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Publication Date

1971-08-01

Submitted to Journal of Molecular
Spectroscopy

LBL-141
Preprint ^{c.1}

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August 1971

AEC Contract No. W-7405-eng-48

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INFRARED ABSORPTION SPECTRA OF ISOTOPIC
OZONE ISOLATED IN RARE GAS MATRICES

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ABSTRACT

Some of the isotopic ozone molecules of different combinations of oxygen-16 and oxygen-18 have been synthesized and isolated in rare gas matrices at 20°K. Their infrared absorption bands have been identified. The isotope effects are calculated for symmetrical as well as unsymmetrical isotopic ozone molecules.

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I. INTRODUCTION

Interest in the products condensed at 20°K from dissociated oxygen (i.e. oxygen which has been passed through an electric discharge) has been stimulated by a number of recent investigations. Both molecular oxygen and atomic oxygen are promising reagents for producing a variety of oxide species in rare gas matrices. The observation¹ of molecular bands upon warming a rare gas matrix in which metallic vapor from a furnace and dissociated oxygen have been condensed at 20°K indicates that the oxygen atoms may be trapped in low temperature matrices. Evidence in favor of this explanation has also been inferred from calorimetric measurements² and infrared absorption.³ Ozone is an expected product in any system containing oxygen atoms. Even when undissociated oxygen is used, ozone can be formed¹ with some reactive metals by the reaction $M + 2O_2 = MO + O_3$. Thus the spectral characterization of the oxide products requires knowledge of spectral behavior of ozone in rare gas matrices. As oxygen isotopic substitution is essential for the identification of the oxide species, the effect of isotopic substitution upon the infrared bands of ozone is presented in this work. Most of these isotopic bands have not been reported in the literature.

II. EXPERIMENTAL

The low temperature systems used have been described in detail elsewhere.¹ The external windows of the vacuum system along the optical path are cesium iodide crystals. The cold target is of cesium bromide.

In the dissociated oxygen experiments, the discharge is initiated in a quartz tube, which has a small orifice of 1 mm diameter. The orifice is about 6 cm away from the collector surface. Air Products and Company research grade oxygen, xenon, and krypton gases are employed without further purification. For isotope studies O_2^{18} of purity 99.85% with 0.13% O_2^{17} from Isomet Corporation, New Jersey, are used. The source of power for the discharge is a 100-w, 2450 Mc microwave generator. A Perkin Elmer 421 infrared spectrometer is used for recording absorption spectra.

III. RESULTS

The observations of infrared absorption bands of ozone in the gaseous phase by D. J. McCaa and J. H. Shaw⁴ and S. A. Clough and F. X. Kneizys,⁵ in solid phase by K. B. Harvey and A. M. Bass³ and by J. L. Brumant, A. Barbe and P. Jouve⁶ and in liquid phase by A. Barbe and P. Jouve⁷, are tabulated in Table I for comparison. The infrared absorption bands of discharged products of oxygen-rare gas mixtures at 20°K are listed in Tables II and III. The spectrograms are shown in Figs. 1 to 4. In general the absorption in the 1030 cm^{-1} region is the most distinctive one. It is assigned to ν_3 of ozone. Bands in the 1100 cm^{-1} and 700 cm^{-1} regions are assigned to ν_1 and ν_2 , respectively. There are red shifts for most of the vibrational absorptions in Kr and Xe matrices and blue shifts in oxygen solid. The calculated isotope effects are also presented in appropriate sections for comparison.

A. O_3^{16} in Kr at 20°K

The most prominent absorption band in krypton matrix is 1035 cm^{-1} . It is assigned to ν_3 of ozone. The appearance of this band as shown in Fig. 1 and Table II is very much like the one in the gas phase. The bands of 1105 cm^{-1} and 700 cm^{-1} are assigned to ν_1 and ν_2 , respectively.

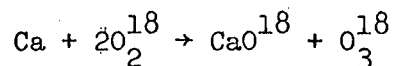
The two bands are relatively weak in comparison with the ν_3 band. There are combination and overtone bands too. They are at 2070 cm^{-1} for $2\nu_3$, 2110 cm^{-1} for $\nu_1 + \nu_3$, and 2150 cm^{-1} for $2\nu_1$. The other assignments are uncertain because they may be due to nitrogen oxides. Traces of OH are indicated by the presence of bands at 3730 and 3710 cm^{-1} . Upon warmup of the matrix only those bands assigned to ozone remain prominent.

