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The Force Constants of Ozone

GEORGE GLOCKLER AND GEORGE MATLACK*

Department of Chemistry and Chemical Engineering, State University of Iowa, Iowa City, Iowa

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A general valency force field treatment has been applied to the ozone molecule, in which it has been possible to obtain values for all four force constants. The values obtained, using a fundamental frequency assignment of Penney and Sutherland, are compared with values obtained from other assignments. In the light of present knowledge concerning the structure of the ozone molecule, the values used by Penney and Sutherland ($\omega_1 = 1043$, $\omega_2 = 710$, $\omega_3 = 1740$ cm^{-1}) are the most consistent, and the force constant of the oxygen-oxygen bond agrees better with the value predicted by Badger's rule than do the others. The oxygen-oxygen bond force constant in ozone lies in the range 0.75 to 0.99 megadyne.

INTRODUCTION

SINCE 1934, various assignments of the fundamental frequencies of the ozone molecule have been made in the attempt to evaluate its force constants.¹⁻⁵ The results obtained from these investigations do not seem satisfactory when compared with the value predicted by Badger's rule⁶ and when the type of O—O bond is considered. This is partly caused by a questionable assignment of fundamental frequencies and partly caused by the fact that a simplified force field treatment was previously used in which some of the force constants were assumed to be zero. It is the purpose of this paper to show that force constants in fair agreement with the predicted values (by Badger's rule) can be obtained by treating the problem with a general valency force field in which none of the force constants is assumed to be zero.

APPLICATION OF THE GENERAL VALENCY FORCE FIELD

The theoretical considerations of the method have been explained in a previous paper.⁷ In general, the six force constants of a triatomic

molecule are reduced to four when the molecule is of the isosceles triangle model type. Since there are only three fundamental frequencies in a triatomic molecule, only three of the four force constants can be evaluated by a direct approach to the problem; the four force constants are: valence bond (c_1), angle bending (c_2), angle-bond interaction (c_3), bond-bond interaction (c_4). In the present method, c_4 , which is nearly always small in magnitude, is assumed to have certain values; c_1 , c_2 , and c_3 may then be calculated from the three equations from the theory of small vibrations, using the three fundamental frequencies, the valence angle, and the value assumed for c_4 as known quantities. When a number of sets of values is thus calculated for c_1 , c_2 , c_3 , and c_4 , it is found that an elliptical relation exists between c_4 and c_3 , between c_4 and c_2 , and a linear relation between c_4 and c_1 . The problem is thereby reduced to one of choosing the appropriate set from all the real sets thus calcu-

TABLE I. Force constants of O₃ calculated from Eq. (2).

| Source | Assignment (cm^{-1}) | | | Range of force constants (megadynes/cm) | | | |
|------------------------------------|---------------------------------|------------|------------|---|-------|-------|--------|
| | ω_1 | ω_2 | ω_3 | c_1 | c_2 | c_3 | c_4 |
| Simpson ^a | 1740 | 1043 | 2105 | 2.030 | 0.312 | 0.378 | 0.432 |
| | | | | 1.242 | 0.588 | 0.136 | -0.356 |
| Hettner ^b | 2105 | 1043 | 710 | 1.894 | 0.366 | 0.554 | 1.712 |
| | | | | 0.533 | 0.840 | 0.136 | -0.351 |
| Adel <i>et al.</i> ^c | 1043 | 710 | 2105 | 1.242 | 0.133 | 0.136 | -0.356 |
| | | | | 1.004 | 0.215 | 0.063 | -0.594 |
| Penney and Sutherland ^d | 1043 | 710 | 1740 | 0.988 | 0.133 | 0.136 | -0.103 |
| | | | | 0.751 | 0.215 | 0.063 | -0.341 |
| — | 1740 | 710 | 1043 | 1.427 | 0.207 | 0.378 | 1.035 |
| | | | | 0.401 | 0.565 | 0.063 | 0.009 |

^a Reference 5.^b Reference 1.^c Reference 3.^d Reference 2.

* From a thesis submitted in partial fulfillment of the requirements for the degree of Master of Science, in the department of chemistry, in the Graduate College of the State University of Iowa.

¹ Hettner, Pohlman, and Schumacher, *Zeits. f. Physik* **91**, 372 (1934); *Zeits. f. Electrochemie* **41**, 524 (1935).

² Penney and Sutherland, *Proc. Roy. Soc. A* **156**, 654, 678 (1936).

³ Adel, Slipher, and Fouts, *Phys. Rev.* **49**, 288 (1936).

⁴ Mulliken, *Rev. Mod. Phys.* **14**, 204 (1942).

⁵ Simpson, *Trans. Faraday Soc.* **41**, 209 (1945).

