

The Vibrational Spectra and Structure of Inorganic Molecules. II. Sulfur S₈, Sulfur Chloride S₂Cl₂, Phosphorous P₄

H. J. Bernstein and J. Powling

Citation: *The Journal of Chemical Physics* **18**, 1018 (1950); doi: 10.1063/1.1747846

View online: <http://dx.doi.org/10.1063/1.1747846>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/18/8?ver=pdfcov>

Published by the *AIP Publishing*

Articles you may be interested in

Erratum: Vibrational Spectra of Inorganic Molecules. II. Infrared Reflection Spectra of Liquid Lithium, Sodium, Potassium, and Silver Nitrates

J. Chem. Phys. **36**, 1088 (1962); 10.1063/1.1732649

Vibrational Spectra of Inorganic Molecules. II. Infrared Reflection Spectra of Liquid Lithium, Sodium, Potassium, and Silver Nitrates

J. Chem. Phys. **35**, 1078 (1961); 10.1063/1.1701184

Erratum: The Vibrational Spectra and Structure of Inorganic Molecules. II. Sulfur S₈, Sulfur Chloride S₂Cl₂, Phosphorous P₄

J. Chem. Phys. **19**, 139 (1951); 10.1063/1.1747976

The Vibrational Spectra and Structure of Inorganic Molecules. III. The InfraRed Spectra of Nitrosyl Chloride and Nitrosyl Bromide from 2.0 to 25 μ

J. Chem. Phys. **18**, 1669 (1950); 10.1063/1.1747559

The Vibrational Spectra and Structure of Inorganic Molecules. I. The InfraRed Spectrum of F₂O from 2.5 to 25 μ

J. Chem. Phys. **18**, 685 (1950); 10.1063/1.1747726



already argued that the third approximation in the Chapman-Enskog expansion would increase the calculated thickness. An experimental decision on this score might be reached by studying the thickness of shock fronts in a monatomic gas and such measurements have been undertaken in argon.

ACKNOWLEDGMENT

We should like gratefully to acknowledge the aid given to us by Dr. Paul M. Fye and the Explosives Division of the Naval Ordnance Laboratory by loaning us the shock tube and much of the recording equipment used in this work.

The Vibrational Spectra and Structure of Inorganic Molecules. II. Sulfur S_8 , Sulfur Chloride S_2Cl_2 , Phosphorous P_4

H. J. BERNSTEIN AND J. POWLING*
National Research Council, Ottawa, Canada
(Received February 27, 1950)

The infra-red spectra from 2-25 μ have been obtained for S_8 as solid and in CS_2 solution; for S_2Cl_2 as liquid and in CS_2 solution; and for P_4 in CS_2 solution. A satisfactory assignment of the Raman and infra-red spectrum of S_8 has been made on the basis of D_{4d} symmetry. The spectrum and valence force calculations are consistent with the C_2 structure for S_2Cl_2 , and together with the electron diffraction data exclude the C_{2v} form. The vibrational spectrum of P_4 is interpreted unequivocally on the basis of the tetrahedral structure (T_d).

I. SULFUR S_8

THE x-ray analysis¹ of rhombic sulfur shows that the molecule is S_8 with symmetry of the D_{4d} point group. The distance between the S atoms is found to be 2.12Å, and the bond angle 105°. Cryoscopic measurements on rhombic sulfur in solution show that the molecule is again S_8 . This is indeed borne out by the similarity between the Raman spectrum of the solid and of sulfur in solution (columns 2, 3, and 4 of Table I).

Table I shows the existing infra-red data of the solid and Raman spectra of solid and solution. Although these data seem extensive, the assignment of the fundamental modes of vibration to the symmetry types of the D_{4d} point group leaves much to be desired. Valence force calculations have been made by Bhagavantam and Venkatarayudu² with a complete quadratic potential function. Using the two strong polarized lines at 470 cm^{-1} and 216 cm^{-1} as the totally symmetrical vibrations approximate values of the principal force constants are calculated for zero value of the interaction constant.² These force constants are then used to indicate that the band at 243 cm^{-1} is a type E_2 vibration. With these three identified frequencies the values of the three force constants were found to be