B. O_3^{16} in Xe at 20°K.

By changing the matrix from Kr to Xe we observe red shifts in all three fundamental frequencies. As shown in Fig. 2 and Table III, ν_3 appears as a doublet. $\nu_1 = 1100 \text{ cm}^{-1}$, $\nu_2 = 695 \text{ cm}^{-1}$, and $\nu_3 = 1030 \text{ cm}^{-1}$. The combination and overtone bands observed in Kr matrix also appear in Xe matrix. They are 2070 cm^{-1} for $2\nu_3$ and 2110 cm^{-1} for $\nu_1 + \nu_3$.

C. O_3^{18} in Kr at 20°K.

Figure 1 has the IR spectrum of the products of Ca + O_2 reaction in Kr matrix. The band at 982 cm^{-1} is considered to be ν_3 of ozone, which is a product of the following reaction



The 756 cm^{-1} band has been identified as the fundamental vibrational frequency of CaO^{18} molecule trapped in Kr matrix,¹ not shown in Fig. 1.

D. O_3^{18} in Xe at 20°K

Figure 2 has the IR spectrum of discharged O_2^{18} /Xe mixture. Bands at 975 cm^{-1} and 660 cm^{-1} are being assigned to ν_3 and ν_2 of ozone molecule respectively. Here ν_3 also appears as a doublet. Bands at 1008 cm^{-1} is considered to be ν_3 of $O_3^{18/O_3^{16}}$.

E. Mixed Isotopic Ozone in Xe Matrix at 20°K

A mixed isotopic oxygen gas with approximately 60% of high purity O_2^{16} and 40% of O_2^{18} was diluted with Xe to become a gas mixture of 4% oxygen by volume. This mixture was passed through a microwave discharge and condensed on a CsBr target at 20°K. The spectrum is shown in Fig. 3. The main absorption features are those of ozone molecules. The absorption bands and their assignment are shown in Table III. The assignments

of ν_3 to each isotopic ozone are made according to the calculated isotopic shifts as shown in Table IV.

Figure 4 shows how the concentration of oxygen-16 effects the relative intensity of the absorption bands. Curve (A) is the blank spectrum before deposition. Curve (B) is the result of a gas mixture with $O_2^{16} : O_2^{18} = 3 : 2$ and Curve (C) is approximately 3 : 1. From the change of relative intensity with the change of isotopic oxygen concentration and the appearance of ν_1 bands of $O^{16}-O^{16}-O^{16}$ and $O^{16}-O^{16}-O^{18}$ we can assign 1030 and 1015 cm^{-1} bands to ozone molecules with higher oxygen-16 contents. The agreements between the observed and the calculated isotopic shifts and the agreements between ν_3 of $O^{16}-O^{16}-O^{16}$ of this work and the previously reported values give us great confidence in our assignments.

In this work the oxygen to rare gas ratio ranged between 0.4% to 100%. The role of rare gas is very important in the production of discharged oxygen. The aim was to maximize the oxygen atoms concentration, so that enough of the different isotopic ozone molecules could be produced and identified.

This work was done under the auspices of the U. S. Atomic Energy Commission.

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Table I. Some infrared absorption bands (in cm^{-1}) of ozone

Gas phase	Calculated ^(a)	In solid O_2 (c) (T=4.8°K)	In solid O_2 (d) (T=10°K)	In liquid Ar (e) (T=98°K)	Assignment
3042 ^(a)	3036	3060	3035	3029	$3\nu_3$
2779 ^(a)	2776	2800	2800	2780	$\nu_1 + \nu_2 + \nu_3$
2110 ^(a)	2106	2100	2105	2107	$\nu_1 + \nu_3$
2043 ^(a)	2054	2060	2047	2046	$2\nu_3$
1728 ^(a)	1722		1720	1716	$\nu_2 + \nu_3$
1103.157 ^(b)		1120	1103.5	1105.5	ν_1
1042.096 ^(b)		1050	1037	1033	ν_3
701.0 ^(a)		705	708.5	702.5	ν_2

(a) Reference 4.

(b) Reference 5.

(c) Reference 3.

(d) Reference 6.

(e) Reference 7.

