LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Isotope Effects in Polyatomic Molecules

The isotope effects of the normal vibrations, of polyatomic molecules can be easily derived from Dennison's general non-central force treatment[1] of the vibrations. We find that the resulting expressions permit the evaluation of the molecular constants without appealing to intensity measurements and also furnish criteria for the assignment of particular spectral frequencies to particular modes of vibration.

For example, compare the symmetrical molecules YX_2 and $\bar{Y}X_2$, where mass of each X atom $=m$, mass of $Y=M$, mass of $\bar{Y}=\bar{M}=M+\Delta M$. Then we find that the isotope effect $\Delta\omega_3/\omega_3$ of the frequency ω_3 (whose electric moment vibrates perpendicularly to the symmetry axis) depends only on the masses and the molecular angle, and once this latter is known from the isotope effect, one of the constants of the potential energy expression can be evaluated from ω_3 itself.

The other three force constants can be evaluated from the frequencies parallel to the symmetry axis and their isotope effects, each of which depends on the constants. But the *sum* of the parallel isotope effects depends only on the masses:

$$\frac{\Delta\omega_1}{\omega_1}+\frac{\Delta\omega_2}{\omega_2}=-\frac{m\Delta M}{\bar{M}(2m+M)},$$

which should prove useful in the analysis of spectra. For a collinear molecule, the isotope effect of the inactive frequency vanishes, the expression on the right becoming that for the active parallel isotope effect alone, say $\Delta\omega_2/\omega_2$, and we also have $\Delta\omega_2/\omega_2=\Delta\omega_3/\omega_3$.

These results are applicable to the electronic absorption bands of chlorine dioxide recently measured by Urey and Johnston.[2] Two frequencies in the normal state showed isotope effects $\Delta\omega/\omega$ whose sum is -0.0124; the value of $-[m\Delta M/\bar{M}(2m+M)]$ for $Cl^{35}O_2$ and $Cl^{37}O_2$ is -0.0129, and therefore those two frequencies represent the parallel vibrations. Since no single isotope effect in the excited or the normal state was even approximately -0.0129, the molecule can not be collinear in either state. Our assignment to parallel vibrations agrees with that of Urey and Johnston, who discuss the matter from the standpoint of valence forces.

For tetratomic molecules YX_3 and $\bar{Y}X_3$, the isotope effect of each normal vibration depends on the six molecular constants and so the frequencies and isotope effects suffice to determine the constants. Again, the sum of the isotope effects of the parallel frequencies depends only on the masses; the sum of the perpendicular effects depends only on the masses and on the ratio of the altitude of the pyramid to the length of side of the triangular base.

Relations for the effects of isotopy of the X atoms are somewhat different, of course. Possibly the most interesting case is the tetratomic molecule, where the small difference in mass of an X atom removes the degeneracy of the motion, so that while YCl_3^{35}, for example, would have four normal frequencies, $YCl_2^{35}Cl^{37}$ would have six.

The expressions upon which the above and other relevant conclusions are based will appear in detail. We take great pleasure in thanking Professor Dennison for advice at various stages of our work.

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[1] D. M. Dennison. Rev. Mod. Phys. **3**, 280 (1931).

[2] H. C. Urey and H. Johnston, Phys. Rev. **38**, 2131 (1931). We are greatly indebted to Professor Urey for the manuscript.