$$K_1=2.309, \quad K_2=0.903, \quad K_3=0.067$$

in units of 10^5 dynes per cm. The above authors then

calculated all the frequencies from these force constants and matched them with the available experimental data as shown in Table II, columns 3, 4, and 5. The discrepancy between $\nu_{10}(\text{calc})$ and $\nu_{10}(\text{obs})$ was later cleared up by further investigation of the Raman spectrum³ when a line was observed at 520 cm^{-1} . However there are two strong objections to the above assignment. Firstly, on the basis of this assignment the strong infra-red band at 150 cm^{-1} and the strong wide band at 200-250 cm^{-1} in the spectrum of the solid (Table I, column 5) cannot be satisfactorily explained and choice of 200 cm^{-1} for one of the fundamentals would seem rather arbitrary. Secondly, since the valence force calculations are accurate to within 10 percent for all frequencies except ν_9 it suggests that since ν_9 is calculated too low the calculated value of ν_8 is too high. The assignment indicated by the calculation then is that ν_8 is 185 cm^{-1} rather than 243 cm^{-1} , and that ν_{11} is 243 cm^{-1} . Because of these criticisms it seemed worth while attempting to improve this assignment both by a new valence force calculation and by investigation of the infra-red spectrum in solid and solution at long paths so that as many overtones and combination tones as possible could be observed.

Experimental

The infra-red spectrum of a 60 percent solution of sulfur in CS_2 and of the crystal was obtained with a Perkin-Elmer spectrometer (Model 12C). The results are shown in Fig. 1 and also included in Table I (columns 6 and 7).

* National Research Laboratories Postdoctorate Fellow 1949-50.

¹ B. E. Warren and J. T. Burwell, J. Chem. Phys. 3, 6 (1935).

² S. Bhagavantam and T. Venkatarayudu, Proc. Ind. Acad. Sci. 8A, 101, 115 (1938).

³ Reported in K. W. F. Kohlrausch, *Ramanspektren* (Edwards Bros., Ann Arbor, Michigan, 1945), p. 394.

TABLE I. Raman and infra-red spectra of S_8 .*

	CS ₂ sol. ^a	Raman C ₁₀ H ₈ sol. ^a	solid ^b	solid ^c	Infra-Red solid ^d	CS ₂ sol. ^d	Assignment
1	°	86(m)	85(5)D				267-185=82(E_2)
2				87(w)			243-152=91(E_1+E_3)
3				103(w)			
4			114(0)				267-152=115(E_2)
5				150(s)			†
6	151(9)	153(m)	152(10)P				$\nu_9(E_2)$
7		184(v.v.w.)	185(0b)D				$\nu_8(E_2)$
8				200-250(s)			†
9	218(11)	217(m)	216(10)P				$\nu_2(A_1)$
10	248(3)	248(v.v.w.)	243(1b)D				$\nu_{11}(E_2)$
11				267(w)			$\nu_4(B_2)$
12	299(1)						$2 \times 152 = 304(A_1+B_1+A_2+B_2)$
13	334(2)?						$185+152=337(A_1+B_1+B_2)$
14				400(w)			$216+190=406(E_1)$
15					435(w)		$190+243=433(B_1+B_2+E_2)$
16	437(1)	437(v.w.)	434(2b)D				$\nu_7(E_2)$
17				465(s)	465(s)	471(s)	$\nu_6(E_1)$
18	474(10)	476(m)	470(10)P				$\nu_1(A_1)$
19					509(w)		$267+243=510(E_1)$
20			520(0) ^f				$\nu_{10}(E_3)$
21					549(w)	544(w)	$2 \times 152 + 243 = 547(E_3+2E_1)$
22		591(v.v.w.)			584(w)	592(w)	$152+434=586(A_1+B_1+A_2+B_2)$
23					618(w)	622(w)	$434+185=619(A_1+B_1+A_2+B_2)$
24					659(w)		$470+190=660(E_1)$
25				686(w)*	678(w)	686(w)	$216+465=681(E_1)$
26					710(w)	714(w)	$190+520=710(B_1+B_2+E_2)$
27				841(m)*	840(m)	854(m)	$2 \times 190 + 465 = 845(E_3+2E_1)$
28					869(w)		$2 \times 434 = 868(A_1+B_1+B_2)$
29					901(w)	912(w)	$465+434=899(E_1+E_3)$
30				932(w)*	937(w)	942(w)	$465+470=935(E_1)$
31					986(w)		$465+520=985(B_1+B_2+E_2)$
32					1052(w)		$532+520=1052(E_1)$
33				1290(w)*	1300(w)	1315(w)	$840+465=1305(B_1+B_2+E_2+E_3+2E_1)$
34					1510(w)		$840+678=1518(B_1+B_2+E_2+E_3+2E_1)$

* D = depolarized, P = polarized, b = diffuse, w = weak, m = medium, s = strong, v = very.

