DETERMINATION OF THE ANHARMONIC POTENTIAL OF SOME LINEAR MOLECULES

T. V. Gosteminskaya, L. V. Belyavskaya, and V. P. Morozov

The coefficients of the anharmonic potential (a polynomial of fourth degree in the generalized coordinates) of the linear molecules CO₂, HCN, and C₂H₂ are calculated. A simple (linear) scheme of calculation is proposed and tested. The spectra of higher orders are satisfactorily reproduced.

In the present paper, using the general theory of vibration—rotation spectra [1], we calculate the anharmonic potential of the molecules CO₂, HCN, and C₂H₂.

The aim of the work is to find and test a simpler method for calculating the anharmonic potential than the traditionally employed least-squares method. The anharmonic potential is sought in the form of a polynomial in the generalized vibrational coordinates up to the fourth degree:

\[ V = \frac{1}{2} \sum_{i,j} F_{ij} q_i q_j + \sum_{i,j,k} F_{ijk} q_i q_j q_k + \sum_{i,j,k,l} F_{ijkl} q_i q_j q_k q_l, \]  

where \( q_i \) are the natural coordinates, and \( F_{ij} = \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right)_e \), \( F_{ijk} = \frac{1}{3!} \left( \frac{\partial^3 V}{\partial q_i \partial q_j \partial q_k} \right)_e \), and \( F_{ijkl} = \frac{1}{4!} \left( \frac{\partial^4 V}{\partial q_i \partial q_j \partial q_k \partial q_l} \right)_e \) are, respectively, the quadratic, cubic, and quartic potential constants.

The choice of the natural coordinates is shown in Fig. 1. Here, \( q_1, q_2, \) and \( q_4 \) are the coordinates of the stretching of the bonds; \( q_3 \) and \( q_5 \) are the coordinates corresponding to variation of the angles.

The basic formulas of the theory of vibration—rotation spectra [1] that we use are

\[ b_{ss}^{(zz)} = \frac{2 \left( B_e^{(zz)} \right)^2}{g_{ss}^0 \omega_s} \left\{ \frac{3A_{zzzz}^{(zz)} - 4 \sum_{s'} K_{zzzz}^{(zz)} q_{ss}^{(zz)} q_{s's's's'}^{(zz)} + \sum_{s' r'} K_{zzzr'} q_{ss}^{(zz)} q_{s's's'r'}^{(zz)} \left( \frac{\omega_{s'}}{\omega_{s'}} \right)^2}{g_{ss}^0 \omega_s} \right\}; \]

\[ X_{s's'} = \sum_{s'} \left[ 6K_{zzzz}^{(zz)} q_{ss}^{(zz)} q_{s's's'}^{(zz)} \left( \frac{\omega_s^2}{\omega_s^2} - \frac{\omega_s^2}{\omega_{s'}^2} \right) \right]; \]

\[ X_{s's'} = \frac{1}{2} \left\{ K_{zzzz}^{(zzz)} - 6K_{zzzz}^{(zzzz)} - 4K_{zzzz}^{(zzz)} \omega_s \frac{\omega_s}{4\omega_s^2 - \omega_{s'}^2} - \sum_{s''} K_{zzzz}^{(zzz)} K_{zzzz}^{(zzz)} \frac{\omega_s}{\omega_{s''}} - \sum_{s''} \frac{K_{zzzz}^{(zzz)} K_{zzzz}^{(zzz)}}{2(g_s + g_{s'} - 2)!} \omega_{s''} \left( \frac{\omega_s^2}{\omega_s^2} - \frac{\omega_s^2}{\omega_{s'}^2} \right) \left( (\omega_s + \omega_{s'}) (\omega_s + \omega_{s'} - \omega_{s''}) \right) \times \right. \]

\[ \left. \left( \frac{\omega_s^2}{\omega_s^2} - \omega_{s''} \right) \left( \frac{\omega_s^2}{\omega_s^2} - \omega_{s''} \right) + \frac{2}{g_s g_{s'}} \sum_{s''} \sum_{s'} \left( q_{ss}^{(zz)} q_{s's's's'}^{(zz)} \left( \frac{\omega_{s''}}{\omega_{s''}} \right) \right) \right\}. \]
### TABLE 1. Zero-Point Frequencies, Anharmonicity Constants and Constants of the Vibration–Rotation Interaction (cm⁻¹), Geometry of the Molecules (Å), and Masses of the Atoms (amu)

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Notes. 1. We calculated X₁₁ for the molecules C₂D₂ using the experimental frequencies of [7].

### TABLE 2. Potential Constants of Carbon Dioxide, Hydrogen Cyanide, and Acetylene (10¹³ dyn/cm², 10²¹ dyn/cm³)

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*) F₁₁₁₁ + F₁₁₁₅ and F₁₁₁₁₁₁ + F₁₁₁₁₅ are given.