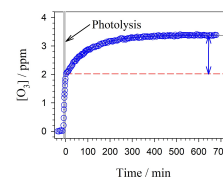


OXYGEN ATOM DIFFUSION BY QUANTUM TUNNELING IN SOLID PARAHYDROGEN: A NEW TOOL TO STUDY LOW TEMPERATURE SOLID STATE REACTIONS

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In quantum crystals such as solid parahydrogen (pH₂), there is considerable overlap between the wavefunctions of molecules in neighboring lattice sites, such that added chemical impurities can exchange positions with nearest-neighbor pH₂ molecules and thereby quantum diffuse through the solid. Our group and others have taken advantage of the quantum diffusion of hydrogen atoms in solid pH₂ to study various low temperature hydrogenation reactions.^a In this talk, we report the first experimental evidence of atomic oxygen diffusion in solid pH₂. O₂ doped pH₂ samples are irradiated at 193 nm to produce O(³P) atoms, and repeated FTIR spectra are collected to map out the temporal behavior during and after photolysis. The experimental proof of mobile O-atoms is provided by the formation of ozone (O₃), which forms via the barrierless $O + O_2 + M \rightarrow O_3 + M$ reaction. After photolysis, while the system is kept in the dark, continued growth in the O₃ concentration with time is detected, indicating that O-atoms are mobile and reacting with O₂ present in the solid. The O₃ growth after photolysis is fit to first-order kinetics equations to extract the rate constant. Kinetics measurements show that the O-atom reaction rate more than doubles in annealed crystals compared to as-deposited crystals. This finding is consistent with the expectation that quantum diffusion is more facile in homogeneous samples with minimum defects. In fact, some proportion of the photo-produced O-atoms get trapped in as-deposited samples and can only be made mobile by annealing the sample. Currently, we are studying the effects of the photolysis conditions, temperature, and doped O₂ concentration on the reaction rate constant. This study shows that O-atoms can be isolated in solid pH₂ and that they are delocalized. Through double doping experiments, we hope to develop this method to study O-atom reactions with other species under controlled low temperature conditions.



^aF. M. Mutunga et al., *J. Chem. Phys.* **154** (2021) 014302.