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Signatures of quantum phase transitions and excited state quantum phase transitions in the vibrational bending dynamics of triatomic molecules

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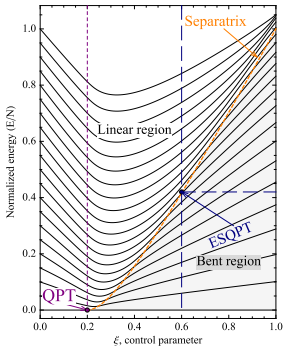
HIGHLIGHTS

- One simple algebraic Hamiltonian describes dierent molecule geometries.
- 2-Dim vibron model describes rigidly linear to rigidly bent molecules.
- The monodromy exhibited by water is shown to represent an excited state quantum phase transition.

GRAPHICAL ABSTRACT



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ABSTRACT

Signatures of quantum phase transitions (QPTs) and excited state quantum phase transitions (ESQPTs) in the bending motion of eight *XYZ* triatomic molecules (HCN, HNC, NiCN; CaOH, CaOD, MgOH, MgOD and OCS), the large-amplitude bending degree of freedom of a tetratomic molecule (HNCS), and four symmetric XY_2 triatomic molecules (H_2O, D_2O, H_2S, H_2Se) are investigated in an attempt to understand their dependence on the composition of the molecular species. It is shown that the isomerizing HCN/HNC system leads to quasi-linearity, that the water molecule H_2O displays a dramatic effect at $E_x \sim 11{,}000\ cm^{-1}$ with clear indication of an ESQPT at about vibrational quantum number $\upsilon_b = 8$, and that the heavy water molecule D_2O is expected to undergo an ESQPT at $\upsilon_b = 10$.

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1. Introduction

In recent years, considerable effort has gone into the study of quantum phase transitions (QPTs) as zero-temperature phase transitions driven by the variation of one or more Hamiltonian parameters called the control parameter(s). Applications to a variety of fields, ranging from Condensed Matter to Nuclear and Particle Physics have been presented [1]. In a simple situation with only one control parameter, ξ, the system's Hamiltonian can be expressed as a combination of two Hamiltonians, $\widehat{H}_1$ and $\widehat{H}_2$, associated with physically different limiting cases

$$\widehat{H} = (1-\xi)\widehat{H}_1 + \xi\widehat{H}_2. \tag{1}$$

In this case the variation of the ξ control parameter from 0 to 1 drives the system from one limit to the other. In some cases an abrupt change of the properties of the system's ground state takes place for small changes around a particular value of the control parameter, called the critical value, ξ_c, which causes qualitative changes in the nature of the system's ground state. These types of

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transitions are also known as "ground state transitions" from the seminal work of Gilmore [2]. The nature of the changes that the system undergoes around the critical value of the control parameter can be studied in close analogy to the formalism of thermodynamic phase transitions and are characterized according to Ehrenfest's classification as transitions of the first order, second order, etc. The equivalence with the abrupt changes that take place in thermodynamic phase transitions is achieved in the limit of very large systems, but finite (mesoscopic) systems can be studied as the precursors of the phase transition and provide a great deal of information on the system.

Very recently the excited state quantum phase transition (ESQPT) concept has extended the QPT formalism to excited states [3]. Whereas a QPT takes place in the system's ground state upon a change of the control parameter, an ESQPT is manifest in excited states of the system as the excitation energy increases. Molecular structure systems offer what is probably the best experimental testing ground for ESQPT, due to the possibility of accessing highly excited states in molecular spectroscopy. The concept of ESQPT is closely related to that of quantum monodromy, introduced in molecular physics by Child, Weston, and Tennyson [4] and observed by Winnewisser et al. [5]. In fact, monodromy in molecular bending degrees of freedom is a particular example of an ESQPT.

QPTs are transitions to different configurations of the system under study. QPTs in molecular structure are transitions between different molecular geometric configurations; in the case discussed in this article the transition occurs between linear and bent molecular geometries associated with a particular bending degree of freedom.

In order to study QPTs and ESQPTs in the bending motion of molecules, we make use of an algebraic model. In such models, molecular degrees of freedom are treated as excitations in a bosonic space (vibrons) [6]. Algebraic models are an ideal tool for the study of precursors of phase transitions in finite systems [7], since the corresponding model Hamiltonian is easily diagonalizable and thus the energies of the quantum states are easily calculable. Extensive reviews of QPTs in algebraic models of atomic nuclei can be found in Refs. [8–10]. The algebraic method used for the study of molecular bending dynamics is the 2-dimensional Vibron Model (2DVM), introduced by one of the authors and Oss [11] and successfully applied to the study of the energy spectrum [12] and transition intensities [13] of non-rigid molecules.

