AIP The Journal of Chemical Physics

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Citation: J. Chem. Phys. **26**, 329 (1957); doi: 10.1063/1.1743293 View online: http://dx.doi.org/10.1063/1.1743293 View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v26/i2 Published by the AIP Publishing LLC.

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Infrared and Raman Spectra of Vanadium Oxytrichloride

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The infrared and Raman frequencies of liquid VOCl₃ (of symmetry C_{3v}) have been measured. The a_1 fundamentals are 1035, 408, and 165 cm⁻¹; those of species e are 504, 249, and 129 cm⁻¹. Most of the fifteen remaining bands can be explained as combinations of these.

INTRODUCTION

7ANADIUM oxytrichloride, VOCl₃, is a pale yellow, mobile liquid which freezes at -79.5° and boils at 127°C.1 It reacts rapidly with moisture, and when it is exposed to the atmosphere a dense yellowish-red cloud of vapor forms, while the liquid turns dark red and bits of solid appear in it.² An electron diffraction study by Palmer³ showed that the molecule has the expected C_{3v} structure. The only report on the spectrum of VOCl₃ is a fairly recent paper by Eichhoff and Weigel⁴ on its Raman spectrum, which we did not see until after our measurements were completed. Our Raman data and conclusions agree very well with theirs. Since the present work also includes polarization measurements on the Raman lines and a determination of the infrared spectrum, it seems worthwhile to present it in its entirety.

EXPERIMENTAL

The sample was made available through the courtesy of the Vanadium Corporation of America. It was prepared by the reaction:

 $V_2O_5 + 3C + 3Cl_2 = 2VOCl_3 + 3CO.$

A mixture of 200 g of cp vanadium pentoxide and 20 g of carbon was heated in a 1000 ml distilling flask in an oil bath to approximately 270°C, and chlorine was passed over the mixture. The condensate obtained from the reaction contained some fine carbon and was redistilled. The purity is not known, but an elemental analysis was quite satisfactory. (Calculated for VOCl₃: V, 29.40%; Cl, 61.37%. Found: V, 29.33%; Cl, 60.62%.)

The infrared spectrum was obtained with a Perkin-Elmer model 112 double pass spectrometer, with prisms of CaF2, NaCl, and CsBr. The pure liquid was used in vapor-tight cells, and all sample handling was done in a dry box. Frequencies are believed to be accurate to $\pm 1 \text{ cm}^{-1}$ from 300–1000, and to $\pm 2 \text{ cm}^{-1}$ from 1000–2000 cm⁻¹.

The visible spectrum, measured on a thin layer of the pure liquid, showed that Hg 4358 was absorbed too strongly to be used as the Raman exciting line, but that Hg 5461 or 5770-5791 would be satisfactory. The former was chosen. Filter solutions of acidic NdCl3 (250 g/1) and basic K₂CrO₄ (80 g/1) were used, each about 1 cm thick. The Raman spectrograph has been described elsewhere.⁵ The photographic plates were Eastman 103a-F.

In filling the Raman tube by vacuum transfer, considerable difficulty was encountered because of the presence of traces of water adsorbed on the walls of the system. Even though the system was evacuated with a diffusion pump and carefully flamed, the vapor reacted to form red spots of solid material on the walls. It was found that the procedure suggested by Wilson⁶ completely solved the problem. This involves admitting to the system a vapor which reacts strongly with water to form gaseous products, which are then evacuated before the sample is admitted. Dimethyldichlorosilane was used for this, and there was no further trouble with the sample; it seems to be stable indefinitely in the sealed-off Raman tube.

For the Raman work the sample volume was about 6 ml. VOCl₃ is an extremely intense Raman scatterer, and exposures did not exceed $\frac{1}{2}$ hour. Qualitative depolarization measurements were made by the method of Edsall and Wilson,⁷ with exposures of about two hours.

The experimental results are summarized in Fig. 1 and Table I. The Raman data of Eichhoff and Weigel⁴ are included for comparison. It is seen that the agreement with them is excellent, except that we did not observe the 1035 cm⁻¹ Raman line. It was known from the infrared spectrum that there was a fundamental here, but in the Raman it is overlaid by the Hg 5791 orange line (whose displacement from Hg 5461 is 1043 cm⁻¹). At this stage the paper by Eichhoff and Weigel was found, and since they had observed 1035 by excitation from the orange lines we did not bother to repeat it.

