PARA-ORTHO HYDROGEN CONVERSION; SOLVING A 90-YEAR OLD MYSTERY

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It is well known among spectroscopists that hydrogen has two modifications: para-H_2 and ortho-H_2. Pure para-H_2 can be produced by leading "normal" H_2, a 3:1 ortho:para mixture, over a catalyst at low temperature. It is perhaps less well known that para-ortho H_2 conversion is also catalyzed by collisions with paramagnetic molecules, such as O_2.

Almost ninety years ago Farkas and Sachsse measured the rate coefficient of para-ortho H_2 conversion in gas mixtures with O_2.[1] In the same year, 1933, it was proposed by Wigner [2] that it is the magnetic dipole-dipole coupling between the electron spin of O_2 and the nuclear spins of the two protons in H_2 that is responsible for the conversion. In asymmetric collisions this coupling makes the two H-nuclei inequivalent and mixes the nuclear spin functions of para- and ortho-H_2, as well as their rotational states with even and odd j values. Another mechanism, suggested to be much more effective, was proposed later: the exchange interaction with the open-shell O_2 induces spin density into the electronic wavefunction of H_2. In most collisions the spin density is different at the two H-nuclei, which makes them inequivalent by different hyperfine interactions through the Fermi contact term.

An important application of para-H_2 is in NMR spectroscopy and its imaging variant, MRI. By adding para-H_2 to the sample the sensitivity of NMR can be increased by four orders of magnitude by a phenomenon called para-hydrogen induced polarization (PHIP). Para-ortho H_2 conversion by O_2 in the gas phase was remeasured in 2014 in view of this application. A detailed and quantitative understanding of the conversion process was still lacking, however.

We theoretically investigated the para-ortho H_2 conversion by collisions with O_2 in a first principles approach.[3] Both mechanisms were taken into account and the corresponding coupling terms were quantitatively evaluated as functions of the geometry of the O_2-H_2 collision complex by means of *ab initio* electronic structure calculations. Then they were included in nearly exact quantum mechanical coupled-channels scattering calculations for the collisions between O_2 and H_2, which yielded the para-ortho H_2 conversion cross sections and the rate coefficients for temperatures up to 400 K. The conversion rate and its temperature dependence are in good agreement with the values measured in H_2-O_2 gas mixtures. The calculations provide detailed insight into the conversion process.

[1] L. Farkas and H. Sachsse, Z. Phys. Chem. B **23**, 1 (1933). [2] E. Wigner, Z. Phys. Chem. B **23**, 28 (1933). [3] X. Zhang, T. Karman, G. C. Groenenboom, and A. van der Avoird, Nat. Sci. (2021); https://doi.org/10.1002/ntls.10002.