† The fundamental $\nu_6=190(E_1)$ interacts with the difference tone $434-243=191(E_1+E_3)$ to give Fermi splitting observed at 150 cm^{-1} and 230 cm^{-1} . The intensity and width of the band at 230 is further enhanced by superposition of $465-243=222(B_1+B_2+E_2)$ and Fermi resonance between 230 and $434-190=244(E_1+E_3)$.

^a H. Gerding and R. Westrik, Rec. Trav. Chim. Pays-Bas, **62**, 68 (1943).

^b C. S. Venkateswaran, Proc. Ind. Acad. Sci. **4A**, 345 (1936).

^c R. B. Barnes, Phys. Rev. **39**, 570 (1932).

^d This work.

^e Overlapped by CS₂ wing, see reference b.

^f Reported in K. W. F. Kohrausch, *Ramanspektren* (Edwards Bros., Ann Arbor, Michigan, 1945), p. 394.

* Taylor and Rideal, Proc. Roy. Soc. (London), **115A**, 589 (1927).

Discussion

It would appear from Table I that all the Raman lines are due to internal vibrations (i.e., not lattice vibrations), since they are present in solution. For this reason it seems not unreasonable to consider the observed infra-red spectrum as entirely due to the S_8 molecule. An assignment of the fundamentals must account therefore for all of the 34 observed infra-red and Raman lines listed in Table I.

From the Raman spectrum of the solid one can readily assign the two strong polarized lines at 470 cm^{-1} and 216 cm^{-1} to ν_1 and ν_2 . Of the three allowed infra-red active fundamentals (ν_4 , ν_5 , ν_6) ν_5 is assigned as 465 cm^{-1} since it corresponds to a stretching mode whereas ν_4 and ν_6 would be much lower since they are bending modes.² Without the aid of a calculation of the frequencies from a quadratic potential function it would be extremely difficult and laborious to assign the remaining 8 frequencies.

With the unambiguous assignment of $\nu_1=470$, $\nu_2=216$ and $\nu_5=465\text{ cm}^{-1}$ the force constants were calcu-

lated from the equations of Bhagavantam and Venkatarayudu² to be

$$K_1=2.042, K_2=0.920, K_3=0.182 \times 10^6 \text{ dynes per cm.}$$

With these force constants all the frequencies were calculated and are given in the last column of Table II. These values differ only very slightly from the values calculated by Bhagavantam and Venkatarayudu (Table II, column 3) because both calculations give a value of $\sim 250\text{ cm}^{-1}$ for ν_8 . As can be seen from Table II the following assignments can be made unambiguously:

$$\nu_4=267, \nu_7=434, \nu_9=152 \text{ and } \nu_{10}=520.^3$$

Again since ν_7 and ν_9 are calculated too low,⁴ the calcu-

⁴ It is not surprising that the equations for the frequencies do not yield better agreement between the observed and calculated frequencies for this symmetry type. All of the equations involve R^2 , R^4 , and R^6 as coefficients where R is the S-S bond distance and is given by $2.12 \pm 0.03\text{ \AA}$. The error in these coefficients may be large but for the first and second degree equations there should be reasonable internal consistency. For a third degree equation, however, the errors have increased and the agreement between observed and calculated frequencies could not be expected to be as good as for equations of lesser degree.

TABLE II. Fundamental vibration frequencies for S_8 .

