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Jenny E. Rosenthal

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Vibrations of Asymmetrical Collinear Triatomic Molecules

JENNY E. ROSENTHAL

Chemistry Department, Columbia University, New York, N. Y.

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Expressions are derived for the vibration frequencies of asymmetrical collinear molecules of the X_2Y and XZY types. They are applied to the calculation of the frequencies of the N_2O^{18} molecule using an appropriate approximate potential function. The ratio of the distribution functions for N_2O^{16} and N_2O^{18} and the value of the equilibrium constant for the reaction $N_2O^{16} + H_2O^{18} \rightleftharpoons N_2O^{18} + H_2O^{16}$ are also given.

WHILE vibrations of three particle systems have been studied by Cross and Van Vleck,¹ their general formulas are not suitable for the particular case of the collinear molecule. Since molecules of this type might be of some interest, however, expressions are derived here for their vibration frequencies.

According to group theory or symmetry considerations two of the vibrations of the X-Z-Y molecule are along the molecular axis, and the frequencies are the roots of a quadratic equation. The vibration perpendicular to the axis is double and the corresponding frequency is a linear function of the force constants.

Explicit formulas will be derived chiefly for the special case of the X-X-Y molecule, since the more general expressions are rather cumbersome. The degree of symmetry of the molecule is unchanged by this simplification so that the discussion concerning the special types of potential energy could also be applied to the X-Z-Y case.

Consider the X_2Y molecule. We denote by s the mutual displacement of the X atoms and by x and y the components of the displacement of the Y atom relative to the center of the X-X distance; x being in the direction of the molecular axis and y perpendicular to it. The most general quadratic potential function consistent with geometrical symmetry is written in terms of four force constants:

$$V = \frac{1}{2}(Ax^2 + Bs^2 + Cy^2 + 2Dxs).$$

Let m be the mass of the X atoms, M that of the Y atom, q_{XX} the (equilibrium) distance between the X atoms, q_{XY} the distance between the Y atom and the X atom nearest to

it, and $q = q_{XX} + q_{XY}$. If $\alpha = q_{XX}/(2q_{XY} + q_{XX})$ and $\mu = M/(M + 2m)$ the kinetic energy has the form:

$$T = \frac{1}{2}m[2\dot{x}^2 + \frac{1}{2}\dot{s}^2 + 2\alpha^2\dot{y}^2(1 + \alpha^2/\mu)^{-1}].$$

If in the more general case we let n be the mass of the Z atom, m and M still referring to the X and Y atoms, respectively, the kinetic energy is expressed as:

$$T = \frac{1}{2}\{(m+n)\mu'\dot{x}^2 + \frac{1}{4}[(m+n) - (m-n)^2\mu'/M]\dot{s}^2 + (m-n)\mu'\dot{x}\dot{s} + 4mn\alpha^2\dot{y}^2[(m+n)(1 + \alpha^2/\mu') + 2\alpha(m-n) - (m-n)^2\alpha^2/M]^{-1}\};$$

$$\mu' = M/(m+n+M).$$

For X_2Y the parallel frequencies ω_1 and ω_3 are the roots of:

$$m^2\lambda^2 - m\lambda(\frac{1}{2}A/\mu + 2B) + (AB - D^2)/\mu = 0,$$

and the perpendicular one ω_2 is given by:

$$m\lambda - \frac{1}{2}C(1/\alpha^2 + 1/\mu) = 0.$$

In the latter case the isotopic shift can be found directly. If asterisks refer to the less abundant isotope, then:

$$\lambda_2/\lambda_2^* = \omega_2^2/\omega_2^{*2} = (\mu^*/\mu)(\mu + \alpha^2)/(\mu^* + \alpha^2).$$

The structural constant α can in principle be obtained from the observed values for the moment of inertia I and the length q of the molecule. The three quantities are related by:

$$I = 2mq^2(\alpha^2 + \mu)/(1 + \alpha)^2.$$

To determine the isotopic shifts for the parallel frequencies a simplifying assumption concerning the intramolecular forces is necessary, since it is impossible to obtain the three constants A , B and D from the two experimentally observed frequencies. As a first approximation it would be natural to suppose that there is no component

¹ P. Cross and J. Van Vleck, *J. Chem. Phys.* **1**, 350 (1933).

of the force between the end atoms parallel to the molecular axis and write

$$V_{\text{parallel}} = \frac{1}{2}(k_{XX}\delta q_{XX}^2 + k_{XY}\delta q_{XY}^2),$$

where the notation is self-explanatory. This assumption is equivalent to letting $D = -\frac{1}{2}A$.

