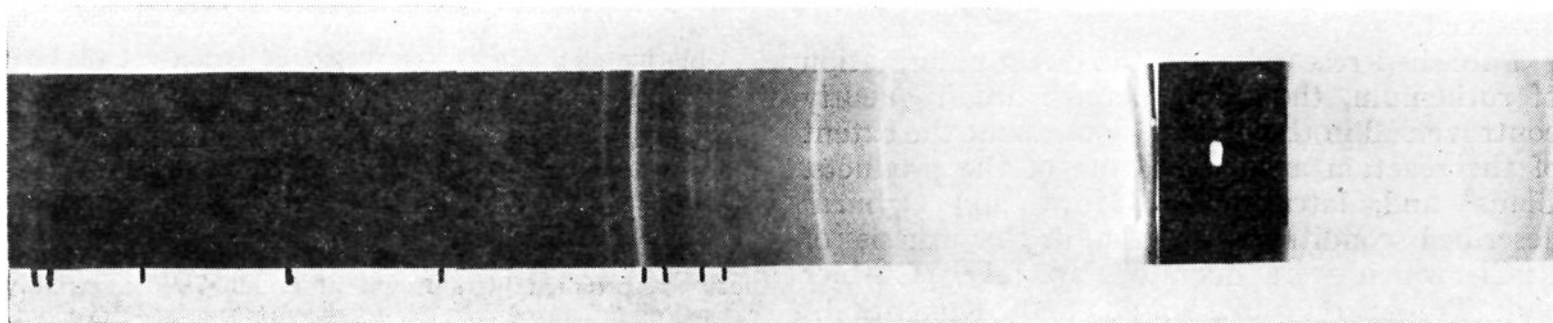
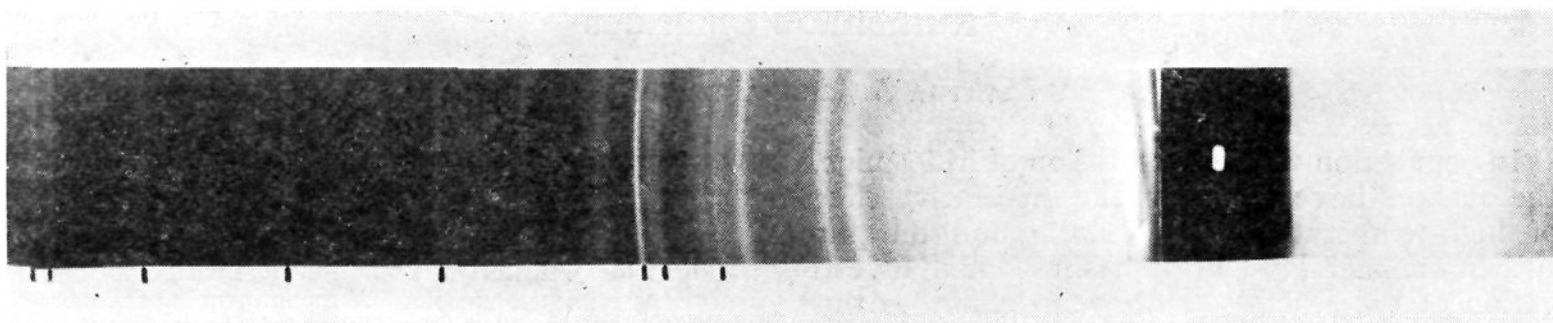


Brown ruthenium trichloride.



Black ruthenium trichloride.

Fig. 1.

reduced to a blue solution by addition of powdered zinc. Absolute ethyl alcohol added to the brown chloride produced a brown liquid which, upon addition of zinc, became green and finally yellow.

Complete conversion of metallic ruthenium to sublimed ruthenium trichloride usually required at least forty-eight hours for a 50-mg. sample, at 700°. Some of the brown trichloride was always obtained, while formation of the black crystals seemed to be favored by conditions which retarded the reaction. Semi-quantitative recovery of ruthenium as sublimate was possible, and the degree of solubility of the product depended on the relative amounts of the two forms of chloride.

Crystal Structure.—Specimens of both brown and black varieties of sublimed ruthenium trichloride were examined by X-ray analysis in the Central Research Laboratory of Canadian Industries, Limited. Figure 1 shows definite and distinctive crystal structures for both materials. The samples were irradiated in the presence of beryllium, the lines of which are indicated.

