The Vibrational Jahn-Teller Effect in $E \otimes e$ Systems

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ABSTRACT

The Jahn-Teller theorem is applied in the vibrational context where degenerate high-frequency vibrational states (E) are considered as adiabatic functions of low-frequency vibrational coordinates (e). For CH_3CN and $\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3$, the global minimum of the non-degenerate electronic potential energy surface occurs at the C_{3v} geometry, but in CH_3OH , the equilibrium geometry is far from the C_{3v} reference geometry. In the former cases, the computed spontaneous Jahn-Teller distortion is exceptionally small. In methanol, the vibrational Jahn-Teller interaction results in the splitting of the degenerate E -type CH stretch into what have been traditionally assigned as the distinct ν_2 and ν_9 vibrational bands. The ab initio vibrational frequencies are fit precisely by a two-state high-order Jahn-Teller Hamiltonian (A. Viel, W. Eisfeld, *J Chem Phys* **120** (2004) 4603-4613). The presence of vibrational conical intersections, including 7 for CH_3OH , has implications for spectroscopy, for geometric phase, and for ultrafast localized non-adiabatic energy transfer.

1. Introduction

The Jahn-Teller theorem [1, 2] states, “*A configuration of a polyatomic molecule for an electronic state having orbital degeneracy cannot be stable with respect to all displacements of the nuclei unless in the original configuration the nuclei all lie on a straight line.*” The existence of non-accidental orbital electronic degeneracy requires a symmetrical nuclear configuration and the instability occurs along a nuclear displacement coordinate that reduces the geometric symmetry. The theorem shows that the electronic energy depends linearly on such a coordinate in the vicinity of the symmetrical configuration, implying that a small displacement in one direction or the other along such a nuclear coordinate will lower the energy. The degeneracy of the electronic state is lifted for such a displacement to yield two non-degenerate electronic states that meet in a conical intersection at the symmetry point.

The experimental observation and theoretical modeling of such spontaneous Jahn-Teller distortions are now well-established aspects of electronic spectroscopy [3-9]. The Jahn-Teller stabilization energies of the distorted structures are typically in the range 500 to 5,000 cm^{-1} [3], which has a profound impact on the electronic spectroscopy of small systems such as C_5H_5 , CH_3O and Ag_3 . The effects of Jahn-Teller distortion can also be very pronounced in transition metal complexes [10, 11]. The impact on their UV-visible and EPR spectra is readily observed and can be applied to understanding the structure of complex inorganic systems, such as in materials and in metalloprotein active sites [12, 13]. Jahn-Teller distortions are known to alter the ligand substitution reactions in some transition metal complexes [14]. The Jahn-Teller effect may result in multiple conical intersections [15], which can become centers for ultrafast energy transfer between the coupled electronic surfaces [16].

The Jahn-Teller theorem exists in the context of the Born-Oppenheimer approximation, that is, the adiabatic separation of the “fast” electronic degrees of freedom from the “slow” nuclear degrees of freedom. In the Jahn-Teller theorem, the quantum states of the fast degrees of freedom are considered to be explicit functions of the slow coordinates. Kellman first pointed out [17] the applicability of the Jahn-Teller theorem to the purely vibrational analog where high-frequency “fast” vibrational modes are adiabatically separated from the low-frequency “slow” vibrational modes. Specifically, he considered van der Waals complexes such as $(\text{SF}_6)_3$, in which the monomer vibrational frequencies are viewed as functions of the van der Waals (inter-monomer) coordinates. For a series of such complexes, he was able to estimate the magnitude of this “vibrational Jahn-Teller effect.”

In this work, we apply the vibrational Jahn-Teller concept to monomer systems with a C_{3v} reference geometry, in which a high-frequency vibrational mode (E) is considered as an explicit function of the low-frequency coordinates (e). The theory and computational methods are outlined in sections 2. and 3., respectively. In section 4., the systems to be considered, CH_3CN and $\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3$, are those for which the global minimum of the (non-degenerate) electronic potential is located at the C_{3v} reference geometry. The magnitude of the spontaneous distortion attributable to the vibrational Jahn-Teller effect is estimated. Then in section 5., the treatment is extended to an example, CH_3OH , where the global minimum of the electronic potential is far from the C_{3v} reference geometry. To demonstrate the vibrational Jahn-Teller effect, the vibrationally adiabatic surfaces are fit to a model Hamiltonian developed for the electronic Jahn-Teller effect. Finally, the limitations of the vibrationally adiabatic concept and the impact of the vibrational Jahn-Teller effect on spectroscopy and dynamics are considered.

2. Theory

In this section, the established theory for the Jahn-Teller effect in $E \otimes e$ systems is adapted and modestly extended for application to the vibrational case. The assumptions inherent in our application of the theory to the vibrational Jahn-Teller effect are noted and evaluated at the relevant points in the text.

In this paper, we address molecular systems that are symmetric under the permutation-inversion operations of the G_6 molecular symmetry group [18], which is isomorphic to the C_{3v} point group. Necessarily, the total wavefunction for each eigenstate, a function of both the fast and slow coordinates, transforms according to one of the irreducible representations, A_1 , A_2 and E , of that group. However, in the context of the vibrationally adiabatic approximation, the fast wavefunctions are solved at each molecular geometry in the slow coordinate space, and therefore these fast wavefunctions transform according to the relevant point group symmetry. Each of the systems considered has a C_{3v} reference geometry and lower symmetries, C_s and C_1 , at other locations in the slow coordinate space. For two systems, CH_3CN and $\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3$, the global minimum of the non-degenerate electronic potential is at the C_{3v} reference geometry. For the third, CH_3OH , there are three equivalent global minima of C_s symmetry that are substantially displaced from the C_{3v} reference geometry; but the overall symmetry of the system is still G_6 , and we will apply the same model Hamiltonian to all three systems.

Relative to the C_{3v} reference geometry, a molecule may distort along degenerate (e) low-frequency vibrational coordinates. The distortion coordinates may be expressed as Cartesian coordinates (x, y) or in polar coordinates (ρ, γ) where the magnitude of the distortion is

$\rho = (x^2 + y^2)^{\frac{1}{2}}$ and γ is the usual polar angle. In the present vibrational case, the high-frequency

states that are degenerate (E) at the reference geometry may include asymmetric CH or CO

stretches. Away from the symmetry point, the degenerate (E) states split, which removes the degeneracy according to the Jahn-Teller effect. We assume (assumption 1) that the energies of the high-frequency vibrational states can be computed as adiabatic functions of the distortion coordinates: $E_{\pm} = E_{\pm}(\rho, \gamma)$. This assumption, which is fundamental to the vibrational Jahn-Teller effect, will be considered further below.

We will follow the development of Viel and Eisfeld (VE) [19], which extends Jahn-Teller theory to include several higher-order couplings that become significant at large distortions. As has been done by some others [15, 20, 21], they limited their treatment of the fast degrees of freedom to two states, assuming that the adiabatic Jahn-Teller surfaces may be approximately described as linear combinations of these two basis states. The validity of this assumption (assumption 2) in the context of the vibrational Jahn-Teller effect will be considered in the sections below. There is no fundamental reason why the number of fast states should be limited to two. Indeed, it is possible to treat multiple fast states, even including higher-order interactions [22, 23]. However, consideration of only two fast states enables the relatively simple closed-form expressions presented below and consequently the physical insight that can be derived from them. We will also find below that these expressions enable high-precision fits to the computed ab initio frequencies.

VE employed Cartesian coordinates and Cartesian basis functions to obtain a real representation of the Hamiltonian that is related to the more usual complex representation [15] by a unitary transformation [19]. The VE Hamiltonian for the high-frequency or “fast” degrees of freedom in this Cartesian basis has the form

$$H = \begin{pmatrix} U+V & 0 \\ 0 & U+V \end{pmatrix} + \begin{pmatrix} W & Z \\ Z & -W \end{pmatrix}. \quad (1)$$

