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Notes on the Infra-Red Spectrum and Molecular Structure of Ozone

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The nature of the fine structure of the band at 14.2μ in the absorption spectrum of ozone has been determined with prism and grating spectrometers. These data, together with the fine structure of the 9.57μ band (previously resolved in the solar spectrum) render possible an unambiguous choice between the divergent views currently held with regard to the structure of the ozone molecule. It is concluded that the form of the isocles triangle is acute, with the apex angle in the neighborhood of 34° .

I. INTRODUCTION

NUMEROUS attempts have been made to analyze the infra-red spectrum and determine the molecular structure of ozone.

Prior to the definitive (although low dispersion) experiments of Hettner, Pohlman, and Schumacher¹ in 1934, these attempts were unsuccessful, mainly because

- (1) they were made in ignorance of the existence of the ozone band at 14.2μ , and
- (2) they mistakenly identified as due to ozone the intense bands of nitrogen-pentoxide (N_2O_5), a contamination difficult to avoid in the preparation of ozone.

Since 1934 the attempts at solving the ozone problem have been inconclusive because of the persisting lack of accurate information regarding the band envelopes and fine structures.

The history of the problem prior to the work of Hettner, Pohlman, and Schumacher¹ is given by Gerhard,² and since that time by Simpson.³ It is sufficient for our present purpose to point out that Hettner, Pohlman, and Schumacher¹ assumed a Q -branch for the 9.57μ band. The envelopes of the bands at 4.75μ and 14.2μ were plainly Q -branch and doublet, respectively. On the assumptions of central forces and the frequency assignment $\nu_1(4.75\mu)$, $\nu_2(9.57\mu)$, $\nu_3(14.2\mu)$ this led to an apical angle of 39 degrees.

Low dispersion solar spectra show, however, an apparently doublet envelope for the band at

9.57μ . Adel, Slipher, and Fouts⁴ showed that, using this identification, imaginary values for the apical angle are obtained on either central or valence forces, provided the bands at 4.75μ , 9.57μ , and 14.2μ are still regarded as fundamentals.

Continuing the assumption of doublet structure for the 9.57μ band (which we believe to be a mistaken one), but substituting the weak band at 5.75μ for the strong one at 4.75μ , and giving preference to a valence force field, Penney and Sutherland⁵ were led by the frequency assignment $\nu_1(9.57\mu)$, $\nu_2(14.2\mu)$, $\nu_3(5.75\mu)$ to an apical angle of 164 degrees.

In a critical discussion of the electronic structure of the ozone molecule Mulliken⁶ favors the acute angle form of the molecule designated by Hettner, Pohlman, and Schumacher.¹ But recently Shand and Spurr⁷ have concluded from electron diffraction experiments that the apical angle of the ozone molecule must be obtuse, 127 ± 3 degrees.

The correctness of this last result was assumed by Miss D. M. Simpson.³ Continuing the tradition of the doublet envelope for 9.57μ she finds the most probable assignment of frequencies to be $\nu_1(5.75\mu)$, $\nu_2(9.57\mu)$, $\nu_3(4.75\mu)$.

In deciding between an acute and an obtuse form for the ozone molecule, the envelope form of the 9.57μ band is crucial. And since, in all analytical attempts to date, this form is at least somewhat uncertain, it is desirable to obtain

¹ G. Hettner, R. Pohlman, and H. J. Schumacher, *Zeits. f. Physik* **91**, 372 (1934).

² S. L. Gerhard, *Phys. Rev.* **42**, 622 (1932).

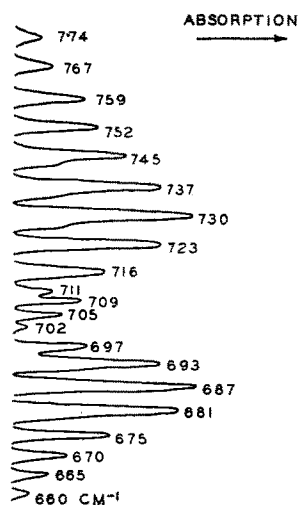
³ D. M. Simpson, *Trans. Faraday Soc.* **41**, 209 (1945).

⁴ A. Adel, V. M. Slipher, and O. Fouts, *Phys. Rev.* **49**, 288 (1936).