Acknowledgment.—The authors are indebted to Dr. F. W. Matthews of the Central Research Laboratory, Canadian Industries, Ltd., MacMasterville, Quebec, for the X-ray analyses.

Summary

Ruthenium is completely converted to the trichloride by dry chlorination at 700°. The trichloride sublimed to two different allotropic modifications with widely different properties. The shiny, black form was the more inert, while the brown product was hygroscopic.

Evidence for the presence of the di- or monochloride in incompletely chlorinated residues was inconclusive.

ONTARIO, CANADA

RECEIVED JANUARY 7, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA, AND THE MINNESOTA MINING AND MANUFACTURING Co.]

The Raman and Infrared Spectra of Perfluoropropane¹

BY WALTER F. EDGELL,² H. DEAN MALLORY AND DONOVAN G. WEIBLEN

Octafluoropropane is a compound which has a number of possible industrial applications, among them being refrigeration. Consequently, its thermodynamic properties are of interest. One common method of obtaining this information for the gas phase is to calculate it statistically from a knowledge of the fundamental frequencies of vibration. To these values are added the corrections for the deviation from ideal gas behavior.

(1) Presented before the Symposium on Fluorine Chemistry of the 116th Meeting of the American Chemical Society.

(2) Chemistry Department, Purdue University, Lafayette, Ind.

With the addition of vapor pressure and heat of vaporization data, the basic Mollier diagram can be constructed. In order to provide the basic information for such a calculation for perfluoropropane, its Raman and infrared spectrum has been studied.

Experimental

The octafluoropropane used in this research was prepared electrochemically by the 3M-Simons process.³ The sample was distilled through a 50-plate stainless steel helix

(3) J. H. Simons and co-workers, *J. Electrochem. Soc.*, **95**, 47 (1949).

packed column, the center portion of the cut boiling at -38° being taken. Most of the work on both the Raman and infrared spectrum was done on this sample. Some evidence for a small amount of impurity was obtained from the infrared spectrum. To remove this, a sample prepared as above was passed over cobalt trifluoride at 500° and the product redistilled.⁴ A comparison of the infrared spectrum of this material with the spectra of the most likely contaminants (C_2F_6H , C_2F_6 , C_4F_{10} , etc.), none of which could be detected, indicate that the sample is probably better than 99.7% pure.

The infrared absorption spectrum was recorded, using a Perkin-Elmer Model 12B spectrometer with sodium chloride and potassium bromide prisms. The pressure ranged from 1.5 to 500 mm. in gas cells 10 cm. in length.

The Raman spectrum was obtained in the liquid state at -65° , using a Lane-Wells spectrograph having a camera aperture of F/3.5. The standard Lane-Wells excitation unit was used with currents through the mercury arcs being varied from 10 to 30 amperes in the various runs. Eastman Tri X Panchromatic film was used for the most part. The slit width was varied from 50 to 200 microns. The Raman tube was placed in an unsilvered dewar with plane windows, which replaced the standard filter jacket of the excitation unit. The sample was maintained at -65° by blowing cold, dry air into the dewar. An optically clear sample of C_3F_8 at this temperature was prepared by thoroughly drying the material and slowly distilling it into the Raman tube. When the sample was prepared in this manner, no background was observed on the films even on long exposures when up to 20 amperes were passed through the arc. The general background was very weak even at higher currents and, consequently, no filters were used.

Results

The transmission curves for the infrared spectrum are shown in Fig. 1. The curves have been corrected for the results obtained with the cobalt trifluoride treated sample. The principal bands in the region of the fundamental frequencies removed by this purification were centered at 801,

929 and 1075 cm^{-1} . The band at 929 consisted of a well resolved triplet with peaks at 923, 929 and 936 cm^{-1} . A broad, very weak absorption still persists at 929 cm^{-1} , and is believed to be due to C_3F_8 .

Table I contains the infrared absorption maxima and "shoulders." Relative intensities are designated by the abbreviations vw, w, m, s, vs and vvs, which stand for very weak, weak, medium, strong, very strong and extremely strong, respectively.

The Raman spectrum is listed in Table II. Line strength is given by estimated values of the relative density. Those with density number 6 or greater have been observed excited at least by the mercury lines 4358 and 4046 Å. Besides those listed, weak lines were found at 216, 257, 282, 680 and 723 cm^{-1} if excited by 4358 Å. These are believed to be 316 excited by 4339, 316 by 4348, 339 by 4348, 780 by 4339 and 780 by 4348, respectively.