Type		Calc. ^a	Obs. ^b		Calc. ^c
			I.R.	R.	
A_1	ν_1	481		470(p)	470
	ν_2	197		216(P)	216
B_1	ν_3	557			524
B_2	ν_4	255	267(w)		277
E_1	ν_5	481	465(s)		465
	ν_6	181	200(s)		202
E_2	ν_7	452		434(D)	410
	ν_8	243		243	258
E_3	ν_9	122		152(D)	131
	ν_{10}	542		114?	515
	ν_{11}	211		185	232

^a Calculated by Bhagavantam and Venkatarayudu from $\nu_1=470$, $\nu_2=216$, $\nu_3=243$.

^b Experimental data used by Bhagavantam and Venkatarayudu.

^c Calculated in this work from $\nu_1=470$, $\nu_2=216$, $\nu_3=465$.

lated value of ν_8 is much too high indicating that ν_8 should be 185 cm^{-1} rather than 243 cm^{-1} . With $\nu_8=185\text{ cm}^{-1}$ and $\nu_{11}=243\text{ cm}^{-1}$ the difference tone $\nu_7-\nu_{11}=434-243=191\text{ cm}^{-1}$ (E_1+E_3) could interact with a fundamental [say $\nu_6=190\text{ cm}^{-1}$ (E_1)] to give Fermi splitting observed at 150 cm^{-1} and 230 cm^{-1} . This would account for the strong band at 150 cm^{-1} and account for a strong band in the region $200\text{--}250\text{ cm}^{-1}$. The width of this band ($200\text{--}250\text{ cm}^{-1}$) could be explained by overlapping with $465-243=222\text{ cm}^{-1}$ ($B_1+B_2+E_2$) and further Fermi resonance between 230 cm^{-1} and $434-190=244\text{ cm}^{-1}$ (E_1+E_2). It is worth emphasizing, that it was found impossible to explain the strong infra-red bands at 150 cm^{-1} and $200\text{--}250\text{ cm}^{-1}$ with any other reasonable choice for ν_6 but $\nu_6=190\text{ cm}^{-1}$. The choice of 150 cm^{-1} and the middle of $200\text{--}250\text{ cm}^{-1}$ as the fundamentals can be excluded as an assignment since the resulting interpretation of the spectrum is highly unsatisfactory.

The only unassigned fundamental is ν_3 which is both Raman and infra-red inactive. However, the band at 1052 cm^{-1} observed in the infra-red spectrum of the solid can be interpreted as a binary combination tone only by combination of $\nu_3+\nu_{10}$ (E_1) from which, by difference $\nu_3=1052-520=532\text{ cm}^{-1}$. This value for ν_3 is further supported by the valence force calculation of $\nu_3\sim 524\text{ cm}^{-1}$. The values of the frequencies of the fundamental modes of solid rhombic sulfur and their assignment to symmetry types as indicated by this work are:

Type			
A_1	$\nu_1=470$	$\nu_2=216$	
B_1	$\nu_3=532$		
B_2	$\nu_4=267$		
E_1	$\nu_5=465$	$\nu_6=190$	
E_2	$\nu_7=434$	$\nu_8=185$	$\nu_9=152$
E_3	$\nu_{10}=520$	$\nu_{11}=243$	

The interpretation of the 34 observed bands and lines is given in the last column of Table I and appears quite satisfactory.

II. SULFUR CHLORIDE S_2Cl_2

The work of Gerding and Westrik⁵ on the Raman spectrum of liquid S_2Cl_2 limits the choice for the structure of S_2Cl_2 molecule to either the planar C_{2v} form or the non-planar C_2 form.

The symmetry types, number of vibrations and selection rules for these point groups are given in Table III.

Both C_{2v} and C_2 models should have 6 lines in their Raman spectrum. For the C_{2v} model, 3 are polarized and 3 depolarized while for the C_2 model 4 are polarized and 2 depolarized.

The Raman spectrum obtained by Gerding and Westrik⁵ gave: 106(depolarized), 245(depolarized), 537(depolarized) 206(polarized) and 443(polarized). Only 5 lines were observed and 3 are depolarized. Since there is no doubt as to the depolarization of 245 cm^{-1} and 537 cm^{-1} and since the above authors quote 106 cm^{-1} as depolarized the C_2 model was rejected and the C_{2v} structure was adopted for S_2Cl_2 .

