

PARA-ORTHO H₂ CONVERSION BY COLLISIONS WITH O₂; A FIRST PRINCIPLES APPROACH

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It is well known among spectroscopists that two modifications of hydrogen exist: para-H₂ and ortho-H₂. Pure para-H₂ can be produced by leading 'normal' H₂, a 1:3 para:ortho mixture, over an iron-containing catalyst at low temperature, and can be kept for a long time also at higher temperature in specially prepared gas cylinders. It is perhaps less well known that para-ortho H₂ conversion is also accelerated by interactions with paramagnetic molecules, such as O₂.

An important application of para-H₂ is in NMR spectroscopy and its imaging variant, MRI. By adding para-H₂ to the sample the sensitivity of NMR can be increased by four orders of magnitude through a phenomenon called para-hydrogen induced polarization (PHIP). The para-ortho H₂ conversion by O₂ was recently measured in view of this application.[1]

Two mechanisms have been suggested for the para-ortho H₂ conversion by collisions with O₂. The first one, proposed in 1933 by Eugene Wigner,[2] is the magnetic dipole-dipole coupling between the electron spin of O₂ and the nuclear spins of the two protons in H₂. In asymmetric collisions this coupling makes the two H-nuclei inequivalent and mixes the nuclear spin functions of para- and ortho-H₂, as well as their rotational states with even and odd j values. Another mechanism, proposed by Minaev and Ågren[3] in 1995, is that the overlap of the O₂ and H₂ wavefunctions in a collision complex transfers some of the spin density of O₂ to the wavefunction of H₂. The spin densities induced at the two H-nuclei may be different, which causes a different hyperfine interaction through the Fermi contact term. Wigner made a crude estimate of the para-ortho H₂ conversion rate with the use of some kinetic gas data. Minaev and Ågren suggested, however, that the second mechanism is much more effective.

We investigated the para-ortho H₂ conversion by collisions with O₂ by a first principles approach. Both mechanisms are included: the corresponding coupling terms are quantitatively evaluated as a function of the geometry of the O₂-H₂ collision complex by means of *ab initio* electronic structure calculations. Then they are included in nearly exact quantum mechanical coupled-channels scattering calculations for the collisions between O₂ and H₂, which yield the para-ortho H₂ conversion cross sections and the rate coefficients for a range of temperatures. The conversion rate at room temperature is compared with the value measured in H₂-O₂ gas mixtures.[1]

[1] S. Wagner, Magn. Reson. Mater. Phys., Biol. Med. **27**, 195 (2014). [2] E. Wigner, Z. Phys. Chem. B **23**, 28 (1933). [3] B. F. Minaev and H. Ågren, J. Phys. Chem **99**, 8936 (1995).