TABLE II

RAMAN SPECTRUM OF C_3F_8			
ω , cm^{-1}	Est. density	ω , cm^{-1}	Est. density
316	20	929*	2
339	18	965*	2
350	18	1005*	2
382	19	1114*	1
537	10	1151*	2
546	10	1207	12
619	16	1250	8
665	18	1271	6
732	3	1315	3
766	6	1350	14
780	23	1369	17
805	2	1460*	1

TABLE I

INFRARED ABSORPTION MAXIMA OF OCTAFLUOROPROPANE

Wave length, μ	Relative intensities	Wave length, μ	Relative intensities	Wave length, μ	Relative intensities
21.64	m	9.12	m	5.34	m
20.26	vw	8.66	vvs	5.145	m
18.78	vs	8.265	vvs	5.03	w
18.62	vs	7.91	vvs	4.89	m
18.42	vs	7.70	s	4.82	w
16.03	m	7.615	s	4.77	w
15.06	s	7.41	vvs	4.695	w
13.77	vvs	7.195	s	4.52	m
13.68	vvs	6.96	m	4.42	m
13.60	vvs	6.44	m	4.24	m
12.85	s	6.32	m	4.14	m
12.37	w	6.175	w	4.09	m
11.76	w	6.11	w	3.98	m
11.35	w	5.98	m	3.91	m
10.77	w	5.84	w	3.815	m
10.23	vw	5.76	w	3.675	vw
9.94	vvs	5.635	m	3.36	vw
9.69	vs	5.50	m	3.16	vw
				2.725	vw

(4) Thanks are due the members of the Central Research Laboratory, Minnesota Mining and Manufacturing Co., for the preparation and purification of the sample.

All lines except those marked with an asterisk have been observed with the cobalt trifluoride treated sample. Films have not been obtained as densely exposed with the treated sample as with the untreated; the asterisk marked lines, consequently, cannot be said to arise from an impurity with any certainty. As a matter of fact the infrared spectrum shows that at least two correspond to fundamentals while only one, 1114 cm^{-1} , corresponds to no infrared absorption.

Discussion

The maximum symmetry that C_3F_8 could have is that corresponding to the point group C_{2v} . Because of repulsion between the F atoms it is not certain that the equilibrium position has any symmetry elements. In any case, all the fundamental modes of vibration would be non-degenerate and Raman active. All these do not appear in the observed Raman spectrum since twenty-four lines are found while there are twenty-seven fundamentals. Reasonably strong infrared absorption occurs at 462 and 1032 cm^{-1} to which no Raman line is found. However, one cannot conclude that these together yield twenty-six of the fundamentals.

