

Analytical formulas for Fermi resonance interactions in continuous distributions of states

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Abstract

Fermi resonance interaction between a distributed fundamental vibrational level and a distributed overtone is considered. The overtone is assumed to be spectrally inactive. Simple analytical expressions are derived for the resulting spectral profile in terms of the distribution functions for the fundamental and overtone. The formulas enable straightforward modeling of spectra with Fermi resonances.

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1. Introduction

Fermi resonances occur frequently in vibrational spectra. The perturbation of the spectral bands caused by the Fermi resonance between two vibrational levels is well understood and can be satisfactorily modeled in instances when the levels are well localized as far as their energies are concerned [1]. However, in many practical situations bands have non-negligible widths, that is, vibrational levels are distributed over a finite energy range. This broadening can be caused by intermolecular interaction (especially for H-bonding molecules), short excited state lifetimes, interaction of vibrational modes with phonons, etc. [2]. In cases like these, the equations governing the perturbation for the localized levels cannot be used. Aside from the full quantum–mechanical approach (e.g. [3]), the solution, as described by Scherer [4], is to approximate the distributions of the interacting vibrational states as collections of discrete levels, and then calculate the contribution of each pair of levels from the two distributions. The end spectrum is then the sum of all such contributions. While workable, this approach normally requires the use of a programming language, as well

as an understanding of the particular implementation that underlies the algorithm.

The current paper presents analytical formulas that can be used to calculate the resulting spectrum from given distributions of the two levels. The advantages are the usual ones associated with the use of analytical forms. Practically any available multi-purpose mathematics software can be employed with these formulas (such as MathCad®, Mathematica®, etc.).

2. Theory

Fermi resonances appear whenever a fundamental vibrational level lies closely in energy to an overtone (or combination) level with the same wavefunction symmetry [1,5]. The two levels are allowed to interact due to the presence of anharmonic terms in the Hamiltonian, and, consequently, the strength of such an interaction will depend on the magnitude of the normal modes' anharmonicity constants [6]. The two original levels mix as a result of the resonance, producing two new levels with spectral intensity of the fundamental distributed between them. Since the overtone is spectrally inactive (or extremely weak) by itself, the resonance leads to the appearance of an additional peak in the spectrum. This

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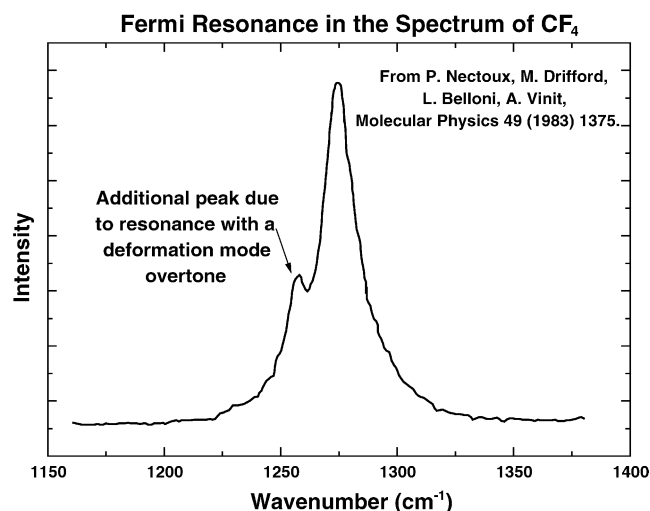


Fig. 1. Fermi resonance in the Raman spectrum of CF_4 in liquid Ar at 84.5 K (from [9]). The weaker band on the low-frequency side of the asymmetric stretch fundamental is due to the resonance with the overtone of the deformation mode at 632 cm^{-1} .

is sometimes viewed as the overtone “borrowing” intensity from the fundamental and becoming visible. A well-known example of Fermi resonance is the presence of two bands in the N–H stretching region of polyamides [7,8], where the two interacting modes are the N–H stretch fundamental and the first overtone of the N–H deformation mode. Vibrational spectrum of CF_4 in the asymmetric stretch region (Fig. 1) also shows a Fermi resonance. It comes from the interaction of the asymmetric stretching mode and the overtone of a deformation mode [9,10].