To account for the 6th line which was not observed they assume that 443 cm^{-1} is the resultant of two co-incident polarized lines due to the S-S and S-Cl symmetrical stretching vibrations. Venkateswaran⁶ working under higher dispersion notes that this line is diffuse on the short wave-length side but obtained no resolution into two lines.

In contradiction to the above interpretation the electron diffraction by the vapor indicates that the structure is C_2 with the S-Cl bonds at 90° with respect to each other.⁷ Since the interpretation of the spectroscopic data does not agree with the results obtained from electron diffraction, we have re-examined the spectroscopic data and have obtained also the infra-red spectrum of S_2Cl_2 .

Results and Discussion

The S_2Cl_2 used in this work was the redistilled product of the General Chemical Company, New York, b.p. $135\text{--}136^\circ\text{C}$. The infra-red spectra from $2\text{--}25\mu$ of S_2Cl_2 as liquid and a solution in CS_2 were obtained with a Perkin-Elmer spectrometer (Model 12C). The results are shown in Fig. 2 and in Table IV.

In dilute solution with CS_2 there are indeed two intense bands at 438 cm^{-1} and 448 cm^{-1} which are presumably fundamentals.

The line at 443 cm^{-1} in the Raman spectrum of the liquid is due to two fundamentals of the same frequency, as surmised by Gerding and Westrik. In dilute solution with CS_2 it is resolved in the infra-red into two bands.

It is interesting that no splitting of the two fundamentals at 443 cm^{-1} was observed in the Raman spec-

⁵ H. Gerding and R. Westrik, Rec. Trav. Chim. Pays-Bas **60**, 702 (1941).

⁶ S. Venkateswaran, Ind. J. Phys. **6**, 275 (1931).

⁷ K. J. Palmer, J. Am. Chem. Soc. **60**, 2360 (1938).

trum due to Fermi resonance.⁸ This is probably due to the fact that there is little interaction between the two vibrations.

In the present authors' opinion it seems highly improbable that Gerding and Westrik could distinguish between a weakly polarized line and a depolarized line at 106 cm^{-1} which shows considerable overlapping with the exciting line on their microphotometer trace.*

If it is assumed then that the line at 106 cm^{-1} is weakly polarized, the spectroscopic data are consistent with the C_2 structure and the assignment is:

Type A	106	206	438	448
Type B	245	537		

Morino and Mizushima⁹ have obtained the secular equations for the vibrations of the S_2Cl_2 molecule of symmetry C_2 in which the S-Cl bonds are at 90° to each other. They employ a quadratic potential function

TABLE III.

C_{2v}				C_2			
Type	No. of vibrations	Raman	I.R.	Type	No. of vibrations	Raman	I.R.
A_1	3	+(pol)	+	A	4	+(pol)	+
A_2	1	+(depol)	—	B	2	+(depol)	+
B_1	2	+(depol)	+		6	6	6
B_2	0	+(depol)	+				
	6	6	5				

with 5 force constants which is independent of azimuthal angle. In this way an expression for the symmetrical frequencies is obtained which does not include the torsional vibration. Using $K_{S-Cl} = 2.42 \times 10^5$ dynes per cm, $K_{S-S} = 1.87 \times 10^5$ dynes per cm, $K' = 0.35 \times 10^5$ dynes per cm, $\delta = 0.30 \times 10^5$ dynes per cm, and $\delta' = 0.00 \times 10^5$ dynes per cm in their expression for the fre-

