

Holding Computations of Conical Intersections to a Gold Standard

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1 Introduction

It is well-known that the electronic potential energy surfaces (PES) of polyatomic molecules can cross even if they are of the same symmetry. More precisely they form a conical intersection (CI) or a $(3N-6-2)$ -dimensional hyperline in the nuclear coordinate space of an N -atom molecule. A very important consequence of the CI for reaction dynamics is that it provides an opportunity for a molecule to move facily from one electronic PES to another.

Reaction mechanisms involving CI's have recently been implicated in a number of well-known photochemical reactions and computational methods to characterize the PES in the vicinity of CI's have been implemented and reviewed.¹ These computations have generally been quite enlightening both as to the nature of the PES and to possible dynamical consequences thereof. However, the gold standard for theoretical predictions, computational or otherwise, has always been experimental verification. Unfortunately, in the present case, it has been exceedingly difficult to apply this standard since most experimental measurements only probe the limits, i.e., reactants and products, of dynamics through the CI. Such measurements are relatively insensitive to the details of the CI.

There is however a clear exception to the above generalization and that is the CI caused by symmetry. Such CI's have long been known and are referred to as Jahn-Teller effects.²⁻⁵ From an experimental point of view, the uniqueness of the Jahn-Teller CI is that it is sampled by bound vibronic eigenfunctions that, along with their corresponding eigenvalues, can be precisely investigated by spectroscopic techniques.

In recent years, in our laboratory we have carried out a number of detailed spectroscopic investigations of the vibronic energy levels of Jahn-Teller active molecules. These experiments provide a gold-standard characterization of the molecular vibronic energy levels which are a sensitive function of the CI and the nearby PES. To apply this gold standard to the PES itself we utilize a somewhat modified version of the traditional analytical model of the PES, and determine experimentally the parameters upon which it depends. This PES can then be compared with those resulting from various quantum chemistry calculations.

2 Nature of the experiments

The goal of experiments is to provide as complete a map as possible of the vibronic energy levels of a Jahn-Teller active state. For a comparison to calculated PES's, it is desirable to utilize the lowest Jahn-Teller active state of a given symmetry. The most popular experimental approach^{6,7} has been to map the vibronic levels via the dispersed fluorescence thereto from a more highly excited state. Oftentimes the molecules are jet-cooled to reduce spectral congestion. Sometimes stimulated emission pumping experiments⁸ have also been performed. If the active state of the lowest symmetry is itself excited, (non-dispersed) laser induced fluorescence can be used to characterize it.⁹ For the ground state of ions, ZEKE and related spectroscopies have also been employed.¹⁰⁻¹⁶ Naturally direct IR absorption to the excited vibronic levels of a Jahn-Teller

active state is a powerful technique; however, the difficulty of achieving substantial populations of reactive, open-shell molecules makes the detection of IR absorption difficult, but not necessarily impossible.^{17, 18}

The above experiments are all performed for isolated molecules. There is voluminous literature involving studies of Jahn-Teller molecules in condensed phases. However if comparison between experimental data and the calculated PES of the isolated molecule is desired, the condensed phase results are usually not appropriate. All too often, environmental effects in the condensed phase distort the PES comparably or greater than the intrinsic Jahn-Teller effect.¹⁹

Until about 25 years ago, there was little or no detailed gas-phase data for the vibronic energy levels of Jahn-Teller active molecules (nor for that matter, a computed PES worthy of comparison). This situation began to change with detailed spectroscopic determinations of the vibronic energy levels of the $\tilde{X}^2E_g^1$ and 2E states, respectively, of hexafluorobenzene and sym-trifluorobenzene (and related halobenzene) cations.²⁰

Although progress has been slow, there is now a substantial amount of precision data on a number of “families” of Jahn-Teller active molecules. In the “near-aromatic” family, the benzene cation²¹ has recently joined its experimentally more accessible halobenzene “siblings.” In addition, the neutral radical “cousins,” cyclopentadienyl^{22, 23} and tropylium²⁴ have also recently been investigated.

Arguably, the \tilde{X}^2E state of the methoxy family, CH_3O , CH_3S , CF_3O , and CF_3S has the most detailed experimental information presently available^{2, 20, 25} of any of the organic families. Somewhat similar but a little less studied are the excited \tilde{A}^2E states of the organometallic family^{2, 9, 26, 27} MCH_3 ($\text{M}=\text{Mg}$, Ca , Zn , and Cd). Both these families introduce a complication into the PES that the “nearly-aromatic” molecules lack. They have significant spin-orbit coupling that, strictly speaking, causes the CI at the symmetric point to become an avoided crossing.

All of the above Jahn-Teller active systems share a common characteristic. The two dimensions along which the electronic degeneracy of the CI is raised lie in a space spanned by several (3 or 4) doubly degenerate normal coordinates transforming according to a unique irreducible representative of the symmetry group characteristic of molecule at the CI. In Jahn-Teller language these are multi-mode problems.

