Fermi resonances in the one-dimensional algebraic model

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Received: 2 April 1995

Abstract. The problem of describing in a systematic fashion anharmonic (Fermi) resonances is addressed in the framework of the one-dimensional vibron model. As a practical example, the resonating manifold of in-plane CH bending modes and CC stretching modes of the ethylene molecule is studied in detail.

PACS: 33.10.-n; 33.10.Cs; 82.20.Rp

I. Introduction

One of the most interesting features characterizing infrared and Raman spectra of molecules containing one or more CH cromophores is the experimental evidence of anharmonic (Fermi) resonances [1]. Such resonances typically involve stretching modes of some (or all) CH bonds and other molecular vibrational modes, like bending modes of the CH bonds themselves. It can happen, for example, that the n-th overtone level of a CH stretch is close in energy to some of the (n + 1)-th combination or overtone bands of CH bending modes. When two of such levels have the same symmetry under transformations of the molecular point group, they can interact through a more or less effective coupling mechanism. As a result, their wave functions are mixed to some extent. In absence of such an interaction, one should observe in the spectrum only a relatively intense line corresponding to the allowed n ~-0 transition of the CH stretching mode, whereas those modes with n + 1 vibrational quanta in the same energy region should result much weaker or even completely dark. When the coupling mechanism is taken into account, part of the electric dipole (or quadrupole) activity of the CH bond is shared among the manifold of interacting levels. The final result is a complex pattern of lines in the observed spectrum (in place of a single one). This is not the only possibility of Fermi resonances of manifest themselves in an experiment. As a matter of fact, this kind of mechanism was initially introduced by Fermi [2] to describe an anomalous infrared spectrum of the CO₂ molecule, in which the symmetric CO stretching mode happens to be strongly mixed with the first overtone of the O–C–O bending mode. Fermi resonances are nowadays playing a remarkable role in the understanding of very complex experimental situations and they result in extremely important support in the construction of effective theoretical models [3]. As an example, Fermi resonances are the natural doorway to the description of IVR processes, which are in turn getting more and more important in the time dependent analysis of molecular dynamics [4].

One of the most widely used approaches, namely the force field method [5], can accommodate a meaningful description of Fermi resonances in terms of cubic, quartic and higher order operators in the space of conventional coordinates (either rectilinear or curvilinear ones). These operators contribute to the usual rovibrational expansion for energy level with off diagonal terms: by considering the previous case of CH stretching modes interacting with CH bending modes, within the force field method the related Fermi operator can be written as

\[ V_F = \phi_{ab} q_s q_b^2. \] (1.1)

In this expression \( q_s \), \( q_b \) denote stretching and bending coordinates, respectively. By making use of perturbation theory, it is possible to show that the operator (1.1) induces an effective Hamiltonian term coupling vibrational states differing in their quantum numbers as expected, that is

\[ \langle v_s, v_b | H_F | v_s - 1, v_b + 2 \rangle = k_{ab} \sqrt{v_s(v_s + 1)} (v_b + 2). \] (1.2)

In this expression, the coupling constant \( k_{ab} \) can be determined by a fitting procedure over the perturbed states. It can then be used to obtain the force field constant \( \phi_{ab} \) appearing in (1.1). It is sometimes possible, in more sophisticated approaches [6], to carry out a direct comparison with ab initio calculated values of the force field constants. Higher order contributions have also been considered [7] to improve the predictions offered by this method. It is of course possible to write down more complex operators than (1.1) or, equivalently, more complex matrix element than (1.2) when dealing with Fermi resonances involving more than just two families of vibrational modes.
In the last few years, several important problems of molecular spectroscopy have been addressed in the framework of a class of methods quite different in their formulation and essence from traditional approaches. Such methods are usually referred to as vibron or algebraic models and they find their basis in the extended use of objects like dynamical symmetries and spectrum generating (Lie) algebras. Algebraic techniques have been introduced, discussed and applied in a number of previous papers dealing with various arguments of molecular spectroscopy ([8] and references therein). These models can be considered somehow in between ab initio techniques and semiempirical methods. They in fact provide a Hamiltonian operator for the physical problem of interest but, at the same time, this Hamiltonian is written as an expansion in powers and/or products of a set of certain algebraic operators. The corresponding expansion parameters have then to be adjusted by means of a fitting procedure. Within this framework, the subject of Fermi resonances has been already dealt with in several papers mainly from a semiclassical viewpoint [9]. In the present paper, we rather pay attention to the specific problem of Fermi resonances in connection with the algebraic description of molecular vibrational spectra. From this point of view, Fermi resonances have already been addressed in some interesting cases, like the prototype situation of the CO$_2$ molecule [10], the problem of the HCCF molecule [11] and IVR processes in the benzene molecule [12]. In these situations, the accent was placed on the specific case at issue, without any attempt to give a more general scheme for describing Fermi anharmonic couplings. This to say that algebraic models, in order to provide a systematic approach to molecular spectroscopy problems, have to include in themselves the complete treatment of anharmonic resonances from the very beginning. In this paper we present the general solution to this question within the simple one-dimensional algebraic model. The convenience of an algebraic (even if one-dimensional) formulation of molecular spectroscopy problems has been already extensively discussed and proven in several occasions. We will not repeat these arguments in the present paper. It should be clear, however, that the inclusion of Fermi interactions in these models will have the effect of dramatically improving the overall description of the vibrational spectrum, yet preserving all the advantages offered by the algebraic approach. A review of the work previously done in this field will also be given. The versatility of this approach will be demonstrated by considering in some detail a non-trivial, practical application to the ethylene molecule.