The first of the two matrices contains the diagonal contributions to the energy that represent the average energy of the two interacting states at each point in the (ρ, γ) large-amplitude space. VE expanded each of the matrix elements, as power series in x and y , and they determined which of the possible terms were allowed by symmetry. For convenience, we divide these diagonal contributions into two parts: U is the electronic energy of the Born-Oppenheimer surface on which the vibrational motion occurs, and V is the average energy of the two fast vibrational states considered. The second of the two matrices in Eq. (1) contains the interaction terms that are of primary interest here. Whereas VE expressed their expansions in terms of the Cartesian coordinates (x, y) , the expansions below are expressed equivalently as Fourier series in γ and power series in ρ , and the terms have been regrouped for the convenience of the present purpose. The Fourier expressions are

$$U = U^{0\gamma} + U^{3\gamma} \cos 3\gamma + U^{6\gamma} \cos 6\gamma + \dots \quad (2)$$

$$V = V^{0\gamma} + V^{3\gamma} \cos 3\gamma + V^{6\gamma} \cos 6\gamma + \dots \quad (3)$$

$$W = W^{1\gamma} \cos \gamma + W^{2\gamma} \cos 2\gamma + W^{4\gamma} \cos 4\gamma + W^{5\gamma} \cos 5\gamma + \dots \quad (4)$$

$$Z = W^{1\gamma} \sin \gamma - W^{2\gamma} \sin 2\gamma + W^{4\gamma} \sin 4\gamma - W^{5\gamma} \sin 5\gamma + \dots \quad (5)$$

with the power series expansions

$$U^{0\gamma} = u_1^{(0)} + \frac{1}{2!} u_1^{(2)} \rho^2 + \frac{1}{4!} u_1^{(4)} \rho^4 + \frac{1}{6!} u_2^{(6)} \rho^6 + \dots \quad (6)$$

$$U^{3\gamma} = \frac{2}{3!} u_1^{(3)} \rho^3 + \frac{2}{5!} u_1^{(5)} \rho^5 + \dots \quad (7)$$

$$U^{6\gamma} = \frac{2}{6!} u_1^{(6)} \rho^6 + \dots \quad (8)$$

$$V^{0\gamma} = a_1^{(0)} + \frac{1}{2!} a_1^{(2)} \rho^2 + \frac{1}{4!} a_1^{(4)} \rho^4 + \frac{1}{6!} a_2^{(6)} \rho^6 + \dots \quad (9)$$

$$V^{3\gamma} = \frac{2}{3!} a_1^{(3)} \rho^3 + \frac{2}{5!} a_1^{(5)} \rho^5 + \dots \quad (10)$$

$$V^{6\gamma} = \frac{2}{6!} a_1^{(6)} \rho^6 + \dots \quad (11)$$

$$W^{1\gamma} = \lambda_1^{(1)} \rho + \frac{1}{3!} \lambda_1^{(3)} \rho^3 + \frac{1}{5!} \lambda_2^{(5)} \rho^5 + \dots \quad (12)$$

$$W^{2\gamma} = \frac{1}{2!} \lambda_1^{(2)} \rho^2 + \frac{1}{4!} \lambda_2^{(4)} \rho^4 + \frac{1}{6!} \lambda_2^{(6)} \rho^6 + \dots \quad (13)$$

$$W^{4\gamma} = \frac{1}{4!} \lambda_1^{(4)} \rho^4 + \frac{1}{6!} \lambda_1^{(6)} \rho^6 + \dots \quad (14)$$

$$W^{5\gamma} = \frac{1}{5!} \lambda_1^{(5)} \rho^5 + \dots \quad (15)$$

Eqs. (9) - (15) use the notation of VE for the expansion coefficients, and Eqs. (6) to (8) follow the same pattern. Notice that the lowest power of ρ in each of Eqs. (6) – (15) corresponds to the order of the Fourier term to which each belongs in Eqs. (2) – (5) and that each series contains only even or only odd powers of ρ . The terms given explicitly in Eqs. (2) – (15) correspond to those given explicitly by VE. The first term in Eq. (12), or its equivalent in the complex basis representation, is designated in the literature [15, 20] as a first-order Jahn-Teller interaction, but here we will extend the concept of a first-order Jahn-Teller interaction (JT1) to include all of the off-diagonal terms $\cos\gamma$, which are embodied the expression of $W^{1\gamma}$ as a power series in ρ (Eq. (12)). Likewise, the first term in Eq. (13), or its equivalent in the complex basis representation, is identified as the second-order Jahn-Teller interaction (JT2), and we will extend that label to the combined effects of all of the terms of the form $W^{2\gamma}\cos2\gamma$ (Eq. (13)). These extensions are consistent with the use of the terms in Ref [24]. In linear molecules ($C_{\infty v}$ and $D_{\infty h}$) where $W^{1\gamma} = 0$, JT2 is that part of the family of Jahn-Teller effects that we know as the Renner-Teller effect [7, 24]. In addition, we have in Eqs. (14) and (15) what one might call fourth-order ($W^{4\gamma}\cos4\gamma$) and fifth-order ($W^{5\gamma}\cos5\gamma$) Jahn-Teller effects. Note that there is no third-order Jahn-Teller effect; that is, off-diagonal terms of the form $W^{3\gamma}\cos3\gamma$ are zero by symmetry [19].

The Hamiltonian represented above is the VE Hamiltonian for the electronic part of the problem, which in the present context becomes the Hamiltonian for the high-frequency

vibrations. The solutions to this part of the problem yield vibrationally adiabatic surfaces that represent the *static* Jahn-Teller effect, our primary concern here. With the inclusion of the nuclear motion in the slow coordinate space and resultant coupling between the adiabatic surfaces, one obtains the *dynamic* Jahn-Teller effect [17]. Based on the form of the adiabatic surfaces, it is possible to deduce some qualitative features of the dynamic Jahn-Teller effect.

For the present applications, we keep the Fourier terms up to $\cos 6\gamma$ in Eqs. (2) and (3) and the Jahn-Teller interactions in Eqs. (4) and (5) up to fourth-order. However, since large distortions from the C_{3v} reference geometry are of interest, higher powers of ρ than shown explicitly in Eqs. (6) – (14) will be included, with additional even or odd powers as appropriate and as many as needed to fit the available data. The eigenvalues of Eq. (1) then become

$$E_{\pm} = (V^{0\gamma} + U^{0\gamma}) + (V^{3\gamma} + U^{3\gamma}) \cos 3\gamma + (V^{6\gamma} + U^{6\gamma}) \cos 6\gamma \\ \pm \left\{ (W^{1\gamma})^2 + (W^{2\gamma})^2 + (W^{4\gamma})^2 + 2W^{1\gamma}(W^{2\gamma} + W^{4\gamma}) \cos 3\gamma + 2W^{2\gamma}W^{4\gamma} \cos 6\gamma \right\}^{\frac{1}{2}} \quad (16)$$

For molecules with the global minimum of the electronic potential in the C_{3v} geometry, the spontaneous distortion caused by the vibrational Jahn-Teller effect can be estimated. Since the form of the Jahn-Teller effect as outlined above is the same in the vibrational and electronic cases, the essence of the spontaneous distortion is also the same, only the physical origin of the parameters and their magnitudes are different. To evaluate the spontaneous distortion attributable to the vibrational Jahn-Teller effect, we consider only terms up to ρ^2 in Eqs. (6) to (14). Then Eq. (16) reduces to

$$E_{\pm} = u_1^{(0)} + \frac{1}{2}u_1^{(2)}\rho^2 + a_1^{(0)} + \frac{1}{2}a_1^{(2)}\rho^2 \pm \left\{ (\lambda_1^{(1)}\rho)^2 + \left(\frac{1}{2}\lambda_1^{(2)}\rho^2\right)^2 + \lambda_1^{(1)}\lambda_1^{(2)}\rho^3 \cos 3\gamma \right\}^{\frac{1}{2}} \quad (17)$$

At this point, it is convenient to define a signed distortion variable ρ^* along a line in (ρ, γ) space such that $\rho^* = +\rho$ for $\gamma = 0^\circ$ and $\rho^* = -\rho$ for $\gamma = 180^\circ$. With this, Eq. (17) gives two intersecting parabolas,

$$E_{\pm} = u_1^{(0)} + a_1^{(0)} + \left(\frac{1}{2}u_1^{(2)} + \frac{1}{2}a_1^{(2)} \mp \frac{1}{2}\lambda_1^{(2)} \right) \rho^{*2} \mp \lambda_1^{(1)} \rho^* \quad (18)$$

In the absence of the vibrational Jahn-Teller effect ($\lambda_1^{(1)} = \lambda_1^{(2)} = 0$), the energy $E_{\pm}$ remains degenerate and the minimum energy is at the C_{3v} geometry ($\rho^* = 0$). But now when $\lambda_1^{(1)} \neq 0$ and $\lambda_1^{(2)} \neq 0$, the minimum is lowered by an amount ΔE_{JT} and is displaced by an amount ρ_{JT} to a location of lower (C_s) symmetry. Relative to the energy at $\rho^* = 0$, the vibrational Jahn-Teller stabilization energy is then

$$\Delta E_{JT} = \frac{1}{2} \left(\lambda_1^{(1)} \right)^2 \left/ \left(u_1^{(2)} + a_1^{(2)} - \left| \lambda_1^{(2)} \right| \right) \right. \quad (19)$$

and the spontaneous vibrational Jahn-Teller distortion is

$$\rho_{JT} = \left| \lambda_1^{(1)} \right| \left/ \left(u_1^{(2)} + a_1^{(2)} - \left| \lambda_1^{(2)} \right| \right) \right. . \quad (20)$$

The values of ΔE_{JT} and ρ_{JT} depend on the strength of the first-order vibrational Jahn-Teller effect. However, the largest contribution to the denominators in Eqs. (19) and (20) comes from the electronic potential in form of the harmonic restoring force constant, $u_1^{(2)}$. Since the purely vibrational effects, as embodied specifically in $\lambda_1^{(1)}$, are much weaker than their electronic counterparts, this leads to leading to very small values of ΔE_{JT} and ρ_{JT} .

