LETTERS TO THE EDITOR

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NOTES

Canonical perturbation theory versus Born–Oppenheimer-type separation of motions: The vibrational dynamics of C_3

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The vibrational spectra of molecules with small (or large) ratios of the fundamental frequencies are difficult to calculate and assign. For example, the bending frequency of the C_3 molecule is as small as $\omega_2 = 63\ \mathrm{cm}^{-1}$ (and the bottom of the surface is very anharmonic), while the frequencies of the symmetric and antisymmetric stretches are of the order of $\omega_1 = 1225\ \mathrm{cm}^{-1}$ and $\omega_3 = 2040\ \mathrm{cm}^{-1}$, respectively.[1] Therefore, the bending vibrational energies of C_3 form dense manifolds, which change considerably from one stretching state to another. In order to tackle this problem, one is naturally tempted to carry out a Born–Oppenheimer (BO) separation between the (slow) bending and the (fast) stretching motions. For this purpose, one first solves the Schrödinger equation for the fast degrees of freedom

$$H_{\mathrm{stretch}}\Phi_k(r_1,r_3|\gamma) = E_k^{\mathrm{BO}}(\gamma)\Phi_k(r_1,r_3|\gamma), \tag{1}$$

where γ denotes the bending angle and r_1 and r_3 the stretch coordinates, H_{stretch} is the stretch Hamiltonian (where γ appears as a fixed parameter and the derivatives with respect to γ are set to zero), k labels stretching states, and $E_k^{\mathrm{BO}}(\gamma)$ and $\Phi_k(r_1,r_3|\gamma)$ are the eigenvalues and eigenvectors of the stretch Hamiltonian, which both depend parametrically on γ. The wave functions $\Psi_{k,m}^{\mathrm{BO}}(r_1,r_3,\gamma)$ of the exact Schrödinger equation are then sought for in the form of products

$$\Psi_{k,m}^{\mathrm{BO}}(r_1,r_3,\gamma) = \Phi_k(r_1,r_3|\gamma)\chi_m(\gamma), \tag{2}$$

where m labels bending states. It is well-known that this kind of approximation breaks down as soon as two surfaces $E_k^{\mathrm{BO}}(\gamma)$ come close together. Unfortunately, this is precisely what happens for C_3, as can be checked in Figs. 1 and 2 of Ref. 2, where BO-type calculations for C_3 are reported. It is seen that the potential energy curves for the stretching states $(n_1,n_3) = (3,0)$ and $(0,2)$ exhibit an avoided crossing, as well as the curves for states (3,1) and (0,3). Tables 3 and 4 of Ref. 2 and Fig. 1 (top) of this Note show that these avoided crossings result in very large errors for the calculated energies of the corresponding bending states, many errors being even larger than the bend frequency. This observation lead the authors to conclude that "for these states the interaction between basis states is extremely important and the only realistic way of calculating them appears to be in a variational calculation."

The purpose of this Note is to emphasize that (i) the avoided crossings and the large errors reported in Ref. 2 are instead just due to the failure of the BO approximation in the case of crossing energy curves, and (2) the canonical perturbation procedure for floppy molecules we have recently derived[3] enables an efficient separation of the degrees of freedom of C_3 up to energies larger than those investigated in Refs. 1, 2.

Since the perturbation procedure is described in detail in Ref. 3, it is sufficient here to recall that the Hamiltonian of Ref. 1 is first expanded in Fourier series along the minimum energy path (MEP), which connects the three extrema of the potential energy surface, and in Taylor series perpendicular to the MEP, leading to

$$H = \sum_{M,P,N,\mathbf{m},\mathbf{n}} h_{MPN\mathbf{mn}}(\cos\gamma)^M \sigma^P (J^2)^N \prod_j (a_j^+)^{m_j}(a_j)^{n_j}, \tag{3}$$

where the a_j and the a_j^+ are the ladder operators for the stretch degrees of freedom, while J^2 and σ denote differential operators with respect to γ.[3] A series of canonical transformations is then performed in order to cancel all the terms such that $\mathbf{m} \neq \mathbf{n}$. At the end of the procedure, one is thus left with a perturbative Hamiltonian of the form

