

The InfraRed Spectrum and Structure of Ozone

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groups would contract to a ring with a diameter of 0.32th of the original chain length.

Similarly we obtain that if in the original chain every 4th, 6th, 8th, 2nth, etc. N^+ ion were neutralized, the chain that contained originally 48, 72, 96, 24n CCN^+ groups, respectively, would close to a ring with a diameter of 0.32th of its former length. Let us, for example, consider a chain containing 12,000 CCN^+ groups. If we neutralized only 12 of the N^+ ions altogether, so that every 1000th N^+ ion would be neutralized, the chain would contract to a ring with a diameter of 0.32th of the original chain length again. This effect is caused in our example by the neutralization of only 1% of the N^+ ions originally present, provided that the ions to be neutralized are distributed equidistant. In the case of equidistant distribution of the 12 neutral N atoms the contraction of the chain is maximal, any other distribution would cause a smaller contraction.

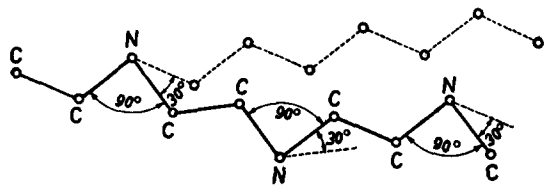
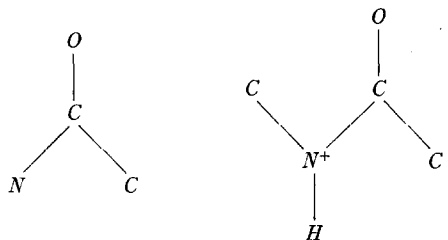


FIG. 1.

The situation is changed if we take into consideration the steric effects too. Taking the spin orientation of the H and O atoms into account, a rough estimation will show us, that the neighboring ($CCN^+CCN^+ \dots CCN$) planes are forming an angle different from zero. It follows that by neutralizing the N^+ ions the chain is twisted to a cylinder as a helical curve; that means that a contraction results also in this case.

Let us now assume that one-half of the C atoms is still in the trigonal while the other half is in the tetragonal state, in accordance with that we replace all CY bonds with the CHR groups. In this case the atoms of the chain are not lying in a plane any more. The atoms of the following configurations,



lie again in planes, which are however inclined to one another. If all the N atoms in this chain were again ionized, the arrangement of the atoms would not be very different from that one in a plane. If the chain contained also neutral N atoms the chain links would become twisted in space. The neutralization of the N^+ ions causes a contraction also in this case.

The single chains are joined together by hydrogen-bonds through the NH and CO groups in the following way: $NH \cdot OC$. This structure shows immediately the impossibility to build up a set of chains in a plane-like surface, and shows that a chain complex must have a spatial structure.

Finally we should like to make a remark on the electron mobility in the chain. In this respect there is an essential difference between the chain containing only N^+ ions and the chain that contains neutral N atoms too. While the first one, owing to its unsaturated resonating π -bonds possesses, like the benzene ring, an electron mobility, that is not the case in the second one where the electrons are localized, because of the 3 saturated valencies of the N atoms. The electron mobility is restricted also in the chain with the CHR groups even in the stretched case.

These calculations are only of informative character. A closer and rather difficult investigation of the energy relations would of course lead to more quantitative results.

¹ K. G. Denbigh, *Nature* **154**, 642 (1944).

The Infra-Red Spectrum and Structure of Ozone

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February 23, 1950

IN the interpretation of the infra-red spectrum of ozone, the appearance of the band envelopes at 1043 cm^{-1} and 2108 cm^{-1} has been questioned¹ and discussed^{2,3} in some detail. Recently we had occasion to examine the infra-red spectrum of ozone while investigating the operation of an "ozoneizer,"⁴ and our observations on the 1043 cm^{-1} and 2108 cm^{-1} bands may be of some general interest. In these observations the contours of the two bands, under the same experimental conditions, are very similar. In particular, the 1043 cm^{-1} band definitely has a Q branch and a detailed comparison with the available data on the 2108 cm^{-1} band indicates the band envelopes are identical in every essential characteristic.