⁵ W. G. Penney and G. B. B. M. Sutherland, *Proc. Roy. Soc. A* **156**, 654, 678 (1936).

⁶ R. S. Mulliken, *Rev. Mod. Phys.* **14**, 204 (1942).

⁷ W. Shand and R. A. Spurr, *J. Am. Chem. Soc.* **65**, 179 (1943).

FIG. 1. Ozone 14.1μ .

new and independent evidence. This has been achieved by comparing the fine structure of the doublet band at 14.2μ with the fine structure of the band at 9.57μ .

The fine structure of 9.57μ is already at hand in the infra-red solar spectrum.⁸ It remained to resolve the band at 14.2μ .

II. EXPERIMENTAL

Ozone was prepared according to the method of Goldstein,⁹ and the 14.2μ band was examined both with a NaCl prism and a 2400-line grating. The prism curve, Fig. 1, is remarkably suggestive of the perpendicular band of a symmetrical top molecule.* Asymmetry in the lines of Fig. 1 suggests a complex line structure, and this is confirmed by the grating analysis, Fig. 2.

The structures of the bands at 9.57μ and 14.2μ are fundamentally dissimilar. And since 14.2μ is a near-perpendicular band, 9.57μ must be a near-parallel band (Q-branch).

As a further aid in discussing the ozone spectrum the envelopes of the bands at 3.28μ and 3.57μ have been re-examined, Fig. 3.

III. DISCUSSION

The first and the most crucial point in the interpretation of the infra-red spectrum of ozone

⁸ A. Adel, *Astrophys. J.* **94**, 451 (1941).

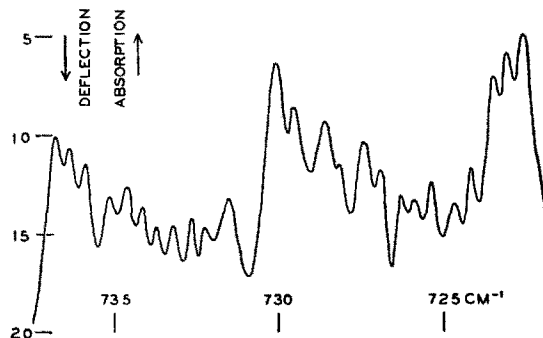
⁹ E. Goldstein, *Ber. d. d. Chem. Ges.* **36**, 3042 (1903).

* We are indebted to Mr. E. A. Boettner of the Wyandotte Chemicals Corporation for the use of their prism spectrometer in obtaining the data for this curve.

is the identification of the fundamental bands. The investigation of Hettner, Pohlman, and Schumacher¹ showed that the most intense regions of absorption are those at 4.75 , 9.57 , and 14.2μ . From 16 to 27μ (the limit of their observations) ozone is almost completely transparent and it is unlikely that any fundamental bands would lie beyond 27μ . It is therefore natural to identify the three regions just mentioned with the three fundamental frequencies of the molecule. An alternate scheme which has been considered by some investigators would be to take the band at 9.57μ as a fundamental but to identify the 4.75μ region as its first overtone. The second overtone must then be assigned to the weak band at 3.28μ . The difficulty with this scheme is that the three frequencies, namely, 1043 , 2108 , and 3050 cm^{-1} cannot be placed in a series of the type demanded by the theory of anharmonic oscillators. This is immediately evident since 2108 is greater than twice 1043 , while 3050 is less than three times 1043 .

For these reasons it seems very probable that the three fundamental frequencies of ozone are $\nu_1 = 2108$, $\nu_2 = 1043$, and $\nu_3 = 705 \text{ cm}^{-1}$, corresponding to the three most intense regions of absorption.

The second crucial point is concerned with the fine structure of the bands. The new experimental evidence reported in this paper sheds a revealing light upon the problem. The long wavelength band at 14.2μ is found to have a structure consisting of widely spaced lines, each of which is multiple. The average value of the coarse spacing is about 5.7 cm^{-1} and is fairly regular although there is a rather large convergence. The magnitude of the coarse spacing indicates

FIG. 2. Ozone 13.7μ .

unequivocally that the electric moment corresponding to this frequency must oscillate along the middle axis of inertia. (The oscillating electric moment of a triatomic molecule can only be directed along either the least or the middle axis of inertia. When it is directed along the middle axis, the rotational selection rules predict a widely spaced series of lines characteristic of the rapid rotations about the least axis of inertia. When the electric moment oscillates along the least axis of inertia, these transitions are forbidden.)