⁶ R. M. Badger, *J. Chem. Phys.* **2**, 128 (1934); **3**, 710 (1935).

⁷ G. Glockler and J. Y. Tung, *J. Chem. Phys.* **13**, 388 (1945).

TABLE II. Badger's rule.

| Substance | State | ω_e (cm ⁻¹) | r_e (Å) | c_1 | $c_1^{-1/3}$ |
|-------------------------------|----------------|--------------------------------|---------------------|-------|--------------|
| O ₂ | $^3\Sigma_g^-$ | 1580.36 ^a | 1.2076 ^a | 1.174 | 0.9479 |
| O ₂ | $^1\Sigma_g^+$ | 1432.62 ^d | 1.223 ^d | 0.965 | 1.012 |
| O ₂ | $^3\Sigma_u^-$ | 710.14 ^d | 1.599 ^d | 0.237 | 1.616 |
| H ₂ O ₂ | | 877 ^b | 1.47 ^c | 0.361 | 1.405 |

^a Herzberg, *Diatomic Molecules* (Prentice-Hall, Inc., New York, 1939).

^b Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, New York, 1945).

^c Giguere and Schomaker, J. Am. Chem. Soc. 65, 2025 (1943).

^d W. Jevons, *Band Spectra of Diatomic Molecules*, (Physical Society, London, 1932).

lated. The range of real values can be found from the condition

$$dc_4/dc_2 = dc_4/dc_3 = 0. \quad (1)$$

The question may be immediately asked: How does one know the range of values to assign to c_4 ? Obviously, it is possible that the assumed value of c_4 may give imaginary values of c_2 and c_3 . Glockler and Tung⁷ have derived explicit relations which define the end-points of the ellipses:

$$\left. \begin{aligned} \text{or} \quad c_1 &= \frac{\lambda_3}{2C} + \frac{C\lambda_1}{2(AC-B^2)} \\ c_1' &= \frac{\lambda_3}{2C} + \frac{C\lambda_2}{2(AC-B^2)}, \\ c_2 &= \frac{\lambda_2}{2C} + \frac{B^2\lambda_1}{2C(AC-B^2)} \\ \text{or} \quad c_2' &= \frac{\lambda_1}{2C} + \frac{B^2\lambda_2}{2C(AC-B^2)}, \\ c_3 &= \frac{B\lambda_1}{2(AC-B^2)} \\ \text{or} \quad c_3' &= \frac{B\lambda_2}{2(AC-B^2)}, \\ c_4 &= c_1 - \frac{\lambda_3}{C} \\ \text{or} \quad c_4' &= c_1' - \frac{\lambda_3}{C}, \end{aligned} \right\} \quad (2)$$

where $A = 1/\mu - \cos \alpha/M$; $B = \sin \alpha/M$; $C = 1/\mu - \cos \alpha/M$; α = valence angle; M = atomic weight of oxygen; μ = reduced mass of two oxygen atoms; $\lambda_i = 4\pi^2\omega_i^2$, where ω_1 is the symmetrical

vibration frequency, ω_2 is the deformation vibration frequency, and ω_3 is the antisymmetrical vibration frequency. The two sets (Eq. (2)) define the end-points of the ellipse where condition (1) holds. In other cases⁷ it appeared possible to choose one of these two sets by the above condition and this set checked isotopic molecules satisfactorily. Up to this point in the argument it can only be said that the O—O bond force constant of ozone must lie within the range of real values (0.75 to 0.99 megadyne).

THE OZONE MOLECULE

Shand and Spurr,⁸ by means of electron diffraction studies, have shown that the ozone molecule exists in the form of an isosceles triangle in which the apical angle is $127^\circ \pm 3^\circ$ and the O—O distance is 1.26 ± 0.02 angstroms. Using the above value for the apical angle, the four force constants were calculated for four different assignments of the fundamental frequencies. The

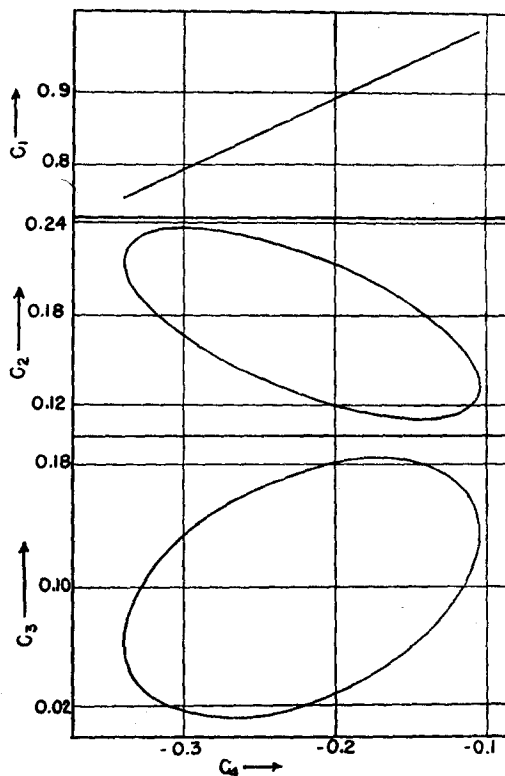


FIG. 1. Possible real values of the force constants of ozone (megadynes/cm).