3. Computational Methods

In this work, a variety of electronic structure methods are used as a means of implementing the assumptions 1 and 2 of the previous section. To approach this problem, the

coordinate space of the molecular vibrations is divided into three parts. There are n_F high-frequency “fast” vibrational modes that are considered as explicit functions of the n_S “slow” coordinates. For a nonlinear molecular system of N atoms, the remaining $n_O = 3N-6-n_F-n_S$ “other” or “inactive” modes are not considered explicitly. In the theory outlined above, we have $n_F = n_S = 2$, but the computational approach outlined here may also be applied for different choices of n_F and n_S . Definition of the means of partitioning a molecule’s $3N-6$ dimensional coordinate space into these three parts and the approximations that result are the major conceptual limitations of this work. This partitioning represents our implementation of assumption (1) above and the practical issues of that implementation result in the additional assumptions (3, 4, 5) outlined below.

The electronic structure methods were used as implemented in the G09 series of programs [25] including a coupled cluster method with an augmented triple zeta basis set (CCSD(T)/aug-cc-pVTZ), Møller-Plesset second-order perturbation theory with a high-angular-momentum basis set (MP2/6-311+G(3df,2p)), and the Becke 3-parameter Lee-Yang-Parr density functional with a small basis set (B3LYP/6-31+G(2d,p)). The first two methods were chosen because they have been used extensively in the literature for methanol [26-31] and the third is an inexpensive level applied here to a transition metal complex, $\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3$ and to test the dependence of the other results on the computational level.

The first step in each calculation is a series of global optimizations, one at each of the relevant stationary points. In every case, one stationary point is the global minimum energy geometry. Where the global minimum is distorted away from the C_{3v} reference geometry (CH_3OH), there are three equivalent global minima and the stationary points also include the three equivalent torsional saddle points and the second-order saddle at the C_{3v} reference

geometry. For all geometry optimizations in this work, the convergence criteria were set to “VERY TIGHT”.

The second step is calculation of the electronic energies of “partially optimized” structures at a variety of points in the n_S -dimensional slow coordinate space, with each of the slow coordinates held fixed at a specified value. The partially optimized structures are obtained by minimizing the electronic energy with respect to the other $3N-6-n_S$ internal coordinates. This step provides the Born-Oppenheimer energies that will be fit to Eq. (2) and the molecular geometries that will be used for computation of the vibrational frequencies. In the present context, the slow coordinates are the torsional angle γ and the distortion ρ . For the molecules with the formula, CH_3XY where $\text{X} = \text{O}, \text{C}$ and $\text{Y} = \text{H}, \text{N}$, we define ρ as the deviation of the CXY angle from linear. To assure the correct symmetry of the results, the symmetrized torsional angle [26] $\gamma = \frac{1}{3}(\gamma_1 + \gamma_2 + \gamma_3)$ is used, where the γ_i , with $i=1, 2, 3$, are the three possible HCXY dihedral angles. Since, with the available software, we were not able to constrain the symmetrized torsional angle during the partial optimization, one of two approaches was applied. In our initial work on CH_3OH [32], only one of the three dihedral angles was constrained and then the symmetrized torsional angle was computed for the analysis. For the symmetric C_s geometries, this approach is equivalent to constraining the symmetrized torsional angle, but for asymmetric geometries (where γ is not a multiple of 60°), the asymmetric constraint of a single dihedral angle leads to a slight distortion of the molecular geometry relative to the partially optimized geometry that would result from the constraint of the symmetrized γ . Therefore in the present work, a second approach was employed to effectively constrain the symmetrized γ . In this approach, all three dihedral angles, γ_1 , γ_2 and γ_3 , were constrained as well as ρ , and a grid of partially optimized calculations was done for each particular value of the symmetrized γ . Then,

the minimum-energy combination of dihedral angles consistent with each symmetrized γ was found within a precision of 0.02° . At the MP2 level, it was found that, along the torsional minimum energy path in methanol, the first approach resulted in a distortion of the unconstrained dihedral angles by typically half a degree relative to the true symmetrized optimization accomplished by the second approach. Along this path, the impact on the computed CH stretch frequencies was small, up to 2.4 cm^{-1} . For the CCSD(T) calculations at each (ρ, γ) combination, all three dihedral angles were constrained at the values found to give the minimum energies in the MP2 calculations.

For the inorganic complex $\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3$, the slow coordinates were defined in terms of the changes in the three Cr-C bond lengths, r_1 , r_2 , and r_3 , and the Cartesian variables,

$$\begin{aligned} x &= \frac{1}{\sqrt{6}}(2\delta r_1 - \delta r_2 - \delta r_3) \\ y &= \frac{1}{\sqrt{2}}(\delta r_2 - \delta r_3) \end{aligned} \quad , \quad (21)$$

which are then converted to the corresponding polar coordinates ρ and γ . Thus in this case,

$\rho = (x^2 + y^2)^{\frac{1}{2}}$ has the units of length, whereas in the H_3CXY molecules, ρ is an angle.

The third step is the calculation of the energies of the one-quantum vibrationally excited states for each of the n_F fast vibrational modes. To do this, we assume (assumption 3) that the fast vibrational modes can be treated harmonically. Our present use of the usual $3N-6$ -dimensional normal mode frequency calculation available in the G09 suite of programs involves the additional assumption (4) that the slow coordinates do not contribute significantly to the fast normal modes in a way that impacts their frequencies. That is, the n_F fast vibrational frequencies determined in this way (and multiplied by h) provide approximations to the energies of the 1-quantum vibrationally excited states of these modes relative to the ground state. The assumptions 3 and 4 are not necessary assumptions in that one could calculate the energies of the

fast states as a function of the slow coordinates in a more rigorous fashion if one was prepared to commit the resources and effort needed to do so. Assumption (3) will be discussed and (4) will be tested in section 5 below.

A fifth assumption (5) is embodied in the use of partially optimized structures, that is, structures whose energy has been minimized with respect to the n_O inactive coordinates as well as the n_F fast coordinates, for calculation of the fast vibrational frequencies. That is, we assume that the inactive degrees of freedom may be handled implicitly by virtue of their slight variation in the partially optimized structures and that the n_F fast coordinates are really effective coordinates that have some curvilinear character in the $(n_F + n_O)$ -dimensional space. The involvement of the inactive coordinates in the effective active coordinates is tested in Section 5 below.

In this work, the variation of the vibrational zero-point energy in the slow coordinate space is neglected. We are primarily interested in the variation of the relative energies of the fast modes in the (ρ, γ) space, and by the form of Eq. (16), the variation of the zero-point energy will not affect those relative energies. For an accurate dynamical calculation on the adiabatic surfaces or on associated diabatic surfaces, one should include the variation of the zero-point energy of the fast modes, and potentially also the variation of the zero-point energies of some or all of the n_O other coordinates.

Once the energies of the one-quantum excited states of the fast modes have been thus computed at an array of points in the slow coordinate space, what remains is to fit the data to Eq. (16) using Eqs. (2) to (14). A non-linear least-squares fit is challenging because the global form of the E_+ and E_- surfaces may be quite complicated, and consequently, the error hypersurface may have a great many secondary minima in the high-dimensional parameter space. Thus, a non-

linear least-squares algorithm is unlikely to converge properly unless the initial parameter values are already quite close to the best-fit values. To simplify the task, the fits to the electronic potential energy surface (Eq. (2) with Eqs. (6) – (8)) and to the vibrational part (the remaining contributions to Eq. (16)) are done separately. At the present level of approximation, the vibrational parts of E_+ and E_- are simply the frequencies of a pair of high-frequency vibrational modes as output by the normal mode analysis of the molecular structure software.