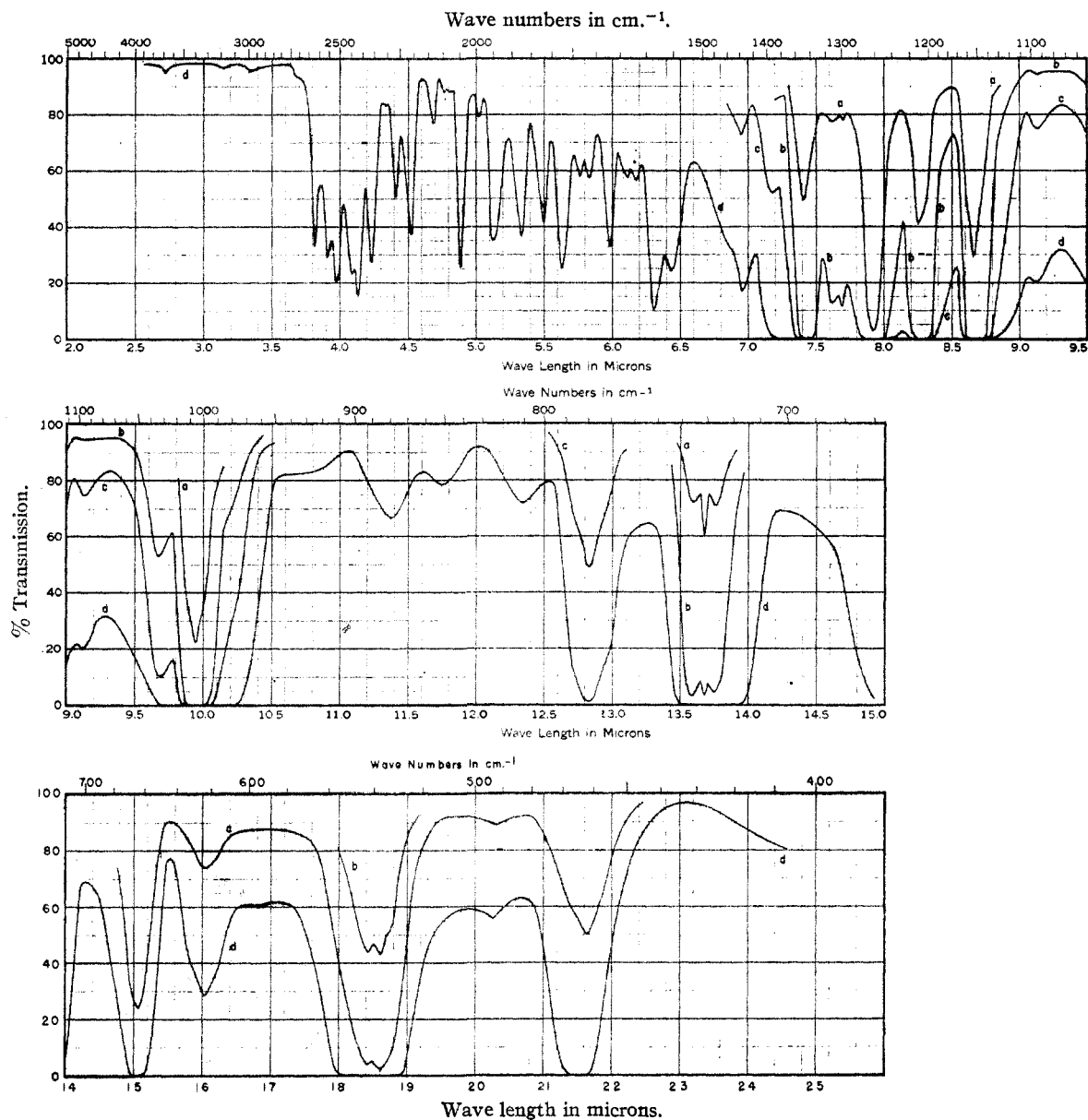


Fig. 1.—Infrared absorption spectrum of octafluoropropane from 2 to 25 μ : cell length, 10 cm.; pressures, a, 1.5, b, 25, c, 100, and d, 500 mm.; temperature, 25°.

It is difficult to predict the character and approximate frequency of the vibrations in this molecule, especially in view of the uncertainty of the effect of the large interaction forces between the fluorine atoms. It would appear, however, that there are more frequencies in the 1000 to 1500 cm^{-1} region than there are fundamentals and the discrepancy increases.

A comparison of the two spectra indicates the following almost surely correspond to fundamental frequencies of vibration: 316, 339, 350, 382, 462, 537, 546, 624, 664, 731, 778, 1006, 1155, 1210, 1250, 1264, 1313, 1350 and 1369 cm^{-1} . To these can probably be added 766, 809 and 1032 cm^{-1} . The remaining five frequencies are uncertain.

It is hoped that work now underway on the force field in certain fluorinated molecules will yield force constants which may be transferred to other molecules with some reliability. If this should prove to be so, it would then be possible to make a reasonable assignment in C_3F_8 by comparing the experimental frequencies with those calculated from these force constants.

A tentative assignment of the observed frequencies suggests that the two torsional vibrations are among those that are missing. In view of the work⁵ on halogenated molecules, a barrier

(5) (a) E. L. Pace and J. G. Aston, *THIS JOURNAL*, **70**, 566 (1948); (b) H. Russel, D. R. V. Golding and D. M. Yost, *ibid.*, **66**, 16 (1944); (c) T. R. Rubin, B. H. Levedahl and D. M. Yost, *ibid.*, **66**, 279 (1944).

height of 3500 calories per mole may be used, in the temperature range of interest, in estimating their thermodynamic contributions from the tables of Pitzer and Gwinn⁶ without introducing an error larger than the other uncertainties. With estimated values for the three remaining frequencies, the thermodynamic properties can be calculated with an accuracy adequate for engineering purposes in the initial or appraisal stages.