The band at 9.57μ has been examined by Adel⁸ in the solar spectrum. Its structure was found to consist of fairly regularly spaced lines with an average spacing constant of around 1 cm^{-1} . Gerhard's² measurements on the 4.75μ band likewise reveal a very narrow spacing which is also of the order of 1 cm^{-1} . Thus for both of these bands the electric moment must oscillate along the least axis of inertia.

These facts admit of only one interpretation. The apical angle of the ozone molecule must be less than 60 degrees. This conclusion is the result of broad and general considerations. A further examination serves to confirm it in detail and leads to the following points.

1. The spacing of the fine structure lines in a band where the electric moment oscillates along the least axis of inertia is of the order of $\Delta\nu = (h/8\pi^2c)(1/I_A + 1/I_B)$. (Of course this molecule is an asymmetric rotator and the spacing of the fine structure lines must be irregular. However, when two of the moments of inertia, in this case the greatest and middle moments, are approximately equal, the above formula gives a rough representation of the fine structure.) Setting in the observed spacing of 1 cm^{-1} , one obtains $2I_AI_B/(I_A + I_B) \cong 56 \times 10^{-40}\text{ g cm}^2$.

The spacing of the fine structure lines in a band with changing electric moment along the middle axis of inertia is of the order of $\Delta\nu = (h/8\pi^2c)(2/I_C - 1/I_A - 1/I_B)$. This approximation is subject to the same limitations as those governing the spacing in the other type of band. In the ozone molecule, the identity of the oxygen nuclei and the fact that their nuclear spin is zero means that every other line will be missing and the observed spacing will have twice the value given above. Setting in the experimental

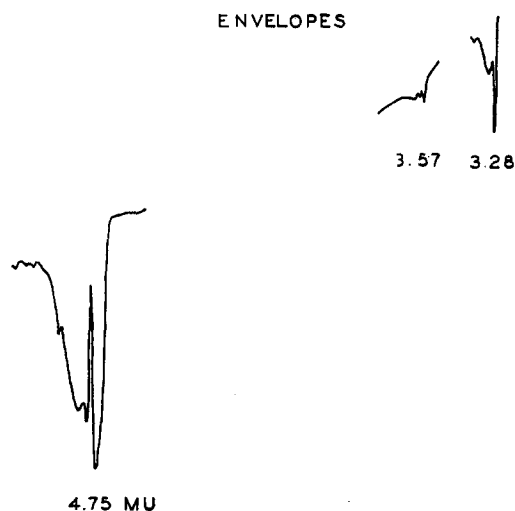


FIG. 3. Ozone envelopes.

value for $\Delta\nu$, combining with the earlier result, and remembering that for a plane molecule $I_A = I_B + I_C$, one obtains $I_A \cong 64 \times 10^{-40}$, $I_B \cong 50 \times 10^{-40}$, and $I_C \cong 14 \times 10^{-40}\text{ g cm}^2$. The corresponding apical angle is 34 degrees. It must be emphasized that these numerical results are extremely rough both from the experimental and the theoretical sides. Our estimate of their order of accuracy is ± 20 percent. In order to obtain the moments of inertia more exactly the most promising procedure appears to be to resolve the complete fine structure of the 14.2μ band with a grating spectrometer. The lines can then be correlated with the energy levels of an asymmetric rotator and the moments of inertia determined. We hope to make this investigation in the near future.

2. If the molecule of ozone has the form of an isosceles triangle with an apical angle of less than 60 degrees, it is quite probable that the forces can be satisfactorily approximated by central forces rather than by valence forces. A calculation of the force constants yields results which are substantially in agreement with those obtained by Hettner, Pohlman, and Schumacher. The apical angle turns out to be 39 degrees, the force constant between the oxygens forming the base of the triangle, $K = 34 \times 10^5\text{ dynes/cm}$ and the constant between the apical and one of the base oxygens, $K' = 6.2 \times 10^5$.

3. The weaker bands of ozone may be expressed as overtones and harmonics of the three fundamentals. These have been assembled in

TABLE I.