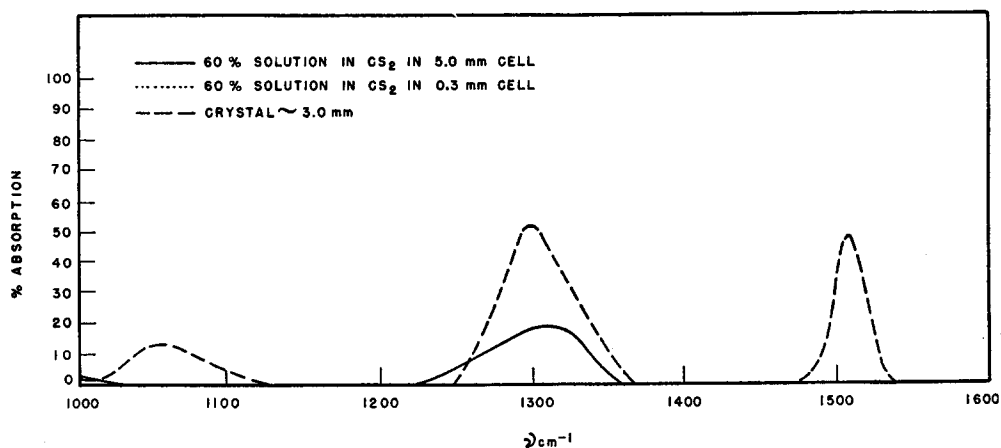
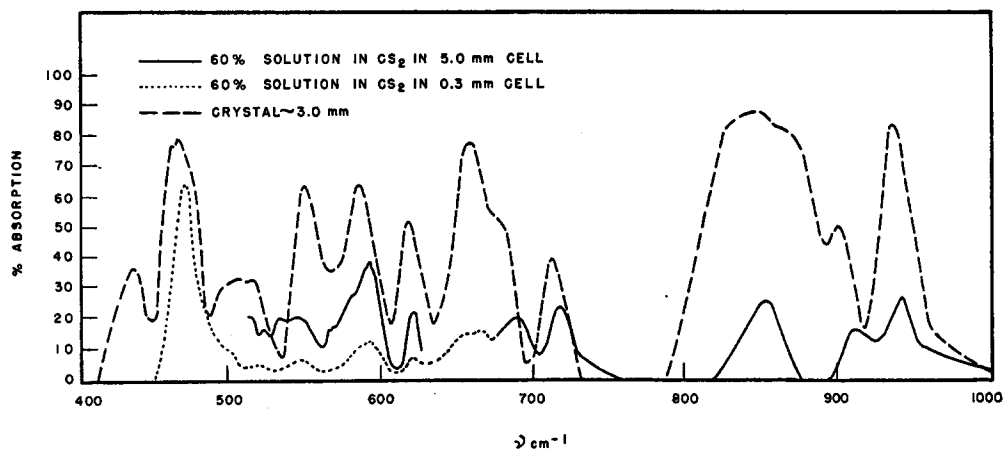


FIG. 1. Infra-red spectrum of solid sulfur and in CS_2 solution.



⁸ G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, New York, 1945), p. 215.

* The earlier measurement by R. Ananthakrishnan, Proc. Ind. Acad. Sci. 5A, 285 (1937) of the polarization of the line at 123 cm^{-1} in the Raman spectrum of dichloroethane showed the line to be depolarized. More recent measurements by Neu, Ottenberg, and Gwinn [J. Chem. Phys. 16, 1004 (1948)] show the line to be weakly polarized ($\rho = 0.63$). The difficulties encountered in obtaining the polarization of lines near the exciting line are well known and doubt as to the depolarization of the line at 106 cm^{-1} in S_2Cl_2 is perhaps justified.

⁹ Y. Morino and S. Mizushima, Sci. Pap. Phys. Chem. Res. Tokyo 32, 220 (1937).

TABLE IV. The vibrational spectrum of liquid S_2Cl_2 .

Raman ^a	ν cm ⁻¹	I.R. ^b	Assignment C_2
106 (depol)			A
206 (pol)			A
245 (depol)			B
443 (pol)	438 s		A
	448 s		A
	538 s		B
537 (depol)	779 w		537+245 (B)
	881 m		448+438 (A)
	984 w		537+448 (B)
	1073 w		537+537 (A)
	1333 w		878+448 (A)

^a Gerding and Westrik, reference 5.^b This work.

quencies the following frequencies for the symmetrical and antisymmetrical modes of the S_2Cl_2 molecule are calculated, *viz.*:

Type A (calc)	493	445	184
(obs)	446	438	208
Type B (calc)	536	242	
(obs)	536	242	

From this one may conclude that the line at 106 cm⁻¹ is due to the torsional oscillation.

The agreement between observed and calculated frequencies is quite good considering the assumptions made and is consistent with the C_2 configuration of S_2Cl_2 .

TABLE V.