In a previous paper [14], two of the authors applied the concepts of QPT and ESQPT to the study of vibrational bending degrees of freedom in different polyatomic species. This work is in the same vein with the study of quasi-linearity pioneered by Winnewisser and Winnewisser and reviewed in Winnewisser et al. [15]. The only difference is that while in [14] the 2-dim vibron model was used, in [15] Hougen, Bunker, and Johns' Rigid-Bender Hamiltonian further enlarged to the Semi-Rigid and Generalized Semi-Rigid Bender Hamiltonian [16] was used to calculate the quantum levels.

In the present paper we focus our attention on the study of QPT and ESQPT in the bending spectra of triatomic molecules, divided into *XYZ* molecules (HCN, HNC, NiCN; CaOH, CaOD; MgOH, MgOD; OCS) and XY_2 molecules (H_2O, D_2O, H_2S, H_2Se), plus the large-amplitude bending mode of a tetratomic molecule (HNCS) which behaves similarly to the *XYZ* molecules. We find that while in the *XYZ* molecules the dynamics of the transition from linear to bent is identical to that previously studied in polyatomic molecules [14], the spectra of XY_2 molecules are more complex, specifically when the molecules are of the form XH_2. This is partly because quantum effects become more important in the lightweight *H* atoms. In particular, the simple quadratic Hamiltonian of [14] is insufficient to describe accurately the spectrum of H_2O. However, with just one higher-order term, we are then able to describe the dynamics fairly well (despite the Fermi resonance and Coriolis interactions which are known to be present in this molecule) and show that this model confirms the experimental evidence that H_2O undergoes an ESQPT. H_2O is to date perhaps the best example of an ESQPT in triatomic molecules, but in our previous paper [14] and especially in [15] it was shown that NCNCS is the best example of an ESQPT in polyatomic molecules, with remarkable experimental evidence (see Fig. 17 of [14]).

After the introductory remarks of this section, an abridged explanation of the basic facts about the 2-dim vibron model and its extension to higher order is given in Section 2. Section 3 is devoted to briefly presenting the spectroscopic signatures that characterize QPT and ESQPT, while Section 4 presents the model results for each of the molecules addressed. Finally, concluding remarks are provided in Section 5.

2. The two-dimensional vibron model (2DVM)

The 2-dim Vibron Model (2DVM) associates a $U(3)$ Lie algebra to one bending degree of freedom [11,12]. For a detailed description of the model see Ref. [17]. The most general rotational and parity-invariant 2DVM Hamiltonian, including one- and two-body operators, is

$$\widehat{\mathcal{H}} = \varepsilon\hat{n} + \alpha\hat{n}(\hat{n}+1) + \beta\hat{\ell}^2 + A\widehat{P}, \tag{2}$$

where the four spectroscopic parameters ε, α, β, and A are adjustable parameters. A numerically convenient basis to compute the Hamiltonian matrix elements is a truncated 2-dim harmonic oscillator basis, $|[N]; n^{\ell}\rangle$, also written as $|N; n, \ell\rangle$, where the parameter N is equal to the total number of bosons (vibrons) in the system and, though it can be related to the total number of bound states, it has been considered an additional adjustable parameter. See Appendix A for a discussion of how values of N are fixed in this study. The quantum numbers n and ℓ are the eigenvalues of the operators $\hat{n}$ and $\hat{\ell}$ and take the values $n = 0, 1, \ldots, N$ and $\ell = \pm n, \pm(n-2), \ldots, \pm 1$ or 0, (n = odd or even). These have the usual interpretation as the number of quanta of excitation in the harmonic oscillator and the 2-dim angular momentum, i.e. the vibrational angular momentum in the particular case of bending dynamics. The vibrational angular momentum quantum number ℓ typically used in linear species corresponds to the projection of the angular momentum in the figure axis K_a for bent species, but both labels can be used interchangeably [11,14,17].

The operators $\hat{n}$ and $\hat{\ell}$ are diagonal in the basis $|N; n, \ell\rangle$ while the action of the pairing operator $\widehat{P}$ on the basis elements is as follows

$$\begin{aligned}\langle N; n', \ell \mid \widehat{P} \mid N; n, \ell\rangle &= \left[(N-n)(N-n-1) + n^2 - \ell^2\right]\delta_{n',n} \\ &+ \sqrt{(N-n+2)(N-n+1)(n+\ell)(n-\ell)}\,\delta_{n',n-2} \\ &+ \sqrt{(N-n)(N-n-1)(n+\ell+2)(n-\ell+2)}\,\delta_{n',n+2}.\end{aligned} \tag{3}$$

The system excitation energies for a fixed value of N and a given set of spectroscopic parameters is computed by diagonalizing the Hamiltonian matrix in the $|N; n, \ell\rangle$basis and performing an iterative nonlinear least squares minimization to maximize the accordance with experimental term values.

The consideration of the classical limit of the algebraic Hamiltonian offers considerable physical insight into the problem under study and this limit can be obtained using the coherent (or intrinsic) state approach, first presented for applications to nuclear physics in Ref. [18], and later applied to molecular physics in Refs. [19,20]. The potential energy functional associated with Hamiltonian (2) is

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