

LEAST-SQUARES MASS-DEPENDENCE MOLECULAR STRUCTURES

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The zero-point moment of inertia of a linear molecule is $I_0 = I_e + \epsilon_0$, where the vibrational contribution ϵ_0 is a complicated function of degree 1/2 in the atomic masses. ^a The substitution method assumes that ϵ_0 is the same for all isotopomers, but least-squares fits of isotopomeric I_0 values assuming constant ϵ_0 give ϵ_0 values that are approximately half of the correct values. On the other hand, fits using $\epsilon_0 = cI_e^{1/2}$, where c is a constant, give essentially identical fits of the data, but with ϵ_0 values close to the correct values. To allow for vibrational effects of atoms with small coordinates, a second vibrational term is required. Here the formula

$$I_0 = I_e + cI_e^{1/2} + d \left(\frac{m_1 m_2 \dots m_N}{M} \right)^{1/(2N-2)}, \quad (1)$$

where c and d are constants, is tested in fits of both synthetic and experimental data. In general, excellent fits in the parts per million range are obtained. The corresponding bond lengths are called $r_m^{(2)}$ to indicate the use of two correction terms. The method is readily generalized to non-linear molecules, and special Laurie-type corrections for hydrogen atoms can be incorporated.

^aJ. K. G. Watson, *J. Mol. Spectrosc.* 48, 479 (1973).