HCl DIMER IN SOLID PARAHYDROGEN REVISITED

MARIO E. FAJARDO and C. MICHAEL LINDSAY, AFRL/MNME, Energetic Materials Branch, Ordnance Division, U. S. Air Force Research Laboratory, 2306 Perimeter Rd., Eglin AFB, FL 32542-5910; DAVID T. ANDERSON, Department of Chemistry, University of Wyoming, Laramie, WY 82071.

We report new polarization dependent high resolution infrared (IR) absorption spectra of HCl dimers isolated in solid parahydrogen (pH₂) produced during annealing of ~ 100 ppm HCl/pH₂ samples at T = 4.5 K. In our 2001 preliminary report, we showed that the isotopic (H/D and ^35Cl/^37Cl) splitting patterns quantitatively match those for gas phase HCl dimers; left unresolved was the origin of an additional ≈ 0.5 cm⁻¹ splitting observed for each isotopolog. In the interim, a number of experiments have demonstrated that annealed rapid-vapor-deposited pH₂ solids consist primarily of "hcp-like" (hcp = hexagonal close packed) regions, with the hcp c-axes oriented preferentially along the surface normal of the cryogenic sample deposition substrate. As a result, HCl dimers occupying adjacent "in-plane" (ip) substitutional vacancies should have their ν₂ vibration transition dipole moments oriented perpendicular to the substrate surface normal, and their IR absorption spectra should show a markedly different polarization dependence than HCl dimers occupying adjacent "out-of-plane" (oop) vacancies. The present polarization dependent IR spectra are in complete agreement with these expectations, settling the mystery of the additional 0.5 cm⁻¹ splitting, and bolstering our previous tentative assignment of the doublet at 2832.902 and 2833.412 cm⁻¹ to the broken symmetry allowed ν₂ transitions of ip and oop isotopically mixed H^35Cl-H^37Cl dimers, respectively. This assignment yields direct measures of the "quantum interconversion" (loosely: "tunneling") splittings for the ν₂ = 1 states of ip and oop H^35Cl-H^37Cl dimers of ΔE_{ip} = 2.250 and ΔE_{oop} = 2.335 cm⁻¹; in the gas phase this splitting is 3.7320(4) cm⁻¹. We believe the ± 0.001 cm⁻¹ uncertainty on our present measurements makes them the most precise determination of tunneling splittings for any condensed phase species to date.

---

b D. T. Anderson, 56th Ohio State University International Symposium on Molecular Spectroscopy, talk RE05 (2001)