$$K = \sum_{M,P,N} k_{MPN}(n_1,n_3)(\cos\gamma)^M \sigma^P J^{2N}, \tag{4}$$

where the k_{MPN}'s are polynomial functions of the stretch quantum numbers n_1 and n_3. Pseudopotential curves $V_{n_1,n_3}(\gamma)$, which are just the equivalent of the $E_k^{\mathrm{BO}}(\gamma)$ curves of the BO theory, are then simply obtained by retaining only the terms such that $P = N = 0$, that is

$$V_{n_1,n_3}(\gamma) = \sum_M k_{M00}(n_1,n_3)(\cos\gamma)^M. \tag{5}$$

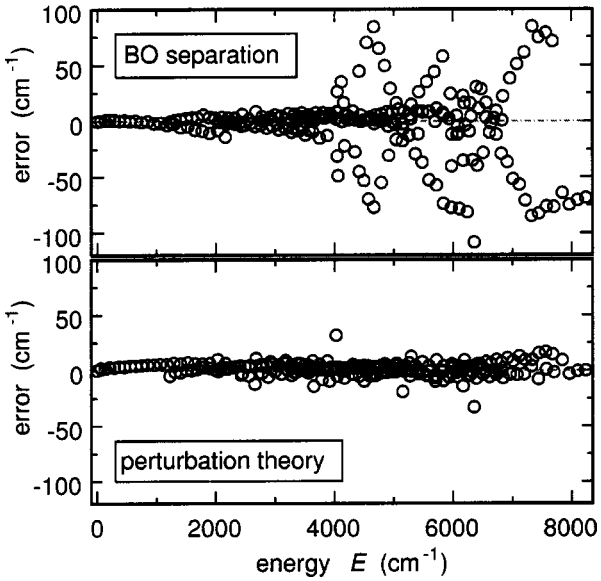

FIG. 1. Plot, as a function of the energy of each state, of the errors with respect to variational energies, which are observed for BO-type calculations (top) and sixth-order perturbative calculations (bottom). Included in the calculations are the 220 states reported in Tables 3 and 4 of Ref. 2, which have up to 21 quanta of excitation in the bending degree of freedom.

The pseudopotential curves obtained after six canonical transformations are shown in Fig. 2 for the couples of stretch quantum numbers (n_1,n_3) displayed in Figs. 1 and 2 of Ref. 2. Contrary to Ref. 2, one now observes a crossing of the curves $V_{3,0}$ and $V_{0,2}$, on one side, and $V_{3,1}$ and $V_{0,3}$, on the other side. Moreover, as can be checked in Fig. 1 (bottom), the energy levels of the sixth-order perturbative Hamiltonian of Eq. (4), which are very easily obtained from the diagonalization of small matrices of size 60×60,[3] are in much better agreement with the variational ones than those derived from the BO procedure.

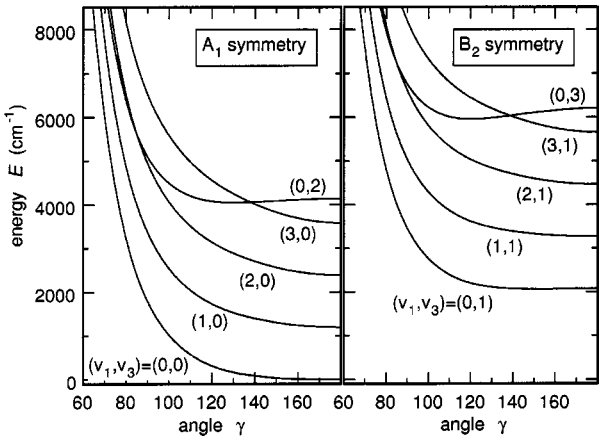

FIG. 2. Plot, as a function of the bending angle γ, of several pseudopotential energy curves $V_{n_1,n_3}(\gamma)$ for the C_3 molecule, obtained from sixth-order perturbative calculations. This figure should be compared with Figs. 1 and 2 of Ref. 2.

Conclusion of this work is twofold: first, the canonical perturbation procedure we have proposed for floppy molecules works better than a BO-type separation of motions when several potential energy curves cross. Moreover, study of the C_3 molecule with this procedure shows that its dynamics is deceptively simple, in the sense that all the degrees of freedom remain essentially decoupled throughout the studied energy range. This implies in turn that vibrational states of C_3 with energies still larger than those investigated here can be obtained with reasonable precision at very low computing costs by using the perturbative Hamiltonian of Eq. (4).

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