

Mode mixing via resonance Raman excitation profiles

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Mode mixing plays an essential role in the reorganization of chemical bonds in molecular systems and impurity centers under electronic transition. Up to now there is no practically useful method which allows to determine this important parameter of vibronic interaction. Here a possibility is proposed which bases on the measurement of resonance Raman excitation profiles. The excitation spectrum of resonance Raman scattering gives information about both the Raman active mode and the entire vibronic coupling. This makes resonance Raman spectroscopy especially important for multimode systems such as polyatomic molecules or solid-state defect systems. The theoretical interpretation of Raman spectra for such systems is complicated as all modes take part in the scattering process. A practical solution to a multimode case is the transform method [1]: the excitation profile of the Raman mode is computed directly from the absorption spectrum, using for that either the Kramers-Kronig transformation (in the frequency domain) or the Fourier transformation (in the time domain). So the multimode information is automatically carried through the calculation via the measured absorption. The comparison of calculated and measured Raman excitation profiles enables to find the parameters of the model.

It appears that in the time domain the transform relations *absorption* \rightarrow *Raman amplitude* (\rightarrow *Raman excitation profile*) can be formulated in a compact and convenient for numerical calculations form [2]. The advantage of the time representation is particularly manifest in more complicated cases when not only the linear vibronic coupling but also the quadratic vibronic coupling (vibrational frequency change and mode mixing at the electronic transition) is taken into account.

In the case of linear+quadratic vibronic coupling with an arbitrary number of configurational coordinates, the exact equation for the resonance Raman amplitude is derived via the absorption Fourier transform. There are some actual cases when this equation has simple solutions: change of vibrational frequency at the electronic transition without mode mixing, mixing of two modes, mixing of modes with close frequency. The corresponding transform relations between Raman amplitudes (\rightarrow excitation profiles) and the absorption are given, which allow to determine the mixing parameters, vibrational frequencies as well as the linear vibronic coupling parameters.

1. V.Hizhnyakov and I.Tehver, J. Raman Spectrosc. **24**, 653 (1993)
2. V.Hizhnyakov and I.Tehver, J. Raman Spectrosc. **28**, 403 (1997)