¹ N. V. Sidgwick, The Chemical Elements and Their Compounds

⁽Clarendon Press, Oxford, 1950), Vol. 1, p. 816. ² J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry (Longmans, Green and Company, New York, 1929), Vol. IX, p. 806.

³ K. J. Palmer, J. Am. Chem. Soc. **60**, 2360 (1938). ⁴ H. J. Eichhoff and F. Weigel, Z. anorg. u. allgem. Chem. **275**, 267 (1954).

⁵ F. A. Miller and R. G. Inskeep, J. Chem. Phys. 18, 1519 (1950). Miller, Cousins, and Hannan, *ibid.* 23, 2127 (1955). ⁶ M. K. Wilson, Rev. Sci. Instr. 25, 1130 (1954). ⁷ J. T. Edsall and E. B. Wilson, Jr., J. Chem. Phys. 6, 124

^{(1938).}



FIG. 1. Infrared and Raman spectra of liquid VOCl₃. For the infrared spectrum A = 0.105 mm, B = 0.185 mm, C = 0.024mm cell. The Raman lines are shown by vertical bars.

VIBRATIONAL ANALYSIS

If vanadium oxytrichloride has symmetry C_{3v} , there will be six fundamental frequencies, all of which will be both Raman and infrared active. They are summarized in Table II. Herzberg's conventions are followed throughout.8

Assignment of the Fundamentals

Our choice for the six fundamental frequencies is included in Table II. Four of the six can be easily selected. Because of the intensity and position of the 1035 cm⁻¹ band, there is no doubt that it is due to ν_1 ,

TABLE I. Infrared and Rame	an spectrum of VOCl ₃ .
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	1	Raman				
E and W4 This work		is work	Infrated			
cm ⁻¹	Int.	cm ⁻¹	Int.	cm ⁻¹	Int.	Assignment
130	10	129	s, dp			VE
164	2	165	m, dp			ν:
249	8	248.5	s, dp			28
				358	real?	?
				374	vw	504 - 129 = 375 129 + 249 = 378
409	100	412	vs. D	408	5	V2
				434	w	2
504	4	504	m. b. d b	~502*	VS	24
				622	m	504 + 129 = 633?
				787	m	1035 - 249 = 786
						129 + 249 + 408 = 78
				840	m	Impurity?
				875 ± 5	vw, sh	1035 - 165 = 870
						129 + 249 + 504 = 88
				903	m	1035 - 129 = 906
						408 + 504 = 912
				~924	vw, sh	165 + 249 + 504 = 93
1035	1	b		1035	vs	ν <u>1</u>
				1162	vw	1035 + 129 = 1164
				1199	vw	1035 + 165 = 1200
				1242	vw	$2 \times 504 + 249 = 1257$
				1280	m	$1033 \pm 249 = 1284$
				2061	vw	$\frac{1}{2} \times 1025 - 2070$

w=weak, m=medium, s=strong, v=very, b=broad, sh=shoulder, =polarized, dp=depolarized, ~=approximate.
Too intense to measure accurately.
Overlaid by Hg 5791.

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

the V=O stretch. The polarization of 408 cm^{-1} indicates that it is ν_2 . ν_3 is presumably either 249, 165, or 129, but since none of these three is detectably polarized the choice is not obvious and will be deferred momentarily.

Two of the three degenerate fundamentals are reasonably taken to be 504 and 129 cm⁻¹. There is no doubt about 504 being ν_4 ; ν_6 is expected to be the lowest of the fundamentals, and 129 is the logical choice.

This leaves only 249 and 165 as possibilities for ν_3 and ν_5 . We chose 249 for ν_5 , and 165 for ν_3 for two reasons. (a) If they were reversed it would put 165 and 129 in the same species. It is unlikely that in a molecule this small, a single species would contain two fundamentals so close together. (b) With this choice the frequency of each degenerate vibration is higher than that of its nondegenerate analog—i.e., $\nu_4 > \nu_2$, and $\nu_5 > \nu_3$. This is known empirically to be quite generally the case.

It may be noted that 249 could conceivably be explained as $2 \times 129 = 258$, but we feel that it is too intense for this. Similarly 165 can be explained as 408-249=159. This can be rejected because of the 6 cm⁻¹ discrepancy between the calculated and observed

TABLE II. Fundamental vibrations of VOCl₃.