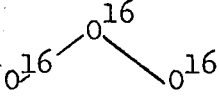
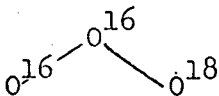
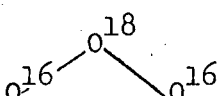
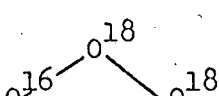
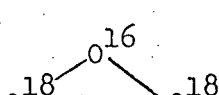
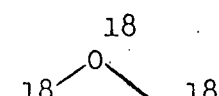
Table II. Infrared absorption bands (in cm^{-1}) of ozone in Kr matrix
at 20°K

$^{16}\text{O}_3$	$^{18}\text{O}_3$	Assignment
2110		$\nu_1 + \nu_3$
1105		ν_1
1035	982	ν_3
700	665	ν_2

Table III. Infrared absorption bands (in cm^{-1}) of ozone in Xe matrix at 20°K

O_3^{16}	$\text{O}^{16}-\text{O}^{16}-\text{O}^{18}$	$\text{O}^{18}-\text{O}^{16}-\text{O}^{18}$	$\text{O}^{16}-\text{O}^{18}-\text{O}^{16}$	O_3^{18}	Assignment
2110				2100	$\nu_1 + \nu_3$
1100				1038	ν_1
1030 } 1025 }	1015	(1008)	995	978 } 970 }	ν_3
695				660	ν_2

Table IV. ν_3 (in cm^{-1}) of Isotopic ozone molecules

Molecules	$\nu(\text{cal.})$	Gas phase	O_2^c	Kr	Xe
		1042	1037	1035	1030
	1030.0 ^a		1023		1015
	1006.0 ^b		1003		995
	994.0 ^a				
	1020.0 ^b				1008
	983.0 ^b			982	978

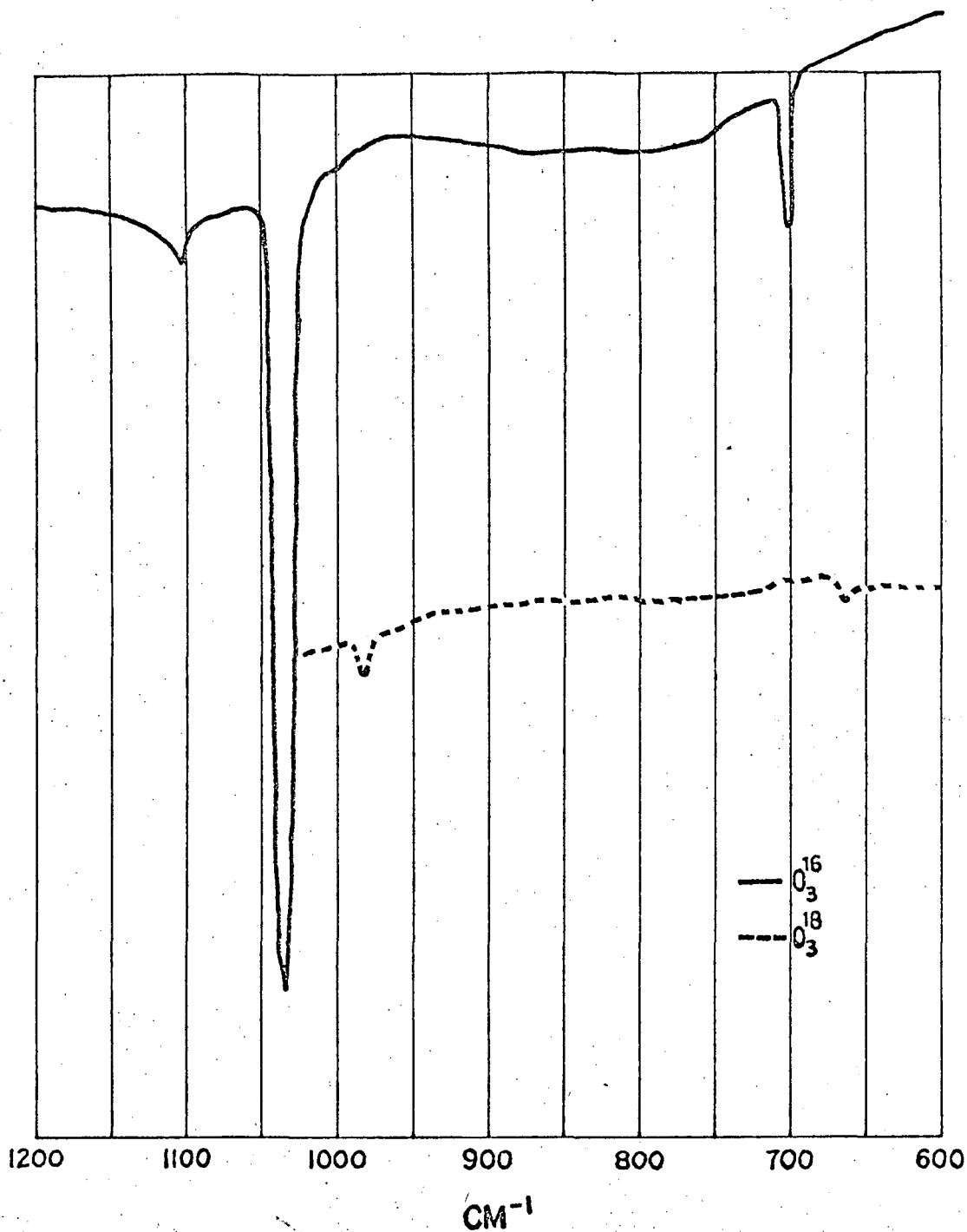
(a) Calculated according to E. O. Salant and J. E. Rosenthal.⁸

