

Ab initio normal-mode vibrational displacement vectors for the three C-H stretching vibrations along the internal rotation path in methanol

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Modern quantum chemistry packages allow for the determination of harmonic vibrational frequencies along a chemical reaction path, primarily for the purpose of correcting fixed-nucleus electronic-state energy differences by including also the differences in their vibrational zero-point energies along the path. This set of commands in the quantum chemistry package can also be used to determine the small-amplitude vibrational frequencies along a large-amplitude internal rotation (torsional) coordinate. In the present work, we are not concerned with the vibrational frequencies themselves, but rather with the form of the vibrational displacement vectors associated with each small-amplitude normal mode, and in particular, we focus only on the Cartesian atomic normal mode displacement vectors $\mathbf{d}_i(\gamma)$ determined by the Gaussian suite of programs for the three CH stretching motions (ν_2 , ν_3 , and ν_9) along the steepest-descent internal rotation path γ in methanol (CH₃OH). These modes are especially interesting because the symmetry environment of each C-H bond changes significantly during the internal rotation, i.e., each of the methyl bonds takes turns passing (twice for a complete torsional revolution) through the plane of symmetry of the COH frame of the molecule.

The first question to be examined concerns the symmetry properties of the $\mathbf{d}_i(\gamma)$ vectors along the torsional coordinate. Graphical displays of these vectors will be used to show that vibrational displacements for atoms in the frame of the molecule have a three-fold periodicity along the torsional coordinate, so that their variations can be expressed by a Fourier series in $\cos 3n\gamma$ for displacements that transform into themselves when $\gamma \rightarrow -\gamma$ or by a series in $\sin 3n\gamma$ for displacements that transform into their negatives when $\gamma \rightarrow -\gamma$ (where n is an integer). On the other hand, vibrational displacements for each hydrogen atom of the methyl group have only a 2π periodicity along the torsional coordinate, so that their variations must be expressed by Fourier series containing terms $\cos n\gamma$ or $\sin n\gamma$ with integer n . In the present work, graphical displays of some calculated displacement vectors are almost noise free, others are very noisy. Furthermore, some variations with γ are rather well described by only the $n = 1$ term in their Fourier expansion, while others contain sharp spike-like features which cannot be well represented by short Fourier series.

The second question to be examined concerns the theoretical understanding of some limiting cases of torsion-vibration coupling that give rise to the $\mathbf{d}_i(\gamma)$ in these graphical displays. It turns out that terms in the Hamiltonian for a simplified theoretical model for this torsion-vibration interaction problem closely resemble terms in the simplified Hamiltonians often used for the better known vibration-electronic Jahn-Teller and Renner-Teller problems. In this analogy, the slow motion is the internal rotation motion here and the vibrational motion in the vibronic Jahn-Teller and Renner-Teller problems. The fast motions are the small-amplitude CH stretching modes here and the electronic motions in the vibronic problems. The torsion-vibration coupling terms for the present problem take the form

$$k_1(e^{+i\gamma}Q_+^2 + e^{-i\gamma}Q_-^2) + k_2(e^{-2i\gamma}Q_+^2 + e^{+2i\gamma}Q_-^2), \quad (1)$$

where $Q_{\pm} = Q_x \pm iQ_y$ represent components of a “doubly-degenerate vibration” formed by combining ν_2 and ν_9 . In the talk, a brief explanation will be given of why these terms are of A_1 symmetry in the permutation-inversion group G_6 , and how the first term is closely analogous to that for the lowest-order Jahn-Teller vibronic coupling term for a C_{3v} molecule, while the second term is closely analogous to that for the lowest-order Renner-Teller vibronic coupling term in a Π electronic state of a linear molecule. In addition, the closed form equations for the $\mathbf{d}_i(\gamma)$ that can be obtained for the limiting cases with either $k_1 = 0$ or $k_2 = 0$ will be discussed. It is of interest to note that if only the first coupling term is present, these $\mathbf{d}_i(\gamma)$ transform into their negatives when the molecule undergoes one full internal rotation; if only the second coupling term is present, these $\mathbf{d}_i(\gamma)$ transform into themselves when the molecule undergoes one full internal rotation. For the CH stretches in methanol the two terms seem to be of almost equal importance, with the second term slightly dominant.

The third question to be examined concerns calculation of the A/E torsional splittings in the excited $\nu = 1$ fundamental states of the three CH stretches from information given by a quantum chemistry calculation. Experimentally, this splitting has the same sign as in the ground state for ν_3 , but has a sign opposite to that in the ground state for ν_2 and ν_9 . Several papers in the literature give theoretical explanations for this sign behavior using perturbation theory based on a diabatic treatment, where the interaction terms are present in the potential energy expression (e.g., the terms given in Eq. (1)). Quantum chemistry output corresponds, however, to an adiabatic situation where all vibration-torsion interaction terms in the potential energy surface have been “diagonalized out.” The complicated (and complicating) torsion-vibration interactions have not really disappeared, however, they have merely been taken out of the potential energy function and relocated in the kinetic energy operator. After this relocation the two terms in Eq. (1) appear as a “new Coriolis interaction term” involving the product of a stretching-vibration angular momentum operator and the torsional angular momentum operator. The coefficient ζ in front of this new Coriolis operator depends on derivatives with respect to γ of the $\mathbf{d}_i(\gamma)$ vectors. Quantum-mechanical situations where all perturbations occur in the kinetic energy operator (rather than in the potential energy operator) are relatively unfamiliar to high-resolution molecular spectroscopists, so the new features in such a calculation will be described briefly.

The present work is not yet finished. The contents of this talk will thus resemble a progress report rather than a presentation of material from a published paper, i.e., results will be somewhat incomplete and conclusions will be somewhat tentative.