

Local modes in vibrational (and rotational) spectroscopy

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The talk is concerned with the description of highly excited vibrational and/or rotational states of molecules in terms of localized vibrations or local modes. Local mode effects are most common in molecules with multiple equivalent H-X bonds, which give rise to equivalent H-X local-mode stretching vibrations, and we discuss the local mode phenomenon using the spectra of such molecules as examples. In the local mode picture of molecular vibration, experimentally observed, initially unexpected near-degeneracies of vibrational states at high vibrational excitation, and of rotation-vibration states at high rotational excitation, can be explained relatively straightforwardly.

The local mode theory predicts relations between the conventional “effective” rotation-vibration parameters whose values are determined in analysis of experimental molecular spectra in least-squares fittings to observed rotation-vibration transition frequencies or wavenumbers. It should be emphasized, however, that such relations are only valid for particular forms of the effective rotation-vibration Hamiltonian used in the spectral analysis. We illustrate the theory with examples of experimental spectroscopic work where local mode effects play an important role in the interpretation of the experimental findings.

The fact that local-mode vibrations not only cause clustering of highly excited vibrational energy levels, but also of highly rotationally excited rotation-vibration energy levels, has been understood fairly recently. We briefly outline the theoretical background for this phenomenon and relate it to the existing experimental work.