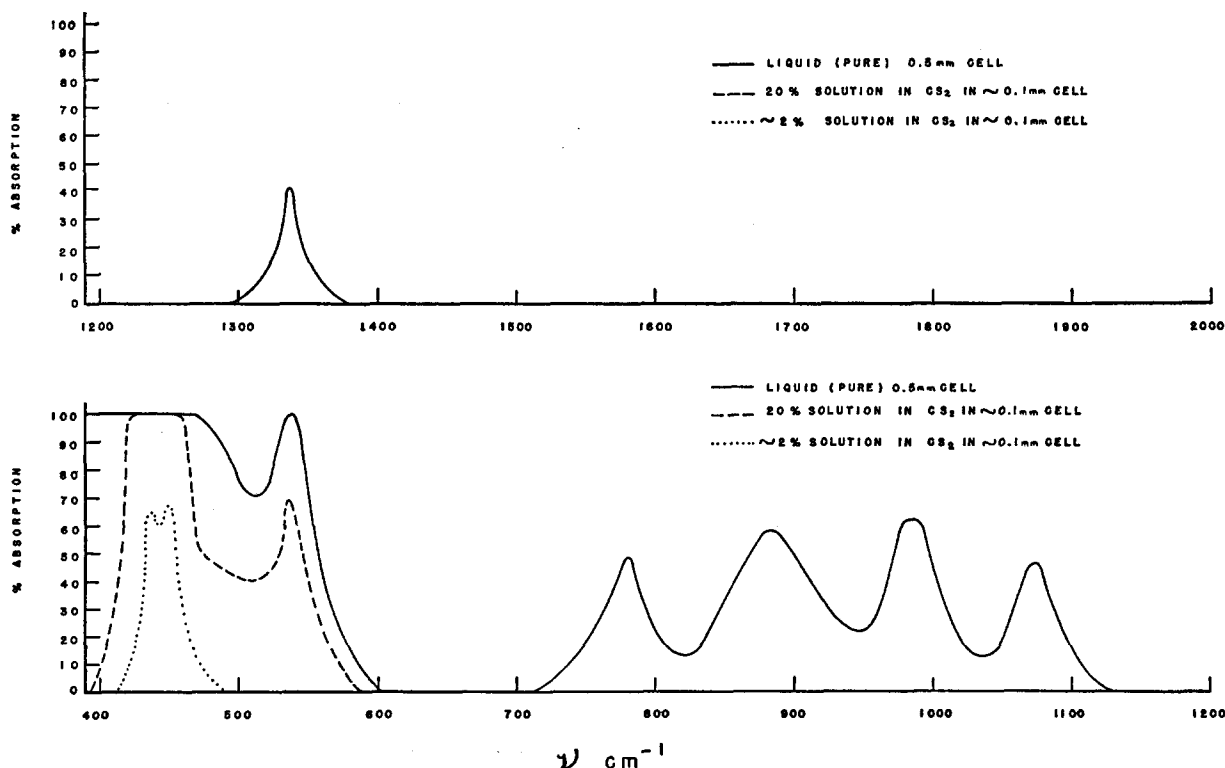
D_{4h}				T_d			
Type	No. of vibrations	Raman	I.R.	Type	No. of vibrations	Raman	I.R.
A_{1g}	1	+(pol)	—	A_1	1	+(pol)	—
B_{1g}	1	+(depol)	—	E	1	+(depol)	—
B_{1u}	1	—	—	F_2	1	+(depol)	+
B_{2g}	1	+(depol)	—		3	3	1
E_u	1	—	+				
	5	3	1				

In Table IV the observed Raman and infra-red spectra are given with an assignment based on the C_2 structure. Although the vibrational spectrum alone is not sufficient to decide the structure of S_2Cl_2 it is not inconsistent with a C_2 structure if the line at 106 cm⁻¹ in the Raman spectrum is taken as weakly polarized rather than depolarized. Also, the calculated frequencies for the C_2 model agree well with those observed. Along with the results obtained from the electron diffraction by the vapor the total evidence favors the C_2 structure rather than C_{2v} .

III. PHOSPHOROUS P_4

If the four P atoms are equivalent, suitable models for P_4 would be the plane square model (D_{4h}) and the tetrahedral model (T_d).

Table V shows the symmetry types, number of vibrations and selection rules for the two models.

FIG. 2. Infra-red spectrum of S_2Cl_2 .