Acknowledgment.—One of us (W. F. E.) wishes to thank the Research Corporation for a

(6) K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

grant which made the purchase of the fast Raman spectrograph possible.

Summary

1. The Raman spectrum of C_3F_8 has been obtained in the liquid state at -65° .

2. The infrared spectrum has been obtained at 25° and at pressures ranging from 1.5 to 500 mm.

3. Although it is not now possible to make an accurate assignment of the observed frequencies, it is believed that twenty-two of the twenty-seven fundamentals have been located.

IOWA CITY, IOWA
ST. PAUL, MINN.

RECEIVED JANUARY 9, 1950

[CONTRIBUTION FROM THE OVALTINE RESEARCH LABORATORIES]

The Ultraviolet Absorption Spectra of Some Hydroxynaphthalenes

BY C. DAGLISH

In a preliminary note¹ it was shown that the "apparent vitamin C"² of the walnut was probably a hydrojuglone derivative. The evidence for this was based on the findings that it could be hydrolyzed to juglone, and that its ultraviolet absorption curve showed similarities with those of α -hydrojuglone and the reduced form of acetoxyjuglone. It is now known that this substance is glycosidal in nature with the sugar moiety attached at the 5-position of α -hydrojuglone. Although a full description of its isolation and the determination of its structure will be published in the near future, several points arose during the spectroscopic examination of similar compounds that suggested further examination of the hydroxynaphthalenes in order to correlate, if possible, structure with absorption curves.

Discussion of Results

Naphthalene in 95% ethanol (Fig. 1), showed three well-defined regions of absorption with the values

λ_{\max} , Å., ca.	2200	2500-2900	2950-3200
$\log \epsilon$	5	3.2-3.7	2.3-2.5

Similar curves have been reported for hexane solutions^{3,4} and the three absorbing regions ascribed⁴ to separate states of electronic excitation of the molecule. The presence of these three regions in the curves of most of the simple derivatives examined suggested that absorption was due to the naphthalene molecule as a whole. However the curve was affected both by the nature and the position in the molecule, of the substituent, as previously shown by de Laszlo.⁵

(1) Daglish and Wokes, *Nature*, **162**, 179 (1948).

(2) Wokes, *et al.*, *ibid.*, **162**, 15 (1948).

(3) Morton and de Gouveia, *J. Chem. Soc.*, 916 (1934).

(4) Hirshberg and Jones, *Can. J. Research*, **27**, Sect. B, 437 (1949).

(5) de Laszlo, *Proc. Roy. Soc. (London)*, **A111**, 355 (1926).

Monohydroxynaphthalenes.—Compared with that of naphthalene, the curve of 1-naphthol in ethanol (Fig. 1) showed a general shift to the red end of the spectrum, with an overlapping of the second and third bands, and a loss of the well-defined subsidiary peaks. The 2200-Å. band was also broadened. However, there was not the increase in intensity found for hexane solutions of the alkyl naphthalenes.³ 2-Naphthol (Fig. 1) showed no such general bathochromic effect save in the third region, which showed also a tenfold increase in intensity. This had the effect of splitting the lower intensity portion of the curve into two. This division was seen in almost all of the further substituted 2-naphthols, and was quite characteristic.

Lewis and Calvin⁶ suggested that light was absorbed by polarized forms which contribute to the general resonance structure of the molecule. By suppressing the electron-donating hydroxyl groups by acetylation, diminution of the particular polarized structures responsible for the curves of 1- and 2-naphthols would be expected. The curves in Fig. 3 of the acetoxynaphthalenes show that there was a reversion to the original naphthalene curve, though with less well-defined subsidiary peaks, the 1-derivative being distinguished by less resolution of the low intensity region. In these acetates, the acetyl group also acted as an electron-acceptor, since the curves obtained were almost identical with those of the corresponding sulfonic acids (Fig. 2).

The distinctions between the 1- and 2-derivatives in neutral and acid solutions were again observed in alkaline solution (Figs. 9 and 14). In both derivatives, although there was a further bathochromic shift and a general smoothing of the curve, the characteristic three peaks were present in 2-naphthol but two only in the 1-derivative.

(6) Lewis and Calvin, *Chem. Revs.*, **25**, 273 (1939).