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Infra-Red Microwave Spectra, Overtones, Degeneracy and Thermal Populations all in one diagram*

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An old drawing, which had an error in it, is re-presented (corrected) for understanding the relationships in diatomic vibrational-rotational interactions at the introductory level.

I. INTRODUCTION

Sometimes, it is difficult for students to put the pieces together in their understanding of elementary topics such as the one under consideration here, rotational-vibrational spectroscopy and thermodynamics. In this note, the various aspects of the problem are collected in a single diagram which illustrates the relationship between microwave transitions, infra-red transitions and overtones, in terms of actual energy levels, as well as the expected populations of the various states at thermal equilibrium which effects intensity relationships in absorption spectroscopy.

II. REVIEWING THE PHYSICS OF THE DIATOMIC MOLECULE UNDER ZERO ORDER APPROXIMATIONS

For a diatomic molecule, the first approximation we make is that the vibration of the molecule is governed by the equivalent harmonic oscillator potential energy function. This means that the potential energy curve is strictly parabolic, and that in this model, dissociation or bond breakage is not allowed.

The vibrational energy levels are given by

$$\epsilon_n = \left(n + \frac{1}{2}\right) h\nu = \left(n + \frac{1}{2}\right) \hbar\omega$$

where $\omega = \sqrt{\frac{k}{\mu}}$. k is the force constant for stretching the molecule (increasing the internuclear distance) and μ is the molecule's reduced mass.

Next, we assume that the rotational part of the motion of the diatomic molecule is at a fixed internuclear distance and is independent of the vibrational motion of

the nuclei. The rotational energy levels are given by

$$\epsilon_J = B(J)(J+1) = \frac{\hbar^2}{2I}(J)(J+1)$$

where $I = \mu r_e^2$, i.e., the moment of inertia (r_e is the equilibrium internuclear (fixed) distance).

The total nuclear motion energy levels becomes, in this zero'th approximation

$$\epsilon_{n,J} = \left(n + \frac{1}{2}\right) h\nu + B(J)(J+1)$$

The degeneracy of these levels is known to be $2J+1$.

III. THE "USEFUL" FIGURE

In 1998, a figure was published on my web sites associated with Physical Chemistry web.uconn.edu/~cdavid and Advanced Physical Chemistry web.uconn.edu/~ch351vc which brought all of the above ideas together in a manner which included the rotational degeneracy levels, and the thermodynamic populations of levels (which is useful in discussing intensity relations in IR and microwave spectroscopy).

Recently, while attempting to clean up these sites, I noticed that the figure was wrong. In the 20 years that these diagrams have been posted, not one single person has e-mailed me to bring this to my attention.

This note is an attempt to rectify the situation. One can see the original at the above cited sites, where there has been added a reference to this note.

A. the actual error

The populations on the l.h.s. of the drawing are wrong. They should have been

$$\frac{\#_{n=1,J=2}}{\#_{n=1,J=1}} = \frac{5 * e^{-\left\{-\left(1+\frac{1}{2}\right)h\nu+B(2)(2+1)\right\}}}{3 * e^{-\left\{\left(1+\frac{1}{2}\right)h\nu+B(1)(1+1)\right\}}}$$

as shown in the current version included herein.

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