Fortunately, it is possible initially to reduce the fit of the rather complicated vibrational part (Eq. (16) minus Eq. (2)) to a series of 1-dimensional fits to Eqs. (9) – (15). To do this, each of the Fourier terms in Eqs. (3) to (5) (excluding $W^{5\gamma}$) at a particular value of ρ is determined explicitly from the ab initio data at that ρ as linear combinations of E_+ and E_- at each of $\gamma = 0^\circ$, 30° , and 60° . At each value of ρ , the 6 Fourier terms in the vibrational part, $V^{0\gamma}$, $V^{3\gamma}$, $V^{6\gamma}$, $W^{1\gamma}$, $W^{2\gamma}$ and $W^{4\gamma}$, can be determined directly from these 6 values of $E_\pm$. This procedure is repeated for many different discrete values of ρ . For CH_3OH , the result is the discrete values plotted as points in Fig. 1. Each of the six Fourier terms is then fit to a 1-dimensional power series in ρ (Eqs. (9) to (14)). The power series parameter values obtained from these 1-dimensional fits are then used as initial values in the final global fit to the vibrational part of Eq. (16) and their final values (Table 1) are found to be very close to these initial values.

For CH_3CN and $\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3$, only the lowest four Fourier terms, $V^{0\gamma}$, $V^{3\gamma}$, $W^{1\gamma}$, and $W^{2\gamma}$, are included. In this simpler case, the values of the four Fourier terms at a specific values of ρ can be computed explicitly as linear combinations of E_+ and E_- obtained from ab initio data for that value of ρ at only $\gamma = 0^\circ$ and 60° . Even in methanol, the higher Fourier terms, $V^{6\gamma}$ and $W^{4\gamma}$, are relatively small and inclusion of only the lowest four terms provides a near-quantitative description of the n_F high vibrational frequencies in the large-amplitude (ρ, γ) space [32].

The ab initio data and fit residuals for the three molecules are tabulated in the supplementary material.

Figure 1. Fourier terms of the Jahn-Teller model Hamiltonian for CH_3OH as functions of the COH bending angle ρ . The markers are calculated directly from the CCSD(T)/aug-cc-pVTZ ab initio data at specific values of ρ . The curves represent the global fit to Eq. (16). The vertical dotted lines indicate the locations of the vibrational conical intersections (CIs), and the vertical dashed line indicates value of ρ at the global minima of the electronic potential. Note that for $W^{1\gamma}$ only, the

negative of its actual value is plotted to show the locations of the CIs as the intersections of the $-W^{1\gamma}$ and the $W^{2\gamma}+W^{4\gamma}$ curves.

Table 1. Jahn-Teller parameters for CH₃OH

Fourier term ^a	Parameter ^b	Value ^c	Fourier term ^a	Parameter ^b	Value ^c
$U^{0\gamma}$	$u_1^{(0)}$	1.15467E4 (3.E-1)	$V^{0\gamma}$	$a_1^{(0)}$	3.07209E3 (7.E-2)
	$u_1^{(2)}$	-3.89044E4 (1.E1)		$a_1^{(2)}$	1.7836E2 (3.E0)
	$u_1^{(4)}$	3.20513E5 (6.E2)		$a_1^{(4)}$	-4.0273E3 (2.E2)
	$u_2^{(6)}$	-4.59193E6 (3.E4)		$a_2^{(6)}$	1.3407E5 (9.E3)
	$u_2^{(8)}$	1.11471E8 (2.E6)		$a_2^{(8)}$	-4.8724E6 (4.E5)
	$u_2^{(10)}$	-3.0397E9 (8.E7)		$a_2^{(10)}$	1.6433E8 (2.E7)
	$u_2^{(12)}$	7.0703E10 (3.E9)		$a_2^{(12)}$	-4.330E9 (6.E8)
	$u_2^{(14)}$	-9.776E11 (5.E10)		$a_2^{(14)}$	6.486E10 (1.E10)
$U^{3\gamma}$	$u_1^{(3)}$	2.8837E3 (3.E1)	$V^{3\gamma}$	$a_1^{(3)}$	-2.47E1 (2.E0)
	$u_1^{(5)}$	-7.9788E4 (2.E3)		$a_1^{(5)}$	8.20E2 (1.E2)
	$u_1^{(7)}$	2.3468E6 (1.E5)		$a_1^{(7)}$	-2.119E4 (4.E3)
	$u_1^{(9)}$	-6.4219E7 (5.E6)		$a_1^{(9)}$	4.06E5 (9.E4)
	$u_1^{(11)}$	1.4130E9 (1.E8)		$a_1^{(11)}$	-4.3E6 (1.E6)
	$u_1^{(13)}$	-1.839E10 (2.E9)	$V^{6\gamma}$	$a_1^{(6)}$	-4.1E2 (10)
$U^{6\gamma}$	$u_1^{(6)}$	5.32E2 (2.E2)		$a_1^{(8)}$	2.6E4 (8)
	$u_1^{(8)}$	-2.05E4 (9.E3)		$a_1^{(10)}$	-8.5E5 (30)
	$u_1^{(10)}$	3.3E5 (2.E5)		$a_1^{(12)}$	1.37E7 (56)
$W^{1\gamma}$	$\lambda_1^{(1)}$	-5.135E1 (4.E-1)	$W^{2\gamma}$	$\lambda_1^{(2)}$	1.2460E2 (3.E0)
	$\lambda_1^{(3)}$	3.830E2 (2.E1)		$\lambda_2^{(4)}$	-3.4810E3 (3.E2)
	$\lambda_2^{(5)}$	-6.116E3 (9.E2)		$\lambda_2^{(6)}$	1.6702E5 (2.E4)
	$\lambda_2^{(7)}$	1.5463E5 (4.E4)		$\lambda_2^{(8)}$	-9.6187E6 (2.E6)
	$\lambda_2^{(9)}$	-4.464E6 (2.E6)		$\lambda_2^{(10)}$	5.4417E8 (1.E8)
	$\lambda_2^{(11)}$	1.076E8 (5.E7)		$\lambda_2^{(12)}$	-2.6502E10 (6.E9)
	$\lambda_2^{(13)}$	-1.49E9 (8.E8)		$\lambda_2^{(14)}$	9.547E11 (2.E11)
$W^{4\gamma}$	$\lambda_1^{(4)}$	-1.550E2 (7.E1)		$\lambda_2^{(16)}$	-1.873E13 (4.E12)
	$\lambda_1^{(6)}$	1.290E4 (6.E3)	Calculation method		CCSD(T)
	$\lambda_1^{(8)}$	-7.039E5 (4.E5)	Basis set		aug-cc-pVTZ
	$\lambda_1^{(10)}$	2.994E7 (2.E7)	RMS (vibrational part) ^d		0.19
	$\lambda_1^{(12)}$	-9.32E8 (8.E8)	RMS (overall) ^d		0.57
	$\lambda_1^{(14)}$	1.61E10 (1.E10)	N_{data} ^e		122

^a The model Hamiltonian (Eqs. (1) and (16)) is given in terms of the Fourier terms in the torsional angle γ (Eqs. (2) – (5)), each of which is a function of ρ , fitted to a power series, Eqs. (6) – (15).

^b The power series coefficients follow the notation of Ref [19]. The power of ρ is given as a superscript.

^c The fit parameters and statistical uncertainty of each (1 σ) are given in units $\text{cm}^{-1}[\rho]^{-n}$ units, where the dimensions of ρ are $[\rho] = \text{radians}$. A sufficient number of significant figures is given to enable the data to be reproduced within the precision of the fit. Other quantities are in cm^{-1} except as indicated.

^d The root-mean-square residual of the fits are given for the vibrational parts only, exclusive of the electronic energy (Eq. (2)) and for the overall fit including the electronic energy.

^e N_{data} is the number of fitted vibrational frequencies in the dataset.

4. Spontaneous Vibrational Jahn-Teller Distortion

Spontaneous vibrational Jahn-Teller distortion will occur when the electronic potential (Eq. (2)) has its global minimum at the C_{3v} geometry. This spontaneous symmetry breaking lowers the symmetry of the minimum of the adiabatic potential (lower energy in Eq. (16)) from C_{3v} to three equivalent minima of C_s symmetry. Two such molecules considered here are CH_3CN and $\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3$.

In CH_3CN , the frequency of the degenerate asymmetric CH stretch is $3,009\text{ cm}^{-1}$ [33] but the degeneracy is lifted when the CCN frame bends away from linear. Here we will consider the resulting two distinct CH stretch frequencies as explicit functions of the two CCN bend coordinates (x, y) , which are expressed as their polar equivalents (ρ, γ) . In the fundamental spectra, the frequency of the degenerate CCN bend is 362 cm^{-1} [33], which allows for about 8x frequency separation between the fast and slow coordinates. Calculations at the MP2 level were completed at the C_{3v} global minimum geometry and in distorted staggered and eclipsed (C_s) geometries. The CH stretch frequencies so obtained were fit to Eq. (16). The resulting parameters are given in Table 2 and the vibrationally adiabatic surfaces are plotted in Fig. 2. The range of the distortion coordinate ρ in Fig. 2 corresponds roughly to twice the CCN zero-point bending amplitude.