The infra-red spectrum of the gas was observed at room temperature with a Perkin-Elmer Model 12B spectrophotometer equipped with rock salt optics. A number of runs were made with equivalent results. Figure 1 gives the spectra observed for: (A)

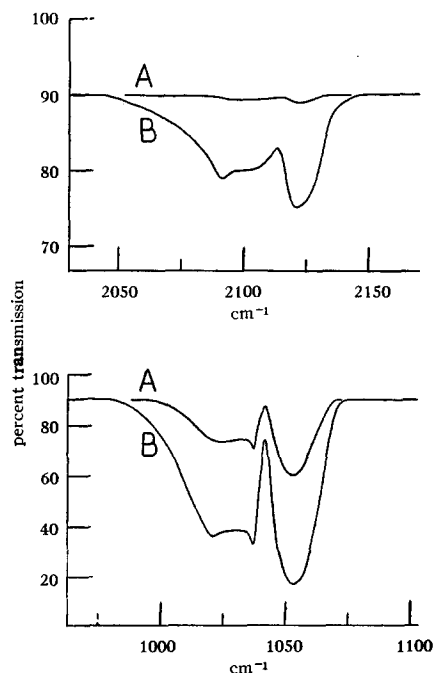


FIG. 1. The 1043 cm^{-1} and 2108 cm^{-1} infra-red absorption bands of ozone.

ozone at a pressure of about 20 cm in a 10-cm gas cell; (B) ozone at an estimated pressure of 10 cm in the spectrometer case containing the primary optics for which the light path is about 40 cm. Under these conditions only the bands at 1043 cm^{-1} and 2108 cm^{-1} were observed in the covered range from 625 cm^{-1} to 4000 cm^{-1} ; in addition, faint traces of absorption were apparent in (B) in the region of the 705 cm^{-1} band.

Both of the band envelopes in Fig. 1 have sharp R branches with considerably broader P branches. The separation of the P

and R maxima is 31 cm^{-1} for the 1043-cm^{-1} band and 28 cm^{-1} for the 2108-cm^{-1} band. As ozone is a near-symmetrical top in either the acute or obtuse-angled model,¹ these separations may be used to estimate the near-equal moments of inertia by means of the expression⁶ $\Delta\nu(P-R)=2.358(TB)^{1/2}$ which applies to parallel type bands. The results of $49\times 10^{-40}\text{ g/cm}^2$ and $60\times 10^{-40}\text{ g/cm}^2$, respectively, are in good agreement with the values ranging from 50 to $60\times 10^{-40}\text{ g/cm}^2$ calculated from the fine structure^{1,3} of the 705-cm^{-1} band and thus the assignment of both the 1043 cm^{-1} and 2108-cm^{-1} bands as parallel type is confirmed. The one disagreement in the band structures in Fig. 1 is the absence of a well-defined Q branch in the 2108-cm^{-1} band. This is probably due to the poorer resolution of the sodium chloride prism in that region as well as to the relative weakness of the band. However, a comparison of the band envelope in Fig. 1 for the 1043-cm^{-1} band with that given by Adel and Dennison³ for the 2108-cm^{-1} band in their Fig. 3 can leave little doubt about these bands being of the same type.

This conclusion, while essential for ozone to have an acute-angled structure,³ is not necessarily inconsistent with the data and frequency assignments of Wilson and Badger² which favor the obtuse-angled model. Although their interpretation is probably the most attractive one, perhaps one should point out that on the basis of available spectral data it is not unique. Table I lists the

TABLE I. The infra-red spectrum of ozone and frequency assignments for acute-angled and obtuse-angled models.

Observed* $\nu\text{ cm}^{-1}$	Acute-angled model†	Obtuse-angled model
705 <i>D</i>	ν_2	ν_2
1043 <i>Q</i>	ν_3	ν_2
1110 <i>D</i>	ν_1	$\nu_1 - \nu_2$; 1062 <i>Q</i>
1740 <i>D?</i>	$\nu_2 + \nu_3$; 1748 <i>Q</i>	$3\nu_3 - \nu_2$; 1072 <i>D</i>
2105 <i>Q</i>	$\nu_1 + \nu_2$; 2153 <i>Q</i>	ν_1
2800 <i>Q?</i>	$\nu_2 + 2\nu_3$; 2791 <i>D</i>	$\nu_1 + \nu_2$; 2810 <i>D</i>
	$\nu_1 + \nu_2 + \nu_3$; 2858 <i>Q</i>	$2\nu_2 + \nu_3$; 2791 <i>D</i>
3050 <i>Q</i>	$3\nu_3$; 3129 <i>Q</i>	$\nu_1 + \nu_2$; 3148 <i>Q</i>
		$3\nu_2$; 3129 <i>Q</i>

* *D*—doublet structure; *Q*—parallel type band with *Q* branch.
† See reference 2.

observed spectrum and band types along with possible frequency assignments on the basis of both structures.