(b) Calculated according to G. Herzberg.⁹

(c) Reference 6.

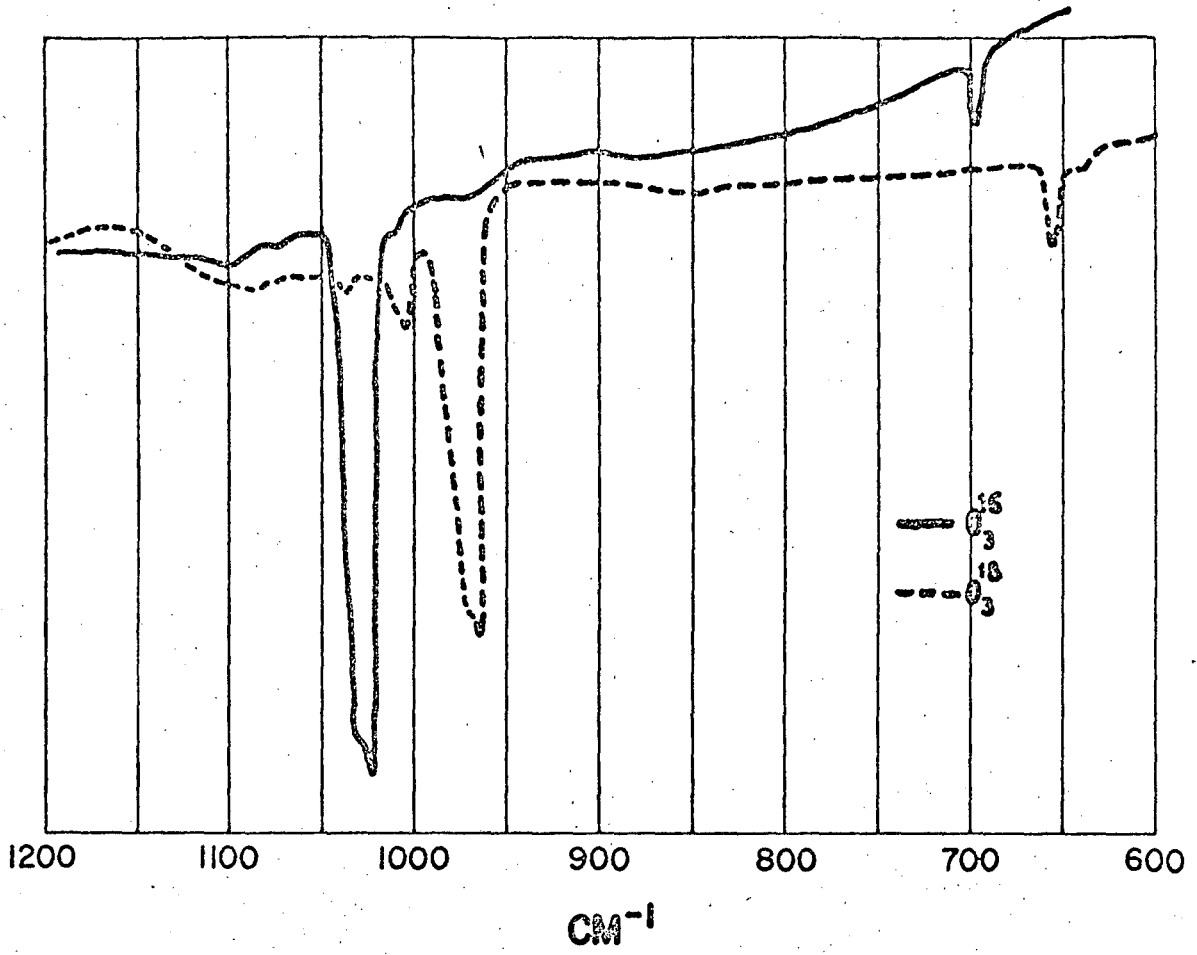
Figure Captions

- Fig. 1. Infrared absorption of O_3^{16} in Kr and O_3^{18} in Kr at 20°K.
- Fig. 2. Infrared absorption of O_3^{16} in Xe and O_3^{18} in Xe at 20°K.