II. Fermi resonances and algebraic models

In this section the most important features of algebraic models accounting for Fermi interactions are described. At present, one can study rovibrational spectra of polyatomic molecules by means of two different algebraic approaches. The first one is a three-dimensional model, in which rotations and vibrations are treated on the same footing. This model, often referred to as U(4) or vibron model, has been used to describe spectroscopic properties of diatomic, three- and four-atomic molecules. The second model is a one-dimensional approach (based on U(2) Lie algebras) in which rotations are completely disregarded. The main advantage of this model is its extreme simplicity from a mathematical point of view. Despite such simplicity, it can be used quite effectively to address complex situations in which the full three-dimensional model requires a more demanding mathematical treatment.

The problem of Fermi resonances has already been outlined, in some special cases, within the framework of both the one- and the three-dimensional algebraic models. Here we want to briefly summarize the story of the algebraic description of Fermi couplings in these last years. The general aspects of molecular algebraic theory can be found elsewhere [8]. To start with, it is important to state that the common denominator of these models is that they (like other models based on effective Hamiltonian operators) provide, as a good effective quantum number, $v_T$, the total number of quanta of vibrational excitation. A typical algebraic Hamiltonian operator will thus have block-diagonal form, each block being labelled by $v_T$. Within each block or polyad, vibrational states result mixed under the action of operators coupling different local modes. This situations is described in an algebraic language in a very compact form. In the dynamical symmetry scheme of algebraic models one has to start from the spectrum generating algebra for $n$ interacting bonds

$$U_1 \oplus U_2 \oplus \cdots \oplus U_n,$$

in which each algebra $U_i$ is either U(4) (in a three-dimensional approach) or U(2) (in a one-dimensional approach). One has then to consider different chains of subalgebras (lattices) closing to a single O(4) coupled algebra (for three-dimensional problems) or to O(2) (for one-dimensional problems). It can be shown that irreducible representations of O(4) (or O(2)) are used to label different blocks of interacting local modes. Such interactions among local modes are described by means of Majorana operators. These operators, which are non-diagonal in the local basis, have the correct properties for describing anharmonic intermode couplings but, at the same time, they break the single U$_i$(4) $\Rightarrow$ O$_i$(4) (or U$_i$(2) $\Rightarrow$ O$_i$(2) dynamical symmetry of each oscillator. This apparent weakness of the dynamical symmetry approach is concurrently its very strength. As already discussed [10], this symmetry breaking is a simple (in the three-dimensional model), yet rigorous mathematical description of how both Darling-Dennison and at least certain Fermi couplings affect vibrational states. This result was used in the vibrational analysis of the CO$_2$ molecule by explicitly taking into account the well known 2:1 Fermi resonance between the states 10'0 and 02'0. The inclusion of such interactions is automatically achieved within the three-dimensional vibron model because of the structure of the matrix elements of the Majorana operator. Due to the specific treatment of bending and stretching vibrations in this model, the sole effective good quantum number for the polyad of interacting levels (in a three-atomic linear molecule) turns out to be (for given $I_2$)

$$v_T = v_1 + v_3 + \frac{(v_2 - I_2)}{2}. \quad (2.2)$$