However, when an attempt is made thus to determine the constants A , B and D for N_2O complex values are obtained. All calculations are based on the following set of experimental data:²

$$\begin{aligned}\omega_1 &= 1288.7 \text{ cm}^{-1}, \\ \omega_2 &= 588.3, \quad I = 66.0 \times 10^{-40} \text{ gcm}^2, \\ \omega_3 &= 2237.9.\end{aligned}$$

Also electron diffraction experiments³ give

$$q = (2.38 \pm 0.08) \times 10^{-8} \text{ cm}.$$

Since our first approximation does not hold for N_2O , we write

$$V_{\text{parallel}} = \frac{1}{2}(k_{XX}\delta q_{XX}^2 + k_{XY}\delta q_{XY}^2 + 2u\delta q_{XX}\delta q_{XY})$$

and assume that the interaction term u has the smallest possible value which gives rise to real values of A , B and D . This assumption has the further advantage of removing the usual ambiguity in the case when the force constant are calculated from a quadratic equation,⁴ for it leads to an equation with a double root. The numerical values obtained on this assumption for the force constants of N_2O are:

$$A = 14.72 \times 10^5 \text{ dynes/cm}, \quad B = 17.20, \quad D = -7.08, \\ \text{or} \quad k_{\text{NN}} = 13.80, \quad k_{\text{NO}} = 14.72, \quad u = 0.278.$$

From these values the parallel frequencies of N_2O^{18} are calculated to be

$$\omega_1^* = 1252.7 \text{ cm}^{-1}, \quad \omega_3^* = 2219.2.$$

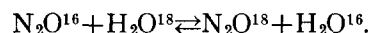
² E. F. Barker, Phys. Rev. **41**, 369 (1932).

³ R. Wierl, Ann. d. Physik **8**, 521 (1931).

⁴ J. E. Rosenthal, Phys. Rev. **49**, 535 (1936).

The numerical evaluation of α is necessary to find the isotope shift for the perpendicular frequency. It so happens, however, that for N_2O the experimentally observed values of I and q give a complex value for α . Since the moment of inertia is known quite accurately, it is necessary that $q \leq 2.31 \times 10^{-8} \text{ cm}$ in order that α be real. If q has its largest possible value, $\alpha = 4/11$. This gives $q_{\text{NN}} > q_{\text{NO}}$ by about 14 percent which may be compared with $q_{\text{NN}} = 1.094 \times 10^{-8} \text{ cm}$ and $q_{\text{NO}} = 1.146$ in the diatomic case. In view of the uncertainty in the value of q it was considered best to assume $q_{\text{NN}} = q_{\text{NO}}$, i.e., $\alpha = 1/3$. This corresponds to a value of q which is smaller than the maximum value by only a few units in the third decimal place. The results are not affected appreciably by any small change in α . If $\alpha = 1/3$, $I^* = 69.83 \times 10^{-40} \text{ gcm}^2$ and $\omega_2^* = 582.4 \text{ cm}^{-1}$.

These values of the isotopic shifts may be used to calculate the ratio of the distribution functions f for N_2O^{16} and N_2O^{18} , also the value of the equilibrium constant K for the reaction



This might be of some interest for the separation of oxygen isotopes. The necessary formulas have been derived by Urey and Greiff.⁵ With the use of their formulas we find that at 273.1° abs. :

$$f(\text{N}_2\text{O}^{18})/f(\text{N}_2\text{O}^{16}) = 1.346.$$

Combining this result with the value⁵

$$f(\text{H}_2\text{O}^{18})/f(\text{H}_2\text{O}^{16}) = 1.274,$$

we find $K = 1.056$.

In conclusion I want to thank Professor Urey who suggested these calculations.

⁵ H. C. Urey and L. J. Greiff, J. Am. Chem. Soc. **57**, 321 (1935).