CRYSTAL FIELD INTERACTIONS OF "LARGE" ROTORS EMBEDDED IN SOLID PARAHYDROGEN

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Matrix isolation has been used for many decades to study the structure and reactivity of species within an inert matrix. In most cases the infrared spectra of the dopants are fairly simple given that the rotational fine structure is usually frozen out by strong anisotropic interactions with the matrix host. In a few noteable cases, quantized rotation in the solid state has been observed spectroscopically, typically occuring when the rotational energy level spacings of the free rotor are large in comparison to the angle dependent barriers imposed by the host solid. The low angular anisotropy and weak interactions of solid parahydrogen has opened up the possibility to study the rotational motion of larger rotators and recently, we have reported that some molecules containing two second row elements, namely CO[a] and HCN,[b] do indeed undergo a hindered rotational motion within the parahydrogen matrix.

In this talk, we discuss our efforts to use infrared spectroscopy to study the rotational dynamics of relatively "large" rotators embedded in solid parahydrogen, *i.e.* molecules that do not rotate in other solid matrices. Parahydrogen matrices containing $\sim 5 - 10$ ppm of CO, NO, HCN, and HCCH are produced using the Rapid Vapor Deposition technique and probed with a high resolution FTIR absorption spectrometer. Analysis of the resulting ro-vibrational spectra show that the crystal field splittings are comparable to the rotational energy level spacings of the free rotor and are sensitive to the vibrational state of the molecule. We analyze this hindered rotational motion using the electrostatic formalism developed by Devonshire[c] and Flygare.[d] Additionally, we examine the magnitude of the various crystal field parameters using ab initio H_2-dopant pair potential energy surfaces.

[a] M. E. Fajardo, *60th Ohio State University International Symposium on Molecular Spectroscopy*, talk RG04 (2005)
[b] C. M. Lindsay and M. E. Fajardo, *61st Ohio State University International Symposium on Molecular Spectroscopy*, talk RD10 (2006)
[c] A. F. Devonshire, *Proc. Roy. Soc. London* A153, 601 (1936).
[d] M. T.Bowers and W. H. Flygare, *J. Chem. Phys.*, 44, 1389 (1966).