A large amount of experimental and theoretical work has been devoted to Fermi resonances in the vibrational spectra of hydrogen-bonded compounds, especially water and hydrates [3,4,11–13], where such resonances are both common and pronounced.

The interaction between the fundamental and the overtone can be viewed as a perturbation of the original non-interacting system [1]. According to the standard first-order perturbation treatment, the new eigenstates of the system can be expressed as linear combinations of the old states:

$$\Psi_1 = \beta\varphi_1 + \sqrt{1 - \beta^2}\varphi_2, \quad \Psi_2 = \sqrt{1 - \beta^2}\varphi_1 - \beta\varphi_2, \quad (1)$$

where φ_1 and φ_2 are the original wavefunctions, Ψ_1 and Ψ_2 the new wavefunctions, and β the mixing coefficient. The new energy eigenvalues of the system can be found by solving the secular equation:

$$\begin{vmatrix} E_1 - E & w \\ w & E_2 - E \end{vmatrix} = 0, \quad (2)$$

where E_1 and E_2 are the energies of states φ_1 and φ_2 , E represents the new energy levels of the system, and the off-diagonal

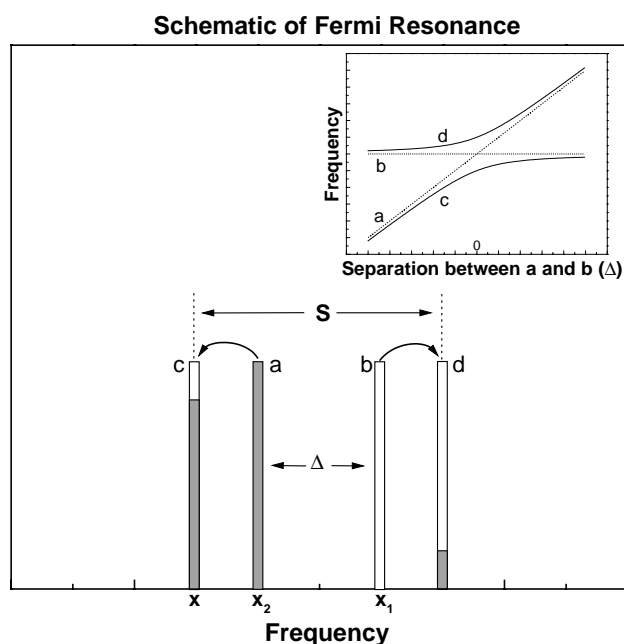


Fig. 2. Effect of Fermi resonance on two interacting vibrational states a and b ; a is spectroscopically visible, b is not. Resonance results in two new eigenstates of the system, c and d , that are linear combinations of a and b . Both c and d are spectroscopically visible. Inset: relative location of states as a function of separation between a and b .

element w is the cross-interaction energy that determines the interaction strength between the two original levels. The solution for (2) is:

$$E = \frac{1}{2}(E_1 + E_2) \pm \frac{1}{2}\sqrt{(E_1 - E_2)^2 + 4w^2}. \quad (3)$$

Fig. 2 schematically shows the effect of the resonance on two infinitely narrow vibrational modes in a spectrum. State a is a fundamental possessing spectral intensity, while state b is a spectrally inactive overtone. This is shown in the figure by the dark shading of state a .

Fermi resonance results in the creation of two new eigenstates of the system, states c and d which, according to (3), are symmetrically displaced with respect to a and b to a new, larger separation S . From (3), S is given by:

$$S = \sqrt{\Delta^2 + 4w^2}, \quad (4)$$

where Δ is the separation between levels a and b .

The admixture coefficient of a in c and d is [cf. with (1)]:

$$f_{c,d}^a = \sqrt{\frac{1}{2} \pm \frac{\Delta}{2S}}, \quad (5)$$

with (+) for c and (–) for d . Both of the new states are spectroscopically active due to admixture of a , with spectral intensity proportional to $(f_{c,d}^a)^2$. As can be seen from (5), no spectral

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