- Fig. 3. Infrared Absorption of isotopic ozone molecules in Xe at 20°K.
- Fig. 4. Infrared absorption of isotopic ozone molecules as a function of oxygen-16/oxygen-18 ratios in Xe at 20°K.



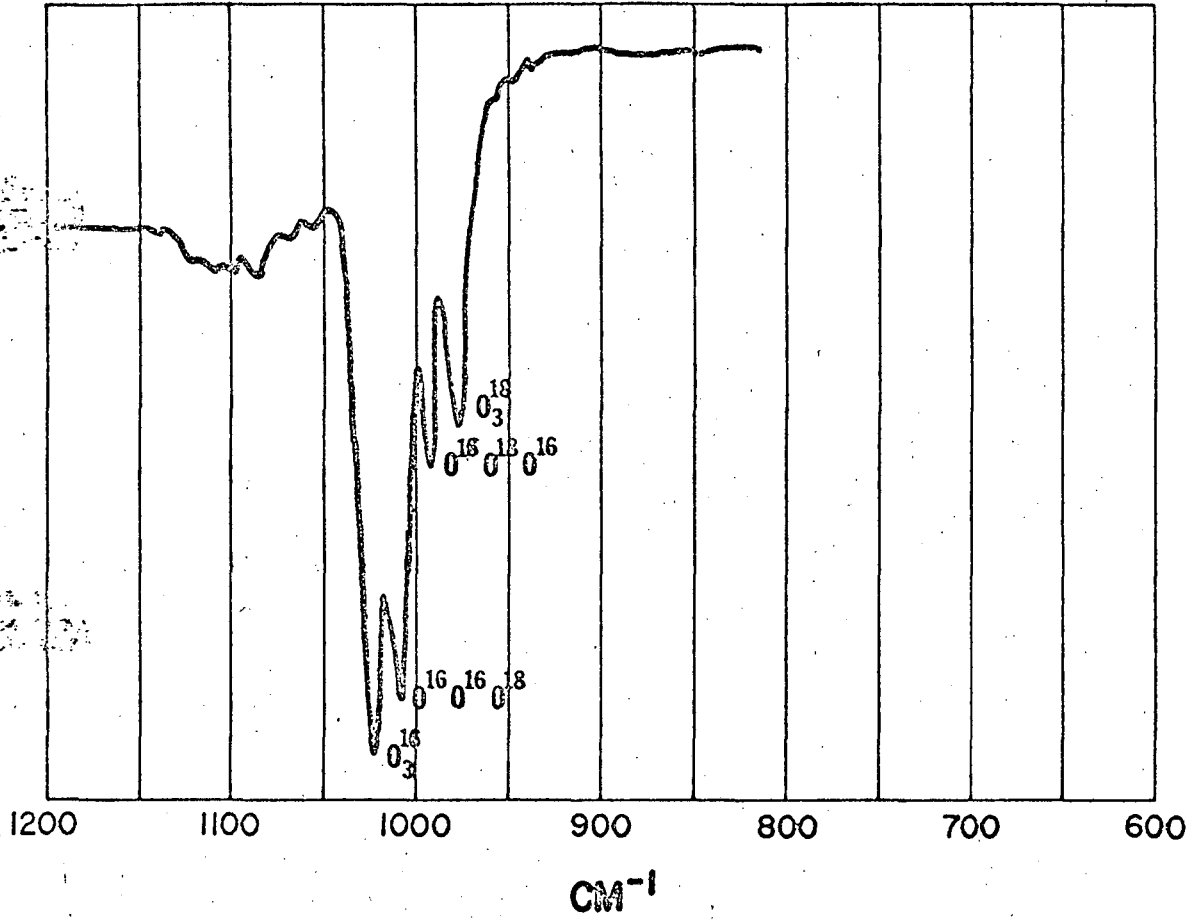
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Fig. 1