¹ D. M. Simpson, *J. Chem. Phys.* **15**, 846 (1947).

² M. K. Wilson and R. M. Badger, *J. Chem. Phys.* **16**, 741 (1948).

³ A. Adel and D. M. Dennison, *J. Chem. Phys.* **14**, 379 (1946).

⁴ We are indebted to Professor Murray Sanders, University of Miami, and Dr. E. J. Ryan, Miami, Florida, for the preparation of the ozone.

⁵ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 391.

The Background Scattering of CO_2 and CCl_4 , Correction

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February 2, 1950

IN a recent paper¹ we stated that the background scattering of electrons for CO_2 and CCl_4 appeared to be in disagreement with theory. The theoretical formula for the background scattering is given by

$$\sum_i S_i/s^4 + \sum_i (Z_i - f_i)^2/s^4, \quad (1)$$

where the summation is over-all atoms in the molecule, S_i is the incoherent atomic scattering factor for x-rays, $(Z_i - f_i)/s^2$ is the

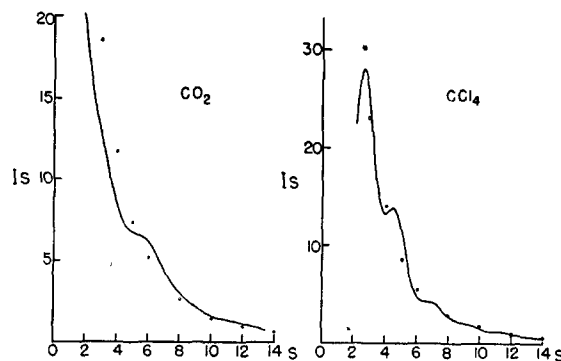


FIG. 1. The solid lines are the experimental scattering curves obtained with a sector whose opening is proportional to s^2 . The dots represent the background scattering calculated from tabulated values.

coherent atomic scattering factor for electrons and s is a function of the angle of scattering. In comparing our experimental results with theory, Eq. (1) was multiplied erroneously by s^2 . The opening in our sector was proportional to s^2 . For comparison Eq. (1) should have been multiplied by s since an opening of s^2 in the sector multiplies the scattered intensity by a factor of $s^2/r \approx ks$ where k is a proportionality constant. The agreement between experiment and the recomputed theoretical curves is seen in Fig. 1.

This correction in no way affects our results for the molecular structure and average vibrational amplitudes, since our method does not involve the use of a theoretical background curve. We obtain one experimentally by drawing a line through the oscillations of the experimental intensity curves. It is assumed that this drawn line represents the correct background scattering. The agreement with theory shown in Fig. 1 is additional evidence for the validity of this assumption.

¹ I. L. Karle and J. Karle, *J. Chem. Phys.* **17**, 1058 (1949).

Microwave Determination of the Structure of Chloroform*

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February 10, 1950

THE $J=6$ to $J=7$ rotational transitions of chloroform (CHCl_3)³⁵ and deuteriochloroform (CDCl_3)³⁶ have been recorded using the Stark modulation technique.¹ In order to obtain the stronger absorptions associated with the high frequencies and low temperatures,² a standard *K*-band two meter Stark cell, provided with cooling and frequency doubling equipment, was used in preference to the longer coiled cell previously utilized in the observations³ of the $J=2$ and $J=3$ and the $J=3$ to $J=4$ rotational transitions of CHCl_3 . Since the chlorine quadrupole moment interacts with the molecular field, the energy levels are split, resulting in weak individual lines. By using pressures near 0.01 millimeter of mercury, the individual lines form an integrated pattern with a single peak and a width of approximately one megacycle at the half power points (see Fig. 1).

Frequency standard⁴ measurements of the peaks of the recorded absorptions yield:

$J=6 \rightarrow 7$	CHCl_3 ³⁵	$46,227.2 \pm 0.15\text{ MC}$
$J=6 \rightarrow 7$	CDCl_3 ³⁶	$45,502.4 \pm 0.15\text{ MC}$

Since the C—H bond in chloroform has some ionic character, the C—H (or C—D) distance was assumed to be $1.090\text{ \AA} \pm 0.005\text{ \AA}$, slightly less than the C—H distance in CH_2Cl_2 ⁵ and CH_4 .⁶ These assumptions, together with the observed frequencies and the corresponding moments of inertia, determine the other molecular