The spontaneous vibrational Jahn-Teller distortion ρ_{JT} is estimated from Eq. (20) to be only 6×10^{-4} degrees. This tiny distortion is the result of a weak first-order Jahn-Teller coupling ($\lambda_1^{(1)}$) in the presence of a relatively robust restoring force constant ($u_1^{(2)}$) in the CCN bend coordinate. Note that the other terms in the denominator of Eq. (20), $a_1^{(2)}$ and $\lambda_1^{(2)}$, have little contribution to ρ_{JT} . Likewise the Jahn-Teller stabilization energy is exceptionally small,

Table 2. Jahn-Teller parameters for C_{3v} molecules

Fourier term ^a	Parameter ^b	CH ₃ CN ^c	Cr(C ₆ H ₆)(CO) ₃ ^c
$U^{0\gamma}$	$u_1^{(0)}$	0.00 (3.E-2)	6.60 (4.E-1)
	$u_1^{(2)}$	1.7318E4 (1.E1)	1.3850E5 (5.E2)
	$u_1^{(4)}$	1.79E4 (2.E3)	6.6234E6 (3.E5)
	$u_2^{(6)}$		-8.856E8 (1.E8)
$U^{3\gamma}$	$u_1^{(3)}$	7.98E2 (1.E2)	-2.6218E5 (9.E3)
	$u_1^{(5)}$	5.7E4 (4.E4)	-2.184E7 (9.E6)
	$u_1^{(7)}$		8.951E9 (4.E9)
$V^{0\gamma}$	$a_1^{(0)}$	3.20311E4 (3.E-4)	1.99524E3 (3.E-2)
	$a_1^{(2)}$	3.95E1 (7.E-2)	-133E2 (2.E1)
	$a_1^{(4)}$	2.1E2 (1.E1))	5.09E4 (1.E4)
	$a_2^{(6)}$		-1.27E7 (5.E6)
$V^{3\gamma}$	$a_1^{(3)}$	-2. (2.E-1)	-4.37E2 (2.E1)
$W^{1\gamma}$	$\lambda_1^{(1)}$	1.05E1 (9.E-3)	1.478E2 (1.E0)
	$\lambda_1^{(3)}$	1.48E2 (1.E0)	-1.54E3 (1.E2)
$W^{2\gamma}$	$\lambda_1^{(2)}$	5.28E1 (1.E-1)	-1.84E2 (1.E1)
	$\lambda_2^{(4)}$	-2.20E2 (3.E1)	3.1E4 (2.E3)
Calculation method		MP2	B3LYP
Basis set		6-311+G(3df,2p)	6-31+G(2d,p)
RMS (vibrational part) ^d		0.0004	0.18
RMS (overall) ^d		0.0028	1.6
N_{data} ^e		148	70
<i>Derived quantities and other information:</i>			
ΔE_{JT} ^f		0.0032	0.079
ρ_{JT} ^f		0.0006°	0.0011 Å

^{a, b, d} See the corresponding footnotes to Table 1.

^c The fit parameters and statistical uncertainty of each (1 σ) are given in units $\text{cm}^{-1}[\rho]^n$ units, where the dimensions of ρ are $[\rho] = \text{radians}$ and $\text{\AA}$ for CH₃CN and Cr(C₆H₆)(CO)₃, respectively. A sufficient number of significant figures is given to enable the data to be reproduced within the precision of the fit. Other quantities are given in cm^{-1} except as indicated.

^e N_{data} is the number of fitted vibrational frequencies in each dataset. For these molecules, the first principles vibrational frequencies were obtained only for molecular geometries with C_s symmetry.

^f Spontaneous distortion parameters derived from Eqs. (19) and (20).

Figure 2. Fitted values of the asymmetric CH stretch frequencies in CH_3CN represented in the two-dimensional coordinate space of the CCN bend angle ρ and the torsional angle γ . Here is ρ represented as the distance from the center of the horizontal coordinate plane and γ is the polar angle. The CH stretch frequencies were calculated at the MP2/6-311+G(3df,2p) level.

$\Delta E_{JT} \approx 0.0032 \text{ cm}^{-1}$. The spontaneous distortion from the electronic Jahn-Teller effect is typically much larger because of the much stronger first-order Jahn-Teller coupling, although the harmonic restoring force may be similar.

In $\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3$, the high-frequency modes considered are the two asymmetric CO stretches near $1,879 \text{ cm}^{-1}$ that become degenerate in the C_{3v} geometry. $\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3$ is sometimes called “piano stool” because of its familiar shape, Fig. 3. The ground electronic state of $\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3$ is non-degenerate, so that no non-zero electronic orbital or spin angular momenta come into play. We will consider the CO stretches as explicit functions of the asymmetric CrC stretch. The frequency of the degenerate CrC stretch is $\sim 492 \text{ cm}^{-1}$, which allows for nearly 4x frequency separation between the fast and slow coordinates. There are other, lower-frequency, coordinates that could be considered as the slow coordinates for the present purpose. However in this complex, the CrC and CO stretches are coupled by back-bonding, which results in stronger coupling than in CH_3CN and a potentially larger first-order Jahn-Teller constant. When a $\text{C}\equiv\text{O}$ bond is lengthened, the probability distribution of one of the electron pairs shifts (slightly) away from the O to create additional bonding between the C and Cr, shortening and strengthening that bond.

Proceeding in a similar fashion as for CH_3CN , the two asymmetric CO frequencies were computed for a range of C_s geometries and fit to Eq. (16). The resulting parameters are given in Table 2 and the vibrationally adiabatic surfaces are plotted in Fig. 4. By comparing Figs. 2 and 4, one can see that the Jahn-Teller splittings are almost an order of magnitude larger reaching about 10 cm^{-1} for distortions in the range of the zero-point CrC amplitude. While the vibrational Jahn-Teller distortion remains very small ($0.001 \text{ \AA}$), it is larger than in CH_3CN .

Figure 3. Structure of $\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3$ optimized at the B3LYP/6-31+G(2d,p) level.

Figure 4. Fitted values of the asymmetric CO stretch frequencies in $\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3$ represented in the coordinate space of the two asymmetric CrC stretches. The magnitude of the CrC displacement from the C_{3v} geometry is represented as ρ , the distance from the center of the horizontal coordinate plane, and γ is the polar angle. The CO stretch frequencies were calculated at the B3LYP/6-31+G(2d,p) level.

relative to the zero-point amplitude. The Jahn-Teller stabilization energy, also still very small, is 20x larger than in CH₃CN.

In each of the above examples, the coordinates (e) of one of the degenerate low-frequency modes were selected as the independent variables and the harmonic frequencies of the highest-frequency vibrational mode (E) were computed as functions of those coordinates. In each molecule there are additional low-frequency degenerate modes that might also have been used as the (e) mode in the same way. That is, there are multiple “Jahn-Teller active” modes in the context of the vibrational Jahn-Teller effect, just as there can be multiple Jahn-Teller active modes in the context of the usual electronic Jahn-Teller effect. We have seen above that the two-state treatment of the $E \otimes e$ Jahn-Teller effect as derived for the electronic context applies equally well to the present vibrational case. Likewise, the situation with multiple Jahn-Teller active modes can also be treated as it is in the electronic case [21].

Based on simple model potential energy surfaces, Kellman [17] was able to estimate the magnitude of the vibrational Jahn-Teller effect in the van der Waals trimmers (SF₆)₃, (Cl₄)₃ and (UF₆)₃. Consistent with the present results, he also found very small stabilization energies, in the range of thousandths to hundredths of a cm⁻¹. While still very small, the spontaneous distortion along the soft van der Waals modes is somewhat larger reaching 0.01 Å. Thus, all of the available examples of the vibrational Jahn-Teller effect show that the magnitudes of the spontaneous distortion and of the stabilization energy are exceedingly small. Although the minimum-energy nuclear geometries have reduced symmetry, the adiabatic surfaces, of which they are a part, have the full permutation-inversion symmetry of the system, and the ground state wavefunction for the slow vibrations will reflect that full symmetry. For such tiny Jahn-Teller distortions, the impact on the total wavefunctions will be slight, likely too small to be directly

measurable. Nonetheless, the splittings between the vibrationally adiabatic surfaces are substantial (1 and 10 cm^{-1} at the zero-point amplitudes in Figs. 2 and 4 respectively), which will impact the energies of the excited states of the low-frequency modes.

5. The Jahn-Teller Effect Far from the Symmetry Point

Because the splittings between the Jahn-Teller adiabatic surfaces increase with the distortion ρ , one can expect the largest impact of the vibrational Jahn-Teller effect in systems that sample the region far from the C_{3v} symmetry point. One class of such systems contains molecules for which the global minimum of the electronic potential occurs at large ρ .

