimics were studied by rotational spectroscopy using laser ablation techniques to produce small metal halide diatomic molecules in a molecular jet. In the complexes with AgCl and AuCl, the binding energy of hydrogen to the metal was rather strong, nearly 160 kJ/mol in the case of H_2-AuCl. [5, 6] High-resolution rotational spectroscopy resolved the spin-spin interaction in the *ortho* hydrogen, and could determine increasing $r_{H\text{-}H}$ bond lengths in these complexes.

While the H_2 metal halide studies were a large and important step in understanding the binding of hydrogen, a large percentage of the surface of most storage materials consists of a π-conjugated system. Our group designed a series of experiments to study hydrogen complexes with small aromatic rings as a stepping stone to large, but still relatively small, mimics of covalent organic frameworks (COF). The general idea, cartooned in Figure 1, is that we find molecules that will represent the linking structures of COF systems.

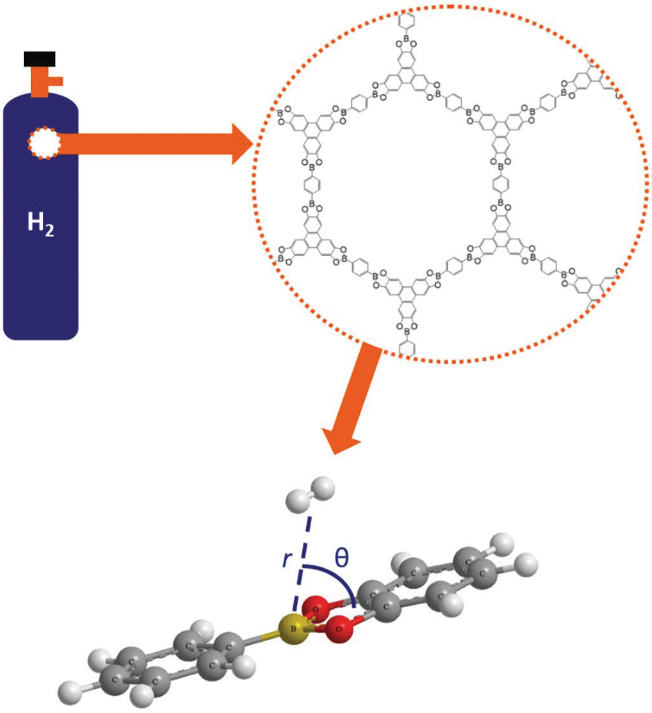

Fig. 1: Simplistic schematic of the fragments of covalent organic frameworks we target in benchmarking hydrogen storage materials (covalent organic frameworks, COF). The structure is not representative of a true observed structure.

This article highlights our work over the past one and a half years as we delve deeper into the structure and spectroscopy of hydrogen complexes. Our work is funded as part of the Benchmark Experiments for Numerical Quantum Chemistry research training group (BENCh). In following the guide practices of benchmarking, we choose systems that explore not just a single structural motif, but a well-designed series. [7] For example, our small aromatic ring targets are those of halogenated benzaldehyde, where we measure the unique structures of

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the complex using the *ortho/meta/para* substituted isomers of the benzaldehyde. We also focus on the boronate ester motif of COF mimics. In this way, we have a clear data set that can be rigorously benchmarked against quantum mechanical methods. In the same regard, we also perform the same experiments with deuterium when possible.

Microwave Rotational Spectroscopy

To measure rotational spectra, our group employs a series of microwave spectrometers from groups around the globe. Our collaboration partners are very gracious and supplement our spectroscopic capabilities. These include the COMPACT spectrometer at DESY, [8] the COBRA and IMPACT spectrometers at the University of Hannover, [9-10] and a reduced-bandwidth chirp pulse spectrometer at Coker College. [11] Our instrumentation at the University of Göttingen is a Balle-Flygare type, Farby-Perot cavity Fourier transform microwave spectrometer. [12] Each has its own capabilities in speed, sensitivity, and resolution. Details on each can be found in the respective citations.

Hydrogen complexes with simple aromatic complexes

In starting with simple halogenated benzaldehyde complexes, we meet many of the needs of a rotational spectroscopy study. The primary requirement is that the observed molecule or complex have a permanent electric dipole in the ground state, where the dipole allows for the observation of pure rotational transitions. A more practical requirement is that the molecule has to be brought to the gas-phase relatively easily. The three common isomers (*o/m/p*) allow for a complete series of benchmarks to be carried out.