Species	Activity	No.	Description	VOCl ₃ cm ⁻¹	POCl3 ª cm ⁻¹
<i>a</i> ₁	<i>R(p</i>), ir	1 2 3	V=O stretch V-Cl stretch VCl ₃ deformation	1035 408 165	1290 p 486 p 267 p?
e	<i>R(dp)</i> , ir	4 5 6	V-Cl stretch VCl₃ deformation Cl₃-V-O rocking	504 249 129	581 dp 337 dp 193 dp

See reference 9.

values. For difference tones, there should be agreement within experimental error. Our values and those of Eichhoff and Weigel are identical to within 1 cm^{-1} for each of the three frequencies 408, 249, and 165. Hence the 6 cm⁻¹ difference is larger than the indicated accuracy will allow. Also there is no sum band at 408+249=657, suggesting that the intensity of the corresponding difference band will be low. Actually 165 cm⁻¹ has medium intensity.

These assignments, which were made independently of Eichhoff and Weigel's, agree completely with theirs. They have pointed out that the close analogy to POCl₃ is useful. The fundamentals for POCl₃⁹ are included in Table II for comparison.

Remaining Bands

 C_{3v} symmetry allows any possible combination tone of VOCl₃ to be both Raman and infrared active. Most of the remaining bands can be satisfactorily accounted for, as shown in Table I. Four exceptions are 434, 840, 1242, and 1797, which are not explainable as binary or ternary combinations of the fundamentals. They may be due to a small amount of an impurity.

⁹ M. L. Delwaulle and F. Francois, Compt. rend. 220, 817 (1945).

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 26, NUMBER 2

FEBRUARY, 1957

Reaction Products of γ Picoline and Iodine*

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From the reaction products of γ picoline and iodine two distinct addition compounds have been isolated and studied by chemical, spectroscopic, and x-ray radial distribution methods. The second of these compounds to be isolated is an intermediate in the formation of the first, and is analogous to the addition compound of pyridine and iodine prepared by many workers. The x-ray radial distribution analysis of the first compound showed that the covalent bond in the iodine molecule had been broken, and the corresponding analysis of the second compound showed that the covalent bond was still present. A mechanism has been postulated for the reaction of the second compound with excess γ picoline to form the first compound.

The applicability of the Geiger counter x-ray diffractometer to the radial distribution method is discussed, and the theory for the radial distribution analysis of diffraction data consisting of discrete peaks is presented.

I. INTRODUCTION

CONSIDERABLE body of experimental evidence ${f A}$ has been collected concerning the complexes between pyridine and its homologs with iodine. The nature of these complexes has been the subject of some discussion. The main problem has been to determine whether the interactions between iodine and the organic base are strong enough to break the iodine-iodine bond, leading to ionization, or whether a covalent iodine molecule still exists in the addition compound. Since a knowledge of this distribution of iodine-iodine distances in the solid complex would be sufficient to resolve this problem, it was thought that an x-ray radial distribution analysis would be applicable, rather than a complete crystal structure determination (as suggested by Reid and Mulliken¹), which would be enormously more laborious. Such questions as the relative spatial orientation of the iodine molecule with respect to the organic base are not answered by the radial distribution method, and fall outside the objectives of the present investigation.

The organic base γ picoline was used rather than pyridine because its addition compounds with iodine were found to be more stable. From the γ picolineiodine system it was possible to isolate two distinct compounds, both of which were investigated chemically, spectroscopically, and by the x-ray radial distribution method.

The first of these was a stable, water-soluble, alcoholinsoluble compound, (I), whose analysis corresponded to two moles of γ picoline per mole of iodine.^{2a,b} The apparent anomalous behavior of this compound when compared with the complexes of iodine with the other picolines and with pyridine led to a search for another compound, essentially covalent, corresponding to the well-known solid pyridine-iodine complex reported by many workers.³ Other evidence which pointed to the existence of a second compound was that solutions of iodine in γ picoline do not set solid until several hours after mixing, whereas the changes produced in the absorption frequencies of γ picoline are immediate.^{2b} These changes in spectra are also entirely analogous to those observed in pyridine and the other picolines upon the addition of iodine. The second compound, (II), was

Contribution No. 2097.

¹C. Reid and R. S. Mulliken, J. Am. Chem. Soc. 46, 3869 (1954).

² (a) Glusker, Thompson, and Mulliken, J. Chem. Phys. 21, 1407 (1953). (b) D. L. Glusker and H. W. Thompson, J. Chem. Soc. 1955, 471

³ For example, see M. Chatelet, Compt. rend. 196, 1421 (1933).