The example that we will consider here is methanol, for which the equilibrium COH angle is $\rho = 71.6^\circ$. Since the molecular symmetry group for methanol is G_6 , the two-state $E \otimes e$ formalism presented above is applicable to methanol as well as to the C_{3v} molecules in Section 4 above. The main difference in the case of methanol is that the electronic potential (Eqs. (2), (6) – (8)) has a second-order saddle at the C_{3v} geometry that is 11,500 cm^{-1} above the global minimum (Fig. 5). Thus at modest excitation energies, the molecule is constrained to explore a circular trough in the vicinity of $\rho = 72^\circ$ that has three equivalent minima in the staggered conformations ($\gamma = 60^\circ, 180^\circ$ and 300°) separated by torsional barriers of about 373 cm^{-1} [34]. This far from the C_{3v} geometry, the degenerate COH bend is represented in terms of the torsional angle γ and the magnitude ρ of the COH bend, the latter being measured as the deviation from linearity. While the torsional frequency is quite low (250 cm^{-1}), the COH bend frequency is higher (1328 cm^{-1}) [35], which is almost 1/2 of the asymmetric CH stretch frequencies ($\nu_2 = 2,999$ and $\nu_9 = 2957 \text{ cm}^{-1}$) [36, 37]. This means a smaller ratio between the high- and low-frequencies than in Section 4 above, and a potentially greater challenge to the validity of

Fig. 5. Fitted electronic potential energy surface for methanol (CCSD(T)/aug-cc-pVTZ) plotted on the vertical axis as a function of the COH bend angle ρ , measured as the deviation from linearity, and the torsional angle γ , represented as the polar angle in the horizontal coordinate plane.

Fig. 6. Relative asymmetric CH stretch frequencies methanol (CCSD(T)/aug-cc-pVTZ), as fitted to the model Jahn-Teller Hamiltonian, and represented as surfaces in the 2-dimensional coordinate space of the COH bend angle ρ and the torsional angle γ . The $V^{0\gamma}$ Fourier term, as well as the entire electronic potential (Fig. 5), have been suppressed in the figure for better viewability.

the adiabatic separation of the high- and low-frequencies. One consequence of dealing with very large ρ is that the power-series expansions in Eqs. (6) – (15) must be extended to quite high powers of ρ .

A great deal of theoretical and computational work on the torsion-vibration dynamics of methanol [24, 26, 27, 29-31, 36, 38-40] has been stimulated by the discovery of inverted torsional tunneling splittings in the CH stretch excited states [37]. Torsional tunneling among the three equivalent minima causes the ground vibrational state to split into A and E tunneling states. Whereas in the vibrational ground state the A state is 9 cm^{-1} below the E state, the E state is below the A state in the ν_2 and ν_9 CH stretch vibrationally excited states [36, 37] and in certain of the other infrared fundamentals [35, 41]. Fehrens et al. [38] applied an adiabatic reaction path Hamiltonian to account for these inverted torsional tunneling splittings. They found that a geometric phase of -1 was accumulated for the CH vibrations ν_2 and ν_9 on a torsional rotation of 2π . In their ab initio treatment of the CH stretch vibrations along the torsional minimum energy path (MEP), Xu et al. [24] have invoked the concepts of Jahn-Teller-like ($\exp(i\gamma)$) and Renner-Teller-like ($\exp(-2i\gamma)$) coupling terms. In the language of the present work, these are the first- and second-order vibrational Jahn-Teller effects, JT1 and JT2. They found that along the MEP, JT2 was actually slightly larger in magnitude than JT1, resulting in the accumulation of a geometric phase of $+1$ for a 2π internal rotation. Recently, two of us (MBD and DSP)[32] applied an extended Zwanziger and Grant Hamiltonian [15] to treat the Jahn-Teller coupling of the ν_2 and ν_9 CH stretches in the 2-dimensional (ρ, γ) large-amplitude space. That work revealed the existence of set of 7 related vibrational conical intersections (CIs), 4 of which are enclosed within the MEP. The Zwanziger and Grant theorem [15] then yields a geometric phase of $(-1)^4 = +1$ for a 2π circuit around four CIs, consistent with the results of Xu et al. The present

application of the VE Hamiltonian represents an extension to include the higher order-terms, $W^{4\gamma}$, $V^{3\gamma}$ and $V^{6\gamma}$, and to implement the noted refinements in the computational method.

The fit of the methanol data to the model Hamiltonian proceeds as described above in Section 3. The values of the 6 vibrational Fourier parameters for methanol were computed directly (without any fit) for specified values of ρ from the ab initio vibrational frequencies at $\gamma = 0^\circ$, 30° , and 60° . These computed values are represented as points in Fig. 1 and values from the global fit to Eq. (16) are shown as lines. The overall dataset included additional ab initio points along the torsional minimum energy path and in the vicinity of each of the conical intersections. It can be seen that the model fits exceptionally well, generally within the thickness of the line in Fig. 1.

As compared to our first published report [32], the inclusion of the fourth order Jahn-Teller coupling $W^{4\gamma}$ results in the $\cos 6\gamma$ term in the eigenvalue expression (Eq. (16)). These model changes, along with refinements to the computational method, cause the RMS residual of the global fit of the vibrational part to be reduced substantially from 0.9 cm^{-1} to 0.19 cm^{-1} . As can be seen from Fig. 1, $W^{4\gamma}$ remains small over the whole range of ρ , which means that the $\cos 6\gamma$ term within the square root makes a small but discernable contribution to Eq. (16). The present fit is good enough that we did not try to include a possible 5th-order Jahn-Teller effect ($W^{5\gamma}$), which would lead to a $\cos 9\gamma$ contribution to the eigenvalue expression. However, a model that included $W^{5\gamma}$ but not $W^{4\gamma}$ would also yield a $\cos 6\gamma$ term in the eigenvalue expression and might be equally good at fitting the data as the present model with only $W^{4\gamma}$. Thus at present, we do not know which of the fourth- or fifth-order Jahn-Teller couplings is more important. It is clear that their combined effects are much smaller than either JT1 or JT2.

The Jahn-Teller parameters are listed in Table 1 and the resulting vibrationally adiabatic surfaces are presented in Fig. 6. These surfaces reproduce the ab initio data within the precision of the fit (0.19 cm^{-1}). With so many terms in each power series, the individual coefficients, other than the leading term in each case, are not particularly well determined. It is noteworthy that the functional form of each Fourier term (each curve in Fig. 1) for small ρ agrees with the respective lowest order power series term as derived by Viel and Einfeld [19] and restated in Eqs. (9) – (14). As is typical when trying to fit an arbitrary curve with a high-order power series, the successive terms in each power series (Eqs. (6) – (15)) alternate positive and negative converging only slowly toward zero, and the fitted coefficients change substantially when one additional term is added to the series. What is well determined and is significant in this problem is the quantitative shape of the curves in Fig. 1. The fit shows that the model Hamiltonian, which was formulated to treat the electronic Jahn-Teller effect, gives an excellent description of the vibrationally adiabatic surfaces (Fig. 6), and thus provides a graphic demonstration of the vibrational Jahn-Teller effect.

The most prominent features in the vibrationally adiabatic CH stretch surfaces for methanol (Fig. 6) are the seven vibrational conical intersections (CIs). These are the locations in the large-amplitude (ρ, γ) space where the two asymmetric CH stretch frequencies, ν_2 and ν_9 , become degenerate. They are degenerate by symmetry at the origin ($\rho = 0^\circ$), but are also degenerate in the eclipsed conformations ($\gamma = 0^\circ, 120^\circ$ and 240°) for $\rho = 62^\circ$ and $\rho = 92^\circ$. The conical intersections at $\rho = 62^\circ$ are quite close to the torsional saddle points ($\rho = 72^\circ$), which are also in the eclipsed conformations. Therefore, these CIs are accessible to the low-energy dynamics.

Fig. 7. In (a) and (b), methanol CH stretch frequencies computed at the CCSD(T)/aug-cc-pVTZ level for the staggered (*s*) and eclipsed (*e*) geometries with a plane of symmetry are plotted as a function of the COH bend angle ρ . The species in the C_s point group are indicated and can be identified with the spectroscopic designations: ν_2 is A' and ν_9 is A'' . The frequencies in (a) are from the usual 12-dimensional normal mode analysis; those in (b) are from a 3-dimensional normal mode analysis that includes only the 3 CH stretch internal coordinates, including the relevant diagonal and off-diagonal f - and g -matrix elements. In (c) are the diagonal force constants for the in-plane (*in*) and out-of-plane (*out*) local CH stretches. The solid lines in (a) represent the global fit to Eq. (16); in the other parts, the dashed lines connecting the points are just a guide to the eye. The vertical dotted lines indicate the locations of the CIs, and the vertical dashed lines indicate value of ρ at the global minima of the electronic potential.

