HCl DIMER IN SOLID PARAHYDROGEN REVISITED

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We report new polarization dependent high resolution infrared (IR) absorption spectra of HCl dimers isolated in solid parahydrogen (pH$_2$) produced during annealing of $\sim$ 100 ppm HCl/pH$_2$ samples at T = 4.5 K.[a] In our 2001 preliminary report,[b] we showed that the isotopic (H/D and ^{35}Cl/^{37}Cl) splitting patterns quantitatively match those for gas phase HCl dimers; left unresolved was the origin of an additional $\approx$ 0.5 cm^{-1} splitting observed for each isotopolog. In the interim, a number of experiments have demonstrated that annealed rapid-vapor-deposited pH$_2$ 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 ν_2 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 $\approx$ 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 ν_2^+ transitions of ip and oop isotopically mixed H^{35}Cl-H^{37}Cl dimers, respectively. This assignment yields direct measures of the "quantum interconversion" (loosely: "tunneling") splittings for the $v_2 = 1$ states of ip and oop H^{35}Cl-H^{37}Cl 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}.[c] We believe the $\pm$ 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.

[a] D. T. Anderson, R. J. Hinde, S. Tam, and M. E. Fajardo, *J. Chem. Phys.* 116, 594 (2002).
[b] D. T. Anderson, *56th Ohio State University International Symposium on Molecular Spectroscopy*, talk RE05 (2001)
[c] M. D. Schuder, C. M. Lovejoy, R. Lascola, and D. J. Nesbitt,*J. Chem. Phys.* 99, 4346 (1993).