

Resonant interactions of normal modes in rotating classical molecules

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During numerical work on classical energy transfer in molecules we found that pairs of normal modes in isolated rotating molecules resonate, i.e., energy is exchanged strongly among modes that have nearly the same frequency. In the case of a degenerate mode pair, energy initially concentrated in one mode, is completely transferred into the other mode after rotating through a characteristic angle

$$\theta_r = \pi/2\xi, \quad (1)$$

where $0 < \xi \leq 1$ is a measure of the Coriolis coupling between the modes. This is found to be true regardless of the magnitude of the angular frequency of rotation Ω , as long as the atomic displacements from their equilibrium positions remain small.

It turns out that, for two modes i and j , $\xi = |e_{ij}|$, where

$$e_{ij} = \hat{n} \cdot \sum_k x_k(i) \times x_k(j). \quad (2)$$

\hat{n} is a unit vector in the direction of the angular velocity Ω , $x_k(i)$ is the eigenvector of the i th mode associated with the k th atom and is obtained from the appropriate force constant matrix of the molecule; the sum is taken over all atoms in the molecule. Coriolis coupling can occur between two modes, therefore, when the cross product of their respective eigenvectors summed over the molecule [i.e., Eq. (2)] does not vanish. This is equivalent to Jahn's rule.¹

Analysis reveals that Newton's equations of motion in the harmonic approximation admit coupled normal vibrations when the Coriolis and centrifugal terms are fully retained, as long as $\Omega \cong \Omega_0 \hat{n}$, where both Ω_0 and \hat{n} are constant. Degenerate normal modes couple strongly through the Coriolis term. Consider, e.g., a pair of in-plane degenerate modes (call them 1 and 2) vibrating at the frequency ω in a planar molecule rotating such that Ω is perpendicular to the molecular plane. For the particular case where the energy is initial-

ly concentrated entirely in mode 1 the energies E_1 and E_2 of the two modes become

$$E_1 = A \cos^2 \xi \Theta(t) + O\left(\frac{\Omega_0}{\omega}\right), \quad (3)$$

$$E_2 = A \sin^2 \xi \Theta(t) + O\left(\frac{\Omega_0}{\omega}\right), \quad (4)$$

where A is a constant and $\Theta = \Omega_0 t$ is the angle through which the molecule has rotated after time t ; the higher order terms oscillate with a frequency slightly shifted from ω . Thus, all the energy is initially concentrated in mode 1 and transfers to mode 2 after the molecule rotates through an angle $\Theta = \theta_r$, where θ_r is defined by Eq. (1). The rate of transition is proportional to $\xi \Omega_0$. It also is true that the sum $E_1 + E_2$ is a constant, except for a correction of the order Ω_0^2/ω^2 . These conclusions are valid no matter how small Ω_0 becomes, as long as Ω_0 is not zero.

The in-plane nondegenerate modes couple also, but much more weakly than do the degenerate modes. It can be shown that the mode energy oscillates with an amplitude of the order $\Omega_0^2 \xi^2 \omega_1 \omega_2 / (\omega_1^2 - \omega_2^2)^2$, for those modes which satisfy the inequality

$$8\Omega_0^2 \xi^2 (\omega_1^2 + \omega_2^2) / (\omega_1^2 - \omega_2^2)^2 \ll 1,$$

where ω_1 and ω_2 are the frequencies of modes 1 and 2. Thus, as the ratio $\Omega_0^2 \xi^2 \omega_1 \omega_2 / (\omega_1^2 - \omega_2^2)^2$ is decreased nondegenerate modes rapidly decouple and the resonance phenomenon disappears.

For molecular rotations oriented at arbitrary angles with respect to the molecular plane, centrifugal couplings and distortions are introduced; however, these effects only cause bond stretching and minor frequency shifts in addition to those encountered in their absence. If ξ is allowed to vanish, the centrifugal coupling of degenerate modes merely lifts the degeneracy since a new linearly independent combina-

tion of the normal coordinates can be found with frequencies split about the degenerate frequency. Thus, we consider the effect of centrifugal couplings to be minor.

It is instructive to evaluate ξ , and thus θ_r , for various molecular models. The equilateral triangular molecule (X_3) has two degenerate modes and a breathing mode in addition to translation and rotation. The eigenvectors for the degenerate modes can be transformed into one another by a 90° rotation. Their cross products are perpendicular to the molecular plane, and the sum over the molecule is unity. Thus, $\xi = |\sin \varphi|$ where φ is the angle Ω makes with the molecular plane, and $\theta_r = \pi/2|\sin \varphi|$ (note that $\varphi = \pi/2$ when motion is confined to two dimensions). In the limiting case of $\varphi = 0$, ξ vanishes and the modes decouple. For any linear $X - Y_2$ molecule, the same transformation property exists among the degenerate mode eigenvectors, so $\theta_r = \pi/2|\sin \varphi|$ again. For nonlinear $X - Y_2$ molecules, the value of ξ will vary depending upon the force constant matrix as well as the relative orientation of Ω and the molecule, but since modes are generally nondegenerate in this case little resonant interaction of modes will occur (unless, of course, there is an accidental degeneracy). The equilateral hexagonal molecule has three pairs of in-plane degenerate modes, call them (1, 2), (3, 4), and (5, 6). Modes 1 and 2 transform as in the X_3 degeneracy, independent of the particular (nontrivial) choice of force

constants, so that $\theta_r = \pi/2|\sin \varphi|$ once again. Pairs (3, 4) and (5, 6) have identical values of e_{ij} which depend upon the force constant matrix. The force constant matrix can be constructed by assuming first and second neighbor Hooke's law forces. The ratio of the second to first neighbor force constants can, in principle, vary from 0 to infinity, which produces a correspondingly wide variation of ξ from 0 to 1. ξ approaches $0.6|\sin \varphi|$ when the ratio is small, and $|\sin \varphi|$ when the ratio is large. We have determined that the force constant ratio 0.2 yields a ratio of mode frequencies appropriate for modeling a benzene ring; for this case $\theta_r = 0.5145|\sin \varphi|$. This yields $\theta_r = 3.05/|\sin \varphi|$.

The phenomenon of resonance among the degenerate modes and the solutions discussed above have been confirmed in numerical simulations and numerical analysis. Although the atomic motions are quite complicated in general, there is one case worth noting in which the atomic motions are very simple. When $\xi = 1$ for two degenerate modes, the amplitude and direction of atomic motions remains fixed in the inertial frame. This case, therefore, mimicks a set of Foucault pendula oscillating in phase about the equilibrium positions of the atoms.

¹H. A. Jahn, Phys. Rev. 56, 680 (1939).