6. Discussion

There are three categories of conical intersections defined according to the role of the local point-group symmetry. The CIs at $\rho = 0^\circ$ in each of the three molecules (located at the centers of Figs. 2, 4 and 6) are required by symmetry and are at the heart of the Jahn-Teller effect. The criteria for a vibrational conical intersection are (i) that the two fast vibrational frequencies become equal and (ii) that the coupling between them is zero. In the C_{3v} geometry at $\rho = 0^\circ$, the asymmetric CH stretches become the degenerate E -type CH stretch and both of the criteria are satisfied by symmetry. Away from $\rho = 0^\circ$ in the staggered and eclipsed conformations, the geometric symmetry is reduced to C_s maintaining only a plane of symmetry. Then the two asymmetric CH stretches transform as A' and A'' in C_s . In general the A' and A'' frequencies are non-degenerate, but the coupling between them is necessarily zero by symmetry. As shown in Fig. 7(a), the A' and A'' frequencies may cross becoming accidentally degenerate at certain values of ρ . The result is “symmetry-allowed” conical intersections at those locations. In methanol, we find such symmetry-allowed conical intersections in the eclipsed conformation near the torsional saddle point, but not in lower-energy staggered conformation. A third possible category of CIs is fully accidental CIs which would occur in non-symmetrical C_1 conformations where both criteria are satisfied accidentally at some point in the large-amplitude coordinate space. We have not found such accidental conical intersections in the systems studied here. In each of Figs. 2 and 4, one sees only the symmetry-required conical intersection at $\rho = 0^\circ$ because the calculations on these C_{3v} molecules were limited to relatively small values of ρ . In Fig. 2, the surfaces are already beginning to curve toward each other at $\rho = 15^\circ$, and CIs at larger ρ can be anticipated although the energies of such CIs might be rather high on the electronic potential energy surface.

Qualitatively, the symmetry-allowed vibrational CIs in methanol result from the cancellation the first- and second-order Jahn-Teller effects (JT1 and JT2) to give a net zero splitting between the adiabatic surfaces at two eclipsed geometries in the general vicinity of the equilibrium COH bending angle. More precisely, in the present treatment there is also a small contribution from the fourth-order Jahn-Teller effect. In terms of the model Hamiltonian, application of Eq. (16) to the C_s geometries reduces all of the cosines to ± 1 and gives the difference between the eigenvalues as

$$\Delta E = 2(W^{2\gamma} + W^{4\gamma} \pm W^{1\gamma}). \quad (22)$$

The upper and lower signs represent the eclipsed and staggered geometries, respectively. The symmetry-allowed CIs occur for $\rho > 0$ where $\Delta E = 0$. For methanol, this happens at two eclipsed geometries as illustrated in Fig. 1 by the crossings of the curve for $-W^{1\gamma}$ (solid red) with the curve for $W^{2\gamma} + W^{4\gamma}$ (dashed). In general, symmetry-allowed CIs occur whenever the magnitudes of the odd- and even-order Jahn-Teller interactions become equal. Thus the locations of the CIs are sensitive probes of the relationship among the different orders of the Jahn-Teller interaction.

In the following paragraphs, the existence and the locations of the conical intersections in methanol are used as benchmarks to gauge the dependence of the results on the computational methods and to gain insight into the nature of the vibrational Jahn-Teller effect. The ρ -dependence of the vibrationally adiabatic frequencies in the staggered and eclipsed conformations (Fig. 7) provides a useful characterization of the results for this purpose.

First of all, little dependence was found on the level of the molecular structure calculations. In methanol, the locations of the CIs at the CCSD(T)/aug-cc-pVTZ level, as evidenced by the crossings in Fig. 7(a) ($\rho = 62.4^\circ$ and 91.9°), are close to those found at the MP2/6-311+G(3df,2p) ($\rho = 61.9^\circ$ and 93.6°) [32] and at the B3LYP/6-31G(d,p) level ($\rho = 60.7^\circ$

and 94.0°)[32]. As expected, the absolute vibrational frequencies are shifted significantly between the different levels, but their relative behavior, including the form of the curves in Fig. 7, is similar at the different levels. This means that the essential features of the phenomenon are captured at the lowest level of calculation. Thus, an initial search for vibrational CIs can be done with an inexpensive calculation and then confirmed, if desired, at a higher level.

The assumptions noted above in sections 2. and 3. deal with different aspects of the separation of the nuclear degrees of freedom into three groups. For methanol, these groups are the asymmetric CH stretches ($n_F = 2$), the slow coordinates ρ and γ ($n_S = 2$), and the other ($n_O = 8$) inactive degrees of freedom. Insight in the role of the 8 inactive degrees of freedom (assumptions 4 and 5) can be obtained by comparing different calculations along the torsional minimum energy path (MEP). Fig. 8 shows the CH frequencies along a partially optimized (POPT) path along which the electronic energy was calculated as a function of the symmetrized torsional angle γ and minimized with respect to the other 11 degrees of freedom. These are seen to be almost coincident with the frequencies along the path of steepest descent (IRC) from a torsional saddle point to a global minimum [24]. That is in Fig. 8, the circles and downward-pointing triangles fall on the same curves within the precision that can be discerned from the figure. However, there is a discernable difference (up to 2.4 cm^{-1}) between the partially optimized points obtained by constraining the symmetrized torsional angle (circles) and those obtained by constraining only a single dihedral angle (squares). As might be expected, the asymmetrical torsional constraint puts a strain on the molecule that results in slightly different partially optimized geometries. A comparison of the two sets of structures along the MEP yields an RMS deviation of up to 0.17° for the angular internal coordinates. This slight difference between the two sets of structures is enough to cause a small but discernable difference in the

Fig. 8. Methanol CH stretch frequencies computed along the torsional minimum energy path from the torsional saddle point ($\gamma = 0^\circ$) to a global minimum ($\gamma = 60^\circ$). To allow comparison of four different ways of calculating the frequencies and to allow a direct comparison with Fig. 9 of Ref. [24], the data are taken from calculations at the MP2/6-311+G(3df,2p) level. The four different types

of ab initio frequency calculations are (i, blue squares) partially optimized structures obtained by constraining a single dihedral angle at each point; (ii, open red circles) partially optimized structures obtained by constraining the symmetrized dihedral angle at each point; (iii, downward pointing green triangles) structures along the path of steepest descent from the torsional saddle point (intrinsic reaction coordinate, “IRC”). For each of these three calculations, an ordinary 12-dimensional (non-projected) normal mode analysis was carried out for each structure to obtain the plotted frequencies; however for (iv, upward pointing black triangles), an 11-dimensional normal mode analysis (as given in Ref. [24]) was done at each point, projecting out the reaction coordinate itself. The line represents the fit (Ref. [32]) to Eq. (16) without inclusion of the $V^{3\gamma}$, $V^{6\gamma}$ and $W^{4\gamma}$ terms. The line is coincident with the model of Ref. [24] as represented by the line in Fig. 9 of that reference.

CH stretch frequencies. This difference goes to zero in the configurations with a plane of symmetry ($\gamma = 0^\circ, 60^\circ, \dots$) where the two types of constraints become equivalent.

Fig. 8 also compares two different frequency calculations along the IRC. One is the CH harmonic frequencies from a 12-dimensional normal mode calculation (downward-pointing triangles), and the other is from 11-dimensional normal mode calculations with the IRC projected out (upward-pointing triangles). These two sets of points are also almost coincident, indicating a negligible involvement of the torsional coordinate in the fast normal modes (ν_2 and ν_9). This result supports our use of 12-D normal mode calculations for determination of the adiabatic CH stretch frequencies (assumption 4).

The validity of the 2-state approximation (assumption 2) is justified in part by the separation of the third CH stretch, called the “symmetric” CH stretch ($\nu_3 = 2845 \text{ cm}^{-1}$) [36, 42], from the two asymmetric CH stretches that are treated by the present model. We find that the ν_3 frequency is substantially lower than the other two over the whole range of the (ρ, γ) space. Additional support comes from the satisfying fit of the 2-state Jahn-Teller model (Eq. (16)) to the ab initio data. However, such a fit yields effective Jahn-Teller parameters that embody the implicit involvement of the other degrees of freedom. A close examination of the MEP shows that the ν_3 normal mode has unequal amplitudes on the three CH bonds and that the relative amplitudes vary by about a factor of two along the MEP. Both the present normal mode calculation and full-dimensional quantum calculations [31] indicate that there is a small but noticeable admixture of the OH stretch in the CH normal modes. The 2-state approximation is not fundamental to the treatment of the vibrational Jahn-Teller effect, but it is frequently used in the domain of the electronic Jahn-Teller effect, and it does enable an appealing closed form analytical expression for the adiabatic energies (Eq. (16)). A model involving all three CH

stretches, and possibly even the OH stretch, could be readily developed [36] with the use of numerical rather than analytical diagonalization of the model Hamiltonian.