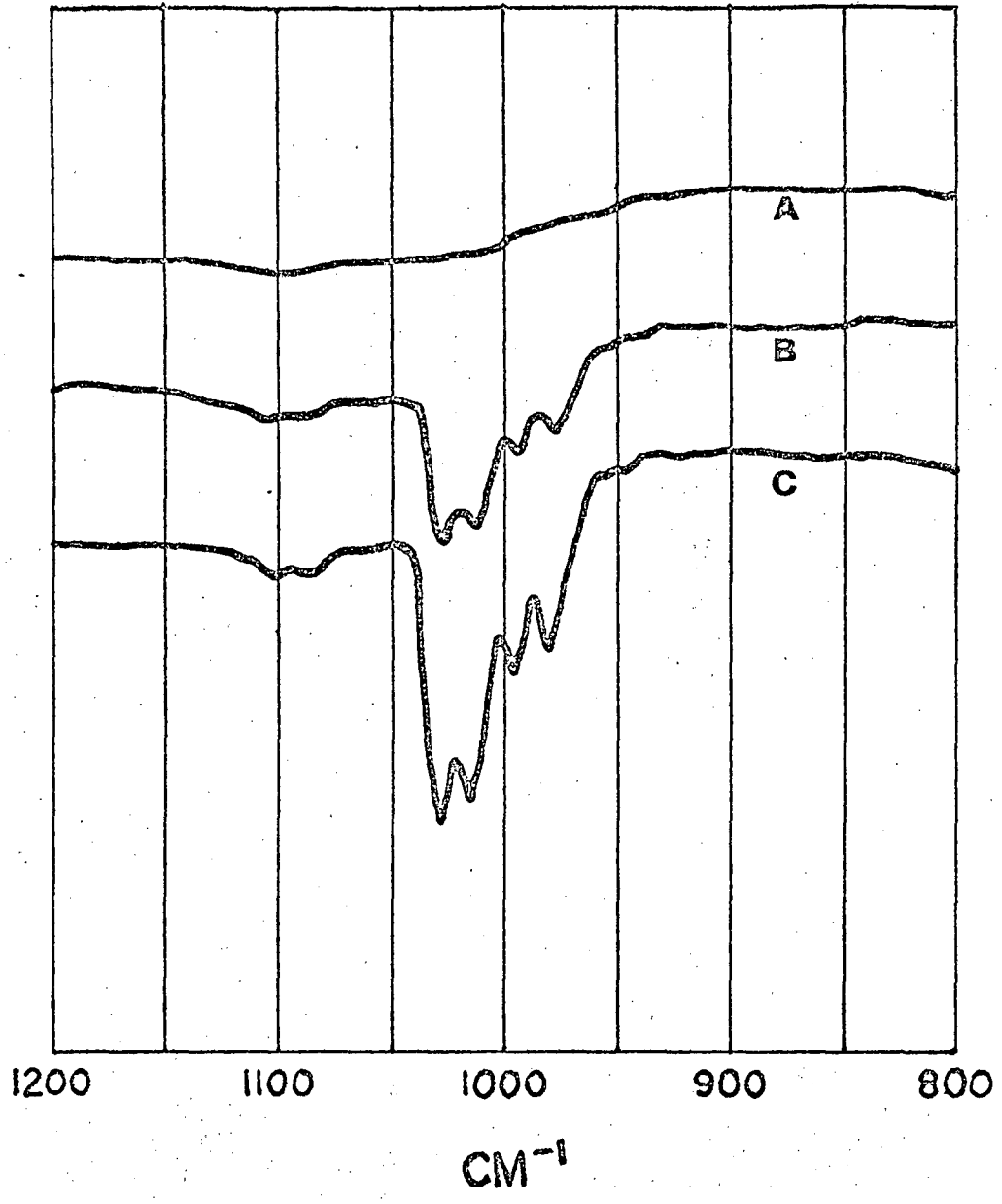
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Fig. 2



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Fig. 3



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Fig. 4

U S G O 1 2 0

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