

On the Force Constants of the XY₂ Molecule

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Citation: [The Journal of Chemical Physics](#) **14**, 294 (1946); doi: 10.1063/1.1724134

View online: <http://dx.doi.org/10.1063/1.1724134>

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On the Force Constants of the XY_2 Molecule

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February 25, 1946

IN a recent paper Glockler and Jo-Yun Tung¹ have suggested a method whereby the four force constants required to describe the behavior of the triatomic molecule XY_2 ($X=M$, $Y=m$) can be determined from its three vibrational frequencies. They employ force constants c_1 , c_2 , c_3 , c_4 defined by the potential field:

$$2V = c_1[\Delta r_1^2 + \Delta r_2^2] + c_2 \cdot r_0^2 [\Delta(2\alpha)]^2 + 2c_3 \cdot r_0 \cdot \Delta(2\alpha) [\Delta r_1 + \Delta r_2] + 2c_4 \cdot \Delta r_1 \cdot \Delta r_2, \quad (1)$$

where Δr_1 , Δr_2 are the changes in length of the XY bonds, equilibrium value r_0 , and $\Delta(2\alpha)$ is the change in the apical angle. These authors discuss the conditions necessary for all four force constants to be real, and suggest that the real value of c_4 should be chosen which makes c_1 approximately the same as the force constant of the corresponding diatomic molecule XY. The limits of reality of c_4 are given by the relationship:

$$\partial c_4 / \partial c_2 = \partial c_4 / \partial c_3 = 0, \quad (2)$$

which also defines its maximum and minimum values. Glockler and Jo-Yun Tung show that if the maximum value of c_4 is chosen, then for molecules such as H_2O and H_2S , c_1 is very similar to the force constants of the radicals OH and SH. The force constants calculated for these triatomic molecules using the three equations for the vibrational frequencies and the maximum value of c_4 are used to derive the frequencies of the isotopic molecules D_2O and D_2S , when good agreement with the observed values is obtained.

The set of force constants defined by Eq. (1) is not unique. Kohlrausch,² for example, uses the potential field:

$$2V = f[\Delta r_1^2 + \Delta r_2^2] + f' \cdot \Delta R^2 + d \cdot r_0^2 [\Delta(2\alpha)]^2 + d' \cdot r_0 \cdot R_0 [\Delta\beta_1^2 + \Delta\beta_2^2], \quad (3)$$

where ΔR is the change of the YY bond length, equilibrium value R_0 , and $\Delta\beta_1$ and $\Delta\beta_2$ are the changes in the basal angles. Both c_1 and f define the behavior of the XY bond, and c_2 and d that of the YXY angle, but they are not

identical for:

$$\begin{aligned} c_1 &= f + f' \sin^2 \alpha + 2d' \cos^2 \alpha, \\ c_2 &= d + d'/2 + f' \cos^2 \alpha. \end{aligned} \quad (4)$$

The method of Glockler and Jo-Yun Tung may be criticized on the following general grounds.

(i) In a polyatomic molecule the force constant of a particular bond will not necessarily be the same as that of the corresponding diatomic molecule, even if the number of electrons involved is identical, for the bond environment must be different in the two cases.

(ii) The force constant of a bond in a polyatomic molecule is not uniquely defined, as is shown by (4) above. There is thus no fundamental reason for preferring to make c_1 rather than f equal to the force constant of the diatomic molecule.

(iii) The relationship (2) gives other relationships if different sets of force constants are used, for example for (3):

$$\partial d' / \partial f' = \tan^2 \alpha / 2. \quad (5)$$

Neither (2) nor (5) seems to have any obvious physical justification.

(iv) Since c_4 is essentially an interaction constant it is surely extraordinary that it should be given its largest possible value.

(v) For the particular case $m=M$ the relationship (2) gives the remarkable condition that $f'=f$ whatever the value of 2α . This conclusion is clearly ridiculous unless 2α is approximately $\pi/3$.

Although Glockler and Jo-Yun Tung have obtained good results for a number of molecules, it would, therefore, appear that their method is not one of general applicability and that the information obtained by using it should not be considered entirely reliable.

¹ G. Glockler and Jo-Yun Tung, J. Chem. Phys. **13**, 388 (1945).

² K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt* (Verlagsbuchhandlung, Julius Springer, Berlin-1938), p. 65.

Comment on "On the Force Constants of the XY_2 Molecule"

GEO. GLOCKLER AND JO-YUN TUNG
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March 1, 1946

WE appreciate the fact that the Editor has permitted us to see the above note by Miss Simpson on "Force Constants of the XY_2 Molecule."

We would like to point out that the idea of the paper by Glockler and Tung was first to indicate a simple representation of all the real values of the force constants of the XY_2 molecule and secondly to make an attempt to find a simple empirical method which might be useful in determining a *unique* set of force constants from all the possible ones. So far the empirical condition studied was shown to hold with seven molecules. We ourselves pointed out that similar considerations would not apply to the COS molecule. Since we are continuing our calculations we will refrain at this time from taking valuable space and will answer the criticism of Miss Simpson at a later date.