A more serious threat to the 2-state approximation comes from the use of the harmonic approximation (assumption 3). One consequence of the harmonic approximation is the neglect of the diagonal anharmonic shift of the CH stretch frequencies that arises primarily from the single-bond anharmonicities. More serious is the neglect of the stretch:bend 1:2 resonances, which are known to be quite strong within the methyl group [31, 43-46]. This means that the vibrational bands that have been recorded experimentally at high-resolution and assigned to the asymmetric CH stretches are in fact mixed states that involve significant HCH bending character. No such interactions are included in the normal-mode model calculations of the present work. Such Fermi and higher-order interactions, which lead to the phenomenon of intramolecular vibrational redistribution (IVR) [45, 46], represent a fundamental limitation to the concept of the separation high- and low-frequency degrees of freedom (assumption 1).

Insights into the nature of the vibrational Jahn-Teller effect can be obtained from comparison of the 12-D normal mode CH stretch frequencies (Fig. 7(a)) with a reduced dimensional normal mode treatment, involving only the Hessian for the three CH stretches and the corresponding g -matrix elements (Fig. 7(b)). Although there is an absolute shift of about 8 cm^{-1} , the pattern of the relative frequencies is almost identical in these two panels. This means that the vibrational Jahn-Teller effect is contained primarily within the CH stretching space and its dependence on the slow coordinates. A further reduction is contained in Fig. 7(c), which plots only the diagonal single-bond force constants of the in-plane and out-of-plane CH bonds. To compare the curves in Fig. 7(a) and (b) with the single-bond force constants in Fig. 7(c), we recognize that the amplitude in these modes is not distributed equally among the three CH bonds.

For the A' CH stretches, there is a larger amplitude on the in-plane CH bond than on the other two CH bonds. For the A'' CH stretches, the amplitude is all on the two out-of-plane CH bonds, none on the in-plane CH bond. Therefore, qualitatively the A' vibrations in Fig. 7(a) and (b) (red) can be compared to the in-plane force constant in Fig. 7(c) (red). Likewise the A'' vibrations (blue) can be compared with the out-of-plane force constants (blue). One can see that these qualitative comparisons hold, implying that the main source of the vibrational Jahn-Teller effect and the set of related CIs is the variation of the single-bond CH stretch force constants in the (ρ, γ) space. The crossings of the two eclipsed curves in Fig. 7(c) do not occur in exactly the same place as in Fig. 7(b), which indicates a discernable but lesser role for the off-diagonal force constants and g -matrix elements connecting the three CH internal coordinates.

A detailed understanding of the impact of the vibrational Jahn-Teller effect will depend on future calculations of the coupled fast and slow nuclear motions, that is, on calculations of the dynamic vibrational Jahn-Teller effect, and on the experiments needed to test them. However, the present static treatment may be used to shed some light on the implications of the vibrational Jahn-Teller effect.

One of the implications of this work is the accumulation of a geometric phase by the high-frequency vibrations along a closed path in the (ρ, γ) space encompassing a conical intersection. In each of the three molecules, a small-radius circular path centered on the C_{3v} symmetry point encloses one CI and thus a geometric phase of -1 is accumulated. In methanol, this applies for $\rho < 62^\circ$. Thus, the wavefunctions for the fast vibrations change sign upon a 2π internal rotation (if they are constrained to be real and to vary smoothly with the torsional angle). In methanol for intermediate ρ ($62^\circ < \rho < 92^\circ$), such a circular path encloses four CIs. According to the theorem proved by Zwanziger and Grant [15], the result is a geometric phase of

+1, which is in agreement with the previous calculations of Xu et al. [26, 28] along the MEP. Beyond the outer CIs ($\rho > 92^\circ$), seven CIs are enclosed and the geometric phase is again -1. Since the CIs at $\rho = 62^\circ$ are relatively close to the MEP, both values of the geometric phase might contribute to fully coupled quantum states as they would be computed, for example, in a full-dimensional quantum calculation of the nuclear motion [29-31].

As is the case for the conical intersections, this vibrational geometric phase exists only in the context of an adiabatic separation of the fast and slow degrees of freedom. Although geometric phase in methanol has been discussed several times in the literature [24, 28, 32, 38, 47], its impact on observable experimental data remains unclear. The connection of the -1 geometric phase to the inverted torsional tunneling splittings in the ν_2 and ν_9 vibrational bands was evident in the nature of the methanol calculations by Fehrens et al. [38]. However, now that we appreciate that JT2 is larger than JT1 along the MEP and that geometric phase is +1, but the torsional tunneling splittings remain inverted [24, 28, 29]. Likewise the JT2 terms are dominant in a series of G_{12} molecules including methylamine and the ethyl radical [48], and in those systems the torsional tunneling patterns are also inverted [49, 50]. The fact of inverted tunneling splittings can be derived from symmetry considerations [39, 49], but there is evidently no direct connection with geometric phase. This begs the question of whether there is any experimentally observable impact of geometric phase in these systems.

A potentially important impact of the vibrational Jahn-Teller effect concerns the propensities for vibrational energy transfer connecting the adiabatic states. In the electronic domain, ultrafast energy transfer between surfaces is localized in the large-amplitude coordinate space to be near the CIs. There are two precedents from the literature to suggest that vibrational conical intersections may play a similar dynamical role. First, localized ultrafast energy transfer

has been predicted by model calculations on vibrational conical intersections [51, 52]. Second, we see in methanol, for example in Fig. 10 of Ref. [24], that the computed composition of the fast vibrations changes sharply, nearly discontinuously, at the eclipsed conformation, which is near the CIs. In quantum mechanical terms, that would become an abrupt change in the character of the vibrational wavefunction as a function of the slow coordinate γ . This suggests a high probability for surface hopping, that is, for non-adiabatic vibrational energy transfer at that point in the large-amplitude coordinate space.

In the context of electronic conical intersections, Ryabinkin et al. [53] have found that impact of the geometric phase on the dynamics was an enhancement of the non-adiabatic transfer rate. It is not yet known whether geometric phase will impact the vibrationally non-adiabatic dynamics in a similar way.

The most readily observable impact of the vibrational Jahn-Teller effect is the splitting of pairs of the high frequency vibrations that would become a single degenerate vibration at the symmetry point. This splitting becomes large, perhaps several tens of cm^{-1} , when the equilibrium geometry is far from the symmetry point. In the G_6 systems considered here, the stretches that are a degenerate E -symmetry vibration at the symmetry point become distinct non-degenerate A' and A'' vibrations away from the symmetry point. In methanol, these A' (ν_2) and A'' (ν_9) CH stretch fundamental frequencies are separated by 42 cm^{-1} [36] and have been historically identified as separate bands [54].

7. Summary

The vibrational Jahn-Teller effect has been demonstrated, both in molecules for which the minimum of the electronic potential has C_{3v} symmetry and for one molecule for which the

minimum of the electronic potential is far from the C_{3v} geometry. In both situations, it was shown that the computed adiabatic energies of the high-frequency vibrational states can be represented accurately by an extended two-state Jahn-Teller model [19] developed for the electronic Jahn-Teller effect. The form of the vibrationally adiabatic surfaces encodes anharmonic couplings between the fast and slow vibrational modes, and the conical intersections connecting them represent localized vibrational resonances. Viewing these couplings through the lens of the adiabatic approximation points to the potential of applying concepts developed in the electronic domain to gain insight into purely vibrational phenomena.

The computed spontaneous distortion of CH_3CN and $\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3$ attributable to the vibrational Jahn-Teller effect is very small, likely too small to yield an observable effect. In methanol, whose geometry is far from the C_{3v} symmetry, the coupling between the fast and slow vibrational modes is much larger. Accordingly, the Jahn-Teller splitting of the vibrationally adiabatic surfaces is also much larger, and gives rise to the substantial splitting of the ν_2 and ν_9 fundamental frequencies. The vibrationally adiabatic surfaces for methanol meet in a related set of vibrational conical intersections, some of which are accessible to the low-energy dynamics.

The vibrational Jahn-Teller effect is an abstraction that only exists within the context of the adiabatic separation of the fast and slow vibrational degrees of freedom. The vibrationally adiabatic approximation is more tenuous than its electronic counterpart, the Born-Oppenheimer approximation, because the frequency separation between the fast and slow degrees of freedom may not be as great and because the fast states may be coupled to low-order combinations of certain intermediate-frequency modes. In fact, the vibrationally adiabatic approximation is sure to fail near a conical intersection where non-adiabatic transitions will be rapid. A test of the usefulness of the vibrational Jahn-Teller concept will be its prediction of observable phenomena,

including ultrafast vibrational energy transfer that is localized in the large-amplitude coordinate space near the vibrational conical intersections.

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Figure 1

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