The *ortho/para* effect of molecular hydrogen is observed in all our collected spectra. Based on the principles of Fermi-Dirac spin statistics, *ortho* hydrogen is required to be rotating in its ground state, while *para* hydrogen is forbidden to rotate. This relationship holds when hydrogen binds to other molecules, where the *ortho* hydrogen complex has a hydrogen internal rotation while the entire complex rotates. In our observed structures, this creates a vastly different set of experimental rotational constants for the *ortho* and *para* with the halogenated benzaldehydes. Rotational transitions appear to be split by several tens of MHz. This is a stark difference to the analogous splitting in H_2O complexes, where the splitting is more commonly on the order of MHz for the equivalent motion. So far, it seems that the best way to treat the rotational fitting of these spectra is that the *ortho* and *para* complexes are two unique species.

This difference is observed in the broadband spectrum of 2-fluorobenzaldehyde with hydrogen gas shown in Figure 2, and is a good example of the *ortho* and *para* splitting. To understand the complexity of the spectrum, the strongest transitions observed in the spectrum are from the monomer, 2-fluorobenzaldehyde, the ^{13}C and ^{18}O isotopes of the monomer and water complexes with 2-fluorobenzaldehyde. The transition of the H_2 complex is generally on the same intensity scale as the isotopic species of the 2-fluorobenzadehyde monomer, making the assignment of transitions rather challenging.

Moving from the broadband data to our cavity data, we observe another interesting feature found only in the *ortho* hydrogen complexes. The coupling of the two spin one-half nuclei of hydrogen produces a hyperfine splitting that is commonly called a “pseudo quadrupole” as the two nuclei behave as a single nucleus of spin equal to one, and couple to rotational transitions in the same way as any spin equal to one nucleus would. The spin-spin coupling tensor has components given by D_{ii},

$$D_{ii} = -7.7\ \text{kHz}\ \text{Å}^3 \times \frac{g_{H_1}g_{H_2}}{r^3_{H-H}} \times \frac{1}{2}\left(3\cos^2(\angle ri) - 1\right) \tag{1}$$

where the g-factors of hydrogen could be replaced by that of deuterium in the case of D_2. The subscripts, *i*, represent the

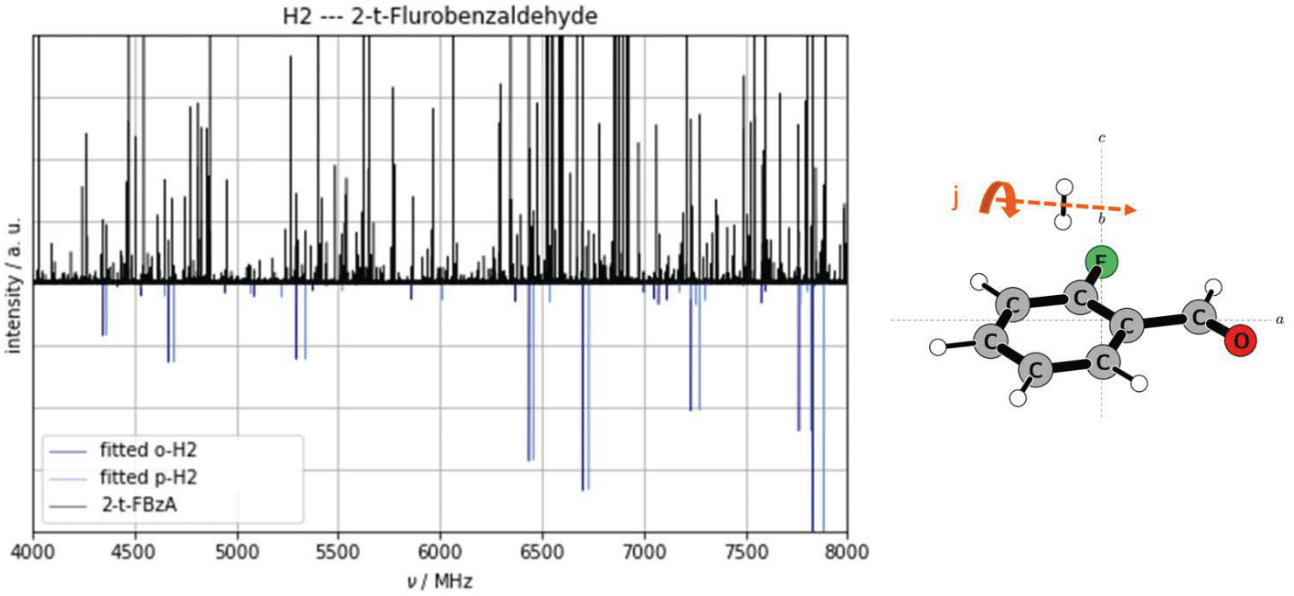

Fig. 2: The fitted spectrum of H_2-2-fluorobenzaldehyde in the *trans* conformer compared to the experimental specturm. Transitions are strong, despite the large intensities shown from the rotational transitions of the monomer.