⁸ W. Shand, Jr., and R. A. Spurr, J. Am. Chem. Soc. 65, 179 (1943).

data are summarized in Table I. Figure 1 illustrates the relation between the force constants which were calculated from the assignment of Sutherland and Penney,² which appears to give results most consistent with the structure of the ozone molecule. The two values for the O—O force constant, 0.988 and 0.751 megadyne (see Fig. 1 and Table I) lie on either side of the value predicted by Badger's rule, or 0.87 (for an O—O distance of 1.26Å), as illustrated in Table II and Fig. 2.

DISCUSSION

Simpson⁵ has reported a value of 1.597 megadynes for the O—O bond force constant in ozone. This value seems too large in view of the presently accepted structure of the ozone molecule. The force constant may be expected to lie between 1.174 (oxygen molecule) and 0.361 (hydrogen peroxide) as can be seen from an inspection of Table II where it is noted that the O—O distance in ozone (1.26Å) lies between the values for hydrogen peroxide and the oxygen molecule.

From Table I it appears that Simpson's assignment is the only one which will give real values for c_2 and c_3 , if c_4 is assumed to be zero, since c_4 must be given some value lying between the two ranges for c_4 given in Table I in order that real values result from c_2 and c_3 . This explains the imaginary values which result when the other assignments are treated by the simple valency force field in which c_4 is assumed to be zero.

The Penney and Sutherland assignment used above is consistent with the modern interpretation of the infra-red spectrum.⁵ The range for c_1 (0.75 to 0.99 megadyne) can be supported by an examination of heats of dissociation.

This consideration which yields information

TABLE III. Heats of dissociation.

| Reaction | D (electron volts) |
|---|----------------------|
| $\text{H}_2\text{O}_2 \rightarrow 2\text{OH}$ | 1.48 ^a |
| $\frac{1}{2}\text{O}_3 \rightarrow \frac{1}{2}\text{O}$ | 3.06 ^{b, c} |
| $\text{O}_2 \rightarrow 2\text{O}$ | 5.08 ^c |

^a L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

^b F. R. Bichowsky and F. D. Rossini, *Thermochemistry of the Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

^c G. Herzberg, *Diatomic Molecules* (Prentice-Hall Inc., New York, 1939).

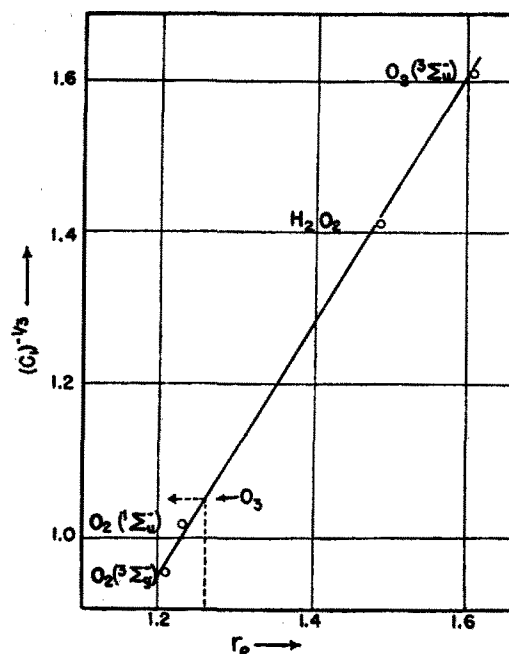


FIG. 2. Badger's rule applied to the O—O bond.

concerning the relative strength of the O—O bonds in the three molecules discussed, concerns the dissociation energy of the three O—O bonds. From Table III it is seen that the ozone bond is intermediate between the O—O bonds of hydrogen peroxide and of oxygen molecule.

The O—O bond energy in ozone has been calculated as follows:



or



The dissociation of the oxygen bond in ozone is intermediate between the dissociation energies of the oxygen bond in hydrogen peroxide and molecular oxygen. Therefore it should be reasonable to expect the force constant in ozone to lie between those in molecular oxygen and hydrogen peroxide. Hence the Penney and Sutherland assignment of fundamental frequencies yielding a force constant for the oxygen bond in ozone between 0.75 and 0.99 megadyne seems most acceptable at present.