Identification	Calc. frequency	Obs. frequency	Obs. type
ν_3	— D	705	Doublet
ν_2	— Z	1043	Zero branch ^a
$\nu_2 + \nu_3$	1748 D	1740	Doublet ^b
ν_1	— Z	2108	Zero branch ^c
$\nu_1 + \nu_3$	2813 D	2800	Zero branch ^d
$\nu_1 + \nu_2$	3151 Z	3050	Zero branch ^d

^a This band has often been thought to be of the doublet type. A study of Adel's curve shows an intense region of absorption at 1041 cm⁻¹ which is undoubtedly a zero branch displaced through convergence.

^b While the resolution is not great, the curve of Hettner, Pohlman, and Schumacher distinctly favors a doublet structure for this band.

^c Gerhard's work, as well as ours, shows that this is clearly a zero-branch band.

^d Figure 3 shows envelopes which more nearly resemble zero branches than doublets. The evidence is inconclusive for both of these overtone bands however.

Table I. The first column gives the designation of the band and the second the calculated frequency and the predicted type (D =doublet band, Z =zero-branch band). The third column lists the observed frequency while the fourth describes its type.

IV. CONCLUSION

The present interpretation of the ozone spectrum is both simple and direct and is, in almost all respects, self-consistent. The three most intense regions of absorption are identified with the three fundamental frequencies. The weaker regions are assigned to those overtone combinations which are normally the most intense, namely, $\nu_2 + \nu_3$, $\nu_1 + \nu_3$ and $\nu_1 + \nu_2$. The calculated frequencies of the overtones are, in each case, slightly larger than the observed frequencies. This again is the usual situation.

The fine structure of the bands leads to an apical angle of 34 degrees which is in good agreement with the apical angle of 39 degrees calculated independently from the positions of the fundamental bands.

The dimensions of the molecule as roughly estimated from the fine structure are reasonable. The distance between the oxygens forming the base of the isosceles triangle is 1.0×10^{-8} cm whereas the distance between the atoms in O_2 is 1.208×10^{-8} . The envelopes of the bands—a distinct doublet for ν_3 and zero-branch bands for ν_1 and ν_2 —are in agreement with the predictions from the theory of the asymmetric rotator.

The force constants are not unreasonable.

The force between the base oxygens is about 5.5 times that between a base and the apical oxygen. The force constant between the base oxygens would predict a vibration frequency of these two atoms taken by themselves of about 2700 cm⁻¹ whereas the vibration frequency of O_2 is 1580 cm⁻¹. It is well known that normal vibrations and interatomic distances follow the approximate law $r_e^n \omega_e = \text{constant}$ where n lies between 2 and 3. In our case the figures lead to a value for n of 2.8. (The above argument must be regarded merely as an indication since the structures of O_2 and of O_3 may be quite dissimilar.)

The Raman spectrum of ozone is very weak and shows no lines which can be identified with certainty.^{10,11} A molecule with an acute apical angle would not be expected to possess a strong Raman spectrum whereas one with an obtuse apical angle would.

There are only two experimental facts which do not appear to be in concordance with our interpretation of the spectrum. (a) The dipole moment of ozone is known to be small,¹² 0.49×10^{-18} . In general a molecule with an acute apical angle should exhibit marked polar qualities although in any particular case other circumstances might tend to reduce the dipole moment. (b) The electron diffraction measurements of Shand and Spurr indicate an apical angle of 127 degrees.

The experiment appears to have been carefully performed and we are unable to suggest any explanation for the discrepancy between the electron diffraction and the infra-red results. It is certainly true, however, that the infra-red spectrum of ozone cannot be identified as belonging to a molecule with an obtuse apical angle without the introduction of what seems to be an artificial series of assumptions and interpretations. It is believed that further precision measurements of the fine structure of the band at 14.2μ will definitely establish the moments of inertia of the molecule.

¹⁰ G. B. B. M. Sutherland, Proc. Roy. Soc. **A141**, 515 (1933).

¹¹ G. B. B. M. Sutherland and S. L. Gerhard, Nature **130**, 241 (1932).

¹² G. L. Lewis and C. P. Smyth, J. Am. Chem. Soc. **61**, 3063 (1939).