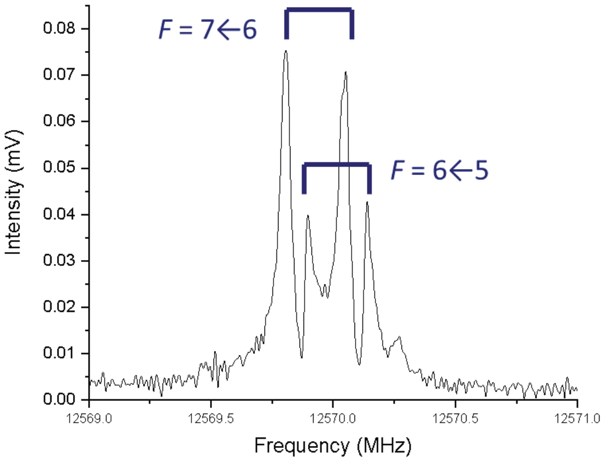

Fig. 3: The 6_{16}-5_{05} transition of *ortho*-H_2 4-fluorobenzaldehyde. Transitions are observed as pairs of Doppler doublets. Hyperfine splitting on top of the Doppler pairs arises from the *ortho*-H_2 spin-spin coupling.

three principal axes (a,b,c) of the molecular system and ∠*ri* is the angle made between the hydrogen bonding axes and the respective principal axis.

From the values in the tensor, we can compare to the values of free-hydrogen and related a change in D_{ii} to a change in the bond length of hydrogen upon forming a complex. This can be very large, as in the case of H_2-AuCl, where the bond was about 0.2 Å longer than in free hydrogen and varied slightly between the observed isotopes. The change can also be small, as it is in the fluorobenzaldehdye complexes, where our preliminary results put the bond length increase at a few hundredths of an Angstrom as determined by spectroscopically observed splitting. The typical splitting pattern shown in Figure 3 shows the relative splitting across all the observed rotational transitions for the *ortho* hydrogen complexes.

Boronate ester complexes with hydrogen

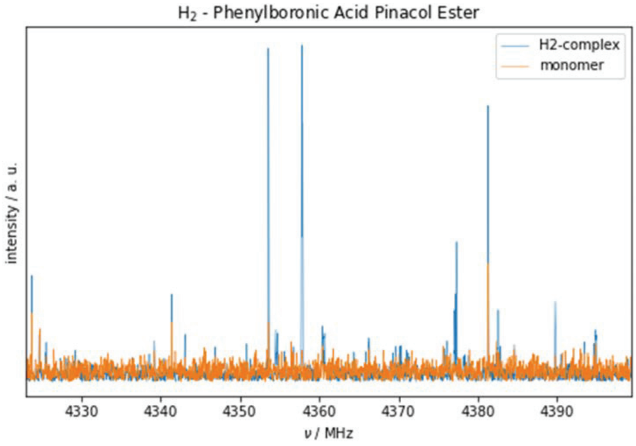

Fig. 4: The broadband spectrum of phenyl boronic acid pinacol ester, with and without H_2. Spectroscopic assignment confirms the transitions unique to the hydrogen data to be of the dimer complex.

Some of the best systems for making quality COF materials are hard to mimic well in the gas phase by rotational spectroscopy. Ideally, benzene would be the best molecule to start with as it is the simplest mimic of the conjugated ring. As benzene has no dipole in the ground state, the induced dipole in its hydrogen complex would be rather small and this makes it difficult to observe. It is best saved for a future study. Alternatively, boronate esters offer a challenging and interesting target system, and still represent a prominent class of COF materials. Once in the gas phase, the large dipole moments of the monomer transfers to the complex and allows for the observation of weakly bound hydrogen complexes. With the initial broadband data, we have already observed the structures of the *ortho* and *para* hydrogen complexes. Future analysis on a cavity microwave spectrometer will yield information on the spin-spin coupling tensor. Here, we will begin to also answer the question of the orientation of hydrogen relative to their binding partners in the complexes, as the angle between the hydrogen nuclei axis and the principal axes required in Equation **1**.

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Daniel Obenchain started his research career developing instrumentation for rotational spectroscopy at Eastern Illinois University, where he received his Bachelor's Degree in Chemistry. He continued in the field of rotational spectroscopy during his PhD at Wesleyan University, where he spent time examining the binding of molecular hydrogen to coinage metals. In 2016, he was awarded an Alexander von Humboldt Postdoc Fellowship at Leibniz University Hannover. In 2018 he had the edifying chance to work in the rotational spectroscopy group in Hamburg, Germany at DESY. Since 2020, he has been building a rotational spectroscopy group (GöRotor Group) at Georg-August University Göttingen in the Institute of Physical Chemistry as a Junior Professor. Their work focuses on benchmarking weakly-bound complexes against other experiments and theory, as well as instructional methods for teaching high-resolution spectroscopy.

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