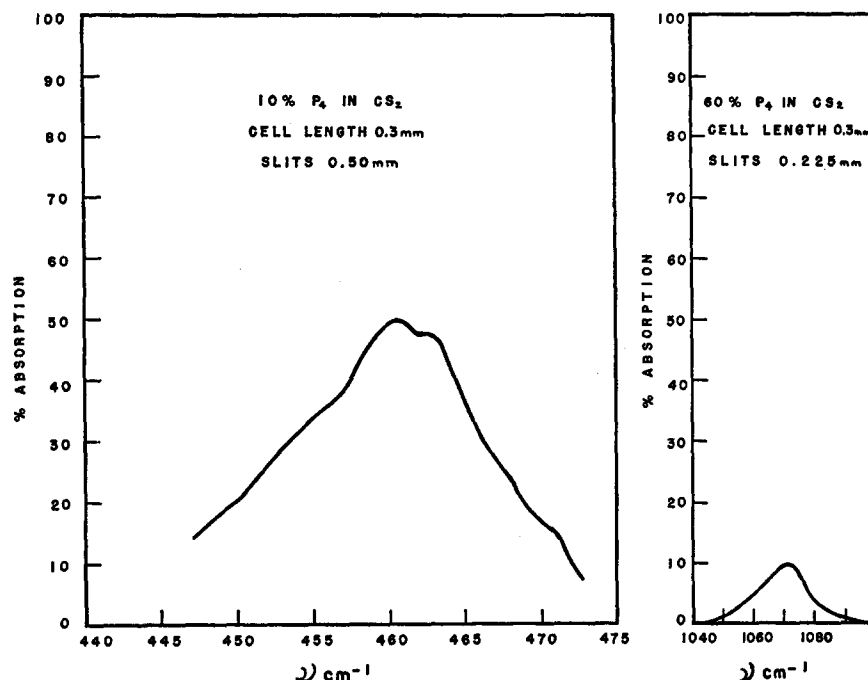


FIG. 3. Infra-red spectrum of phosphorus. [The abscissae in the smaller figure should be moved one division to the right.]

In both cases there should be one polarized line and two depolarized lines in the Raman spectrum.

In the infra-red spectrum there should be no correspondence with a Raman band for the D_{4h} model, whereas, the infra-red active fundamental should correspond to one of the two depolarized Raman lines for the T_d model.

The infra-red spectrum of a solution of yellow phosphorous P_4 in CS_2 was obtained in a 0.3 mm cell with a Perkin-Elmer model 12C spectrometer.

One strong band was observed at 461 cm^{-1} and a weak one at 1062 cm^{-1} (see Fig. 3). Since the Raman spectrum of liquid phosphorous¹⁰ contains a polarized line at 606 cm^{-1} and two depolarized lines at 363 cm^{-1} and 465 cm^{-1} it seems quite definite that the infra-red band at 461 cm^{-1} (in CS_2 solution) corresponds to the Raman line at 465 cm^{-1} (liquid) and that this frequency corresponds to the type F_2 vibration of the T_d model.

Since 606 cm^{-1} is polarized it is necessarily of type A_1 so that 363 cm^{-1} is of type E .

Furthermore since $A_1 + F_2$ is infra-red active the weak band observed at 1062 cm^{-1} is $606 + 461 = 1067$. The Raman and infra-red spectra of yellow P_4 clearly indicate then the T_d structure.

Calculations of the frequencies of the tetrahedral model from a two constant quadratic potential function¹¹ show also that 465 cm^{-1} is of type F_2 and 363 cm^{-1} is of type E when 606 cm^{-1} is taken as type A_1 .

Further, the tetrahedral structure has been deduced from the electron diffraction data.¹²

ACKNOWLEDGMENT

Thanks are due W. Le B. Ross of the University of British Columbia for obtaining the infra-red spectrum of S_8 in CS_2 solution and to Miss E. Miller for reducing the spectra.

¹¹ S. Bhagavantam and T. Venkatarayudu, Proc. Ind. Acad. Sci. 8A, 119 (1938).

¹² Maxwell, Hendricks, and Mosely, J. Chem. Phys. 3, 699 (1935).

¹⁰ C. S. Venkateswaran, Proc. Ind. Acad. Sci. 2A, 260 (1935); 4A, 345 (1936).