QUANTITATIVE MODELING OF THE ν_3 INFRARED SPECTRUM OF SF_6 IN AN Ar MATRIX

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An infrared active polyatomic molecule has several vibrational modes, each of which has a characteristic frequency. If the molecule is trapped in a matrix of perturbing atoms, those vibrational frequencies will shift, and if the vibrational mode is degenerate, the perturbation may lift the degeneracy. Such shifts and splittings are due to the dependence of the chromophore/matrix-atom interaction potential on the internal vibrational motion of the chromophore. Applying a previously-developed model for the shifting and splitting of the triply degenerate ν_3 mode of SF_6 perturbed by a rare gas atom,[a] we use Monte Carlo simulations to find the most stable configurations for SF_6 in an Ar matrix and to predict the associated thermally averaged perturbed IR spectra. Since the experimental spectrum has 10 peaks[b] while the triply degenerate ν_3 mode of SF_6 in a particular environment could have at most 3 peaks, the observed spectrum must be a combination of spectra for SF_6 trapped in different types of lattice sites. A fit to experiment of simulated spectra generated from a family of lattice sites determines the relative importance of the various sites, and accurately reproduces the experimental spectrum.

[a] D. Eichenauer and R.J. Le Roy, *J. Chem. Phys.* **88**, 2898 (1988).
[b] B.I. Swanson and L.H. Jones, *J. Chem. Phys.* **74**, 3205 (1981).