VIBRATIONAL FREQUENCIES

Obtained by determining the second derivative of the potential energy function with respect to the Cartesian coordinates of the nuclear positions, transforming to mass weighted coordinates and diagonalizing the resulting (force constant) matrix.

$$E(x_1, x_2, \cdots x_{3N}) = E_0 + \frac{1}{2}\sum_{K}^{3N}\sum_{L}^{3N} F_{KL}(x_K - x_K^0)(x_L - x_L^0)$$

The eigenvalues of the 3Nx3N matrix with elements

$$F_{KL}\Big/\sqrt{M_K M_L} \qquad \textbf{\textit{are}} \quad \omega_i^2 \quad \textbf{i=1, 3N}$$

In principle there should be 6 zero vibrations due to the translation of the center of mass and the rotation of the molecule about the center of mass. If all 3n coordinates are used one often sees small but non-zero frequencies corresponding to these degrees of freedom.