The remaining Jahn-Teller active families for which there is presently considerable experimental data available²⁸ are the metal trimer systems. These fall into two categories, the alkali metal trimers (Li_3 , Na_3 , and K_3) and the coinage metal trimers (Cu_3 , Ag_3 , Au_3). There is a well-known spectroscopic transition $^2E'' - \tilde{X}^2E'$, which has produced considerably more information on the excited state, although information on the \tilde{X}^2E' state is slowly forthcoming. Clearly these systems all have the possibility of spin-orbit coupling turning the CI into an avoided crossing. However they all also share an important simplifying feature. There is only a single normal mode of e' symmetry that is Jahn-Teller active. Thus the problem of determining the orientation of the 2-dimensional Jahn-Teller distortion vector in the normal coordinate space is rendered trivial.

All the molecules discussed above have an n -fold symmetry axis where n ranges from 3 to 7 and correspondingly a Jahn-Teller active state that transforms according to one of the doubly degenerate E representations. For spectroscopic applications it has been traditional to represent the Jahn-Teller PES (U_{\pm}) as a function of the normal coordinates (in the vicinity of the CI) by an analytical expression of the form,²⁸

$$\begin{aligned}
 U_{\pm} &= \sum_{i=1}^{M-r} \frac{1}{2} \lambda_i Q_i^2 + \sum_{i=M-r+1}^M \frac{1}{2} \lambda_i \rho_i^2 \pm \rho_i k_i \left(1 + \frac{2g_{ii}\rho_i}{k_i} \cos(n\phi_i) + \frac{g_{ii}^2 \rho_i^2}{k_i^2} \right)^{1/2} \\
 &\approx \sum_{i=1}^{M-r} \frac{1}{2} \lambda_i Q_i^2 + \sum_{i=M-r+1}^M \frac{1}{2} \lambda_i \rho_i^2 \pm [k_i \rho_i + g_{ii} \rho_i^2 \cos(n\phi_i)]
 \end{aligned} \tag{1}$$

where we have introduced for the r degrees of freedom that remove the degeneracy, polar normal coordinates $Q_{i,\pm} = \rho_i e^{\pm\sqrt{-1}\phi_i}$ that span the space, $k_i = \left(\frac{\partial U}{\partial Q_{i,\pm}} \right)_0$, and $g_{ii} = \left(\frac{\partial^2 U}{\partial Q_{i,\pm}^2} \right)_0$ and reference the zero of energy to the vibrationless level of the $(M-r)$ modes that are not Jahn-Teller active. Note that n in $\cos(n\phi_i)$ is determined by the point group symmetry of the molecule. The terms indicated above are typically included in the expression for the PES, although some may be zero for a particular molecule. In some cases additional terms are included^{28, 29} in the expansion of the PES.

The form above corresponds to the traditional champagne bottle PES, in the space of the Jahn-Teller distortion coordinates. If $g = 0$ the CI lies above an equal potential moat (along ϕ). The separation of the

moat from the CI is the linear Jahn-Teller stabilization energy, ϵ^1 . For $g \neq 0$ the moat has barriers, ϵ^2 , caused by separating equivalent local minima, the quadratic Jahn-Teller effect. While the vibronic energy levels are sensitive to all aspects of the PES, it is usually considered to be characterized experimentally if values are obtained for the quantities ϵ^1 , ϵ^2 , and the geometry of the distorted minimum, the latter allowing the magnitude of the Jahn-Teller effect for each of the normal modes to be determined.

These same quantities are of course obtainable from quantum chemistry calculations of the PES and comparison of them to the experimental values constitutes an important benchmark for the computed surface. There are of course numerous procedures and programs (see below) for computing the electronic energies. Once that has been done, we have used three separate approaches to obtain values for comparison to experiments. (i) The simplest, but most computationally intensive (oftentimes prohibitively intensive) is simply to calculate a grid of points over the entire portion of the PES of interest.²¹ Given this grid, it is straightforward to extract values for ϵ^1 , ϵ^2 , the geometry of the global minimum, etc. (ii) A second approach is to calculate only the energies of the CI and the global minimum and the latter's geometry.³⁰ The difference of the calculated energies gives the Jahn-Teller stabilization energy. The geometry of the global minimum gives the direction of the Jahn-Teller distortion. (iii) The third approach is to calculate only the global minimum and distorted geometry.³⁰ Given that the geometry of the CI is known, all the desired quantities can be calculated using an assumed analytical form of the PES, e.g., Eq. (1). The last approach is computationally simplest and has been surprisingly successful in replicating experimental results, perhaps because the electronic computation involves only the global minimum, where it is expected to perform well.

The choice of the computational method is of course highly dependent upon the molecule. Methods we have employed include density functional theory for the global minimum, the approach of Robb, et al.,¹ as contained in Gaussian 98 for the CI, and state-averaged CASSCF calculations using the Columbus package. Normal coordinate vectors at the CI also must be determined and Cadpark and ACESII have been employed for this purpose.

3 Outlook

In the past few years the first notable successes have occurred with good agreement having been obtained between calculated PES's and semi-empirical ones obtained from spectroscopic measurements. The results for the ground PES's of C_5H_5 and $C_6H_6^+$ are excellent examples of such successes.

However many issues remain to be clarified. The general problem of computing a PES near a CI is far from a routine task. Many more molecules will need to be investigated before the best and least computationally expensive approaches can be selected with a degree of certainty.

Experimentally more data is needed but the open-shell nature of Jahn-Teller active states make the experiments difficult. Questions also abound concerning the sufficiency of the simple spectroscopic models to describe the actual PES of many molecules. Only more experiments and comparisons to calculations can answer these questions.

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