[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Vacuum Ultraviolet Absorption Spectra of Some Halogen Derivatives of Methane. Correlation of the Spectra[1]

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Vacuum ultraviolet absorption spectra of CH_2Cl_2 and $CHCl_3$ were obtained for the first time, under high dispersion. Incomplete measurements of former workers on CCl_4, CCl_2F_2 and CF_4 were amplified and extended to the shortest wave lengths at which significant absorption occurred. A correlation of the electronic energy levels of these compounds, and comparison with previously observed levels of CH_3Cl, suggested that in all molecules containing chlorine the spectra were due to excitation of non-bonding electrons on chlorine. This idea was supported by the fact that Rydberg series observed in CH_2Cl_2 and in CCl_2F_2 converged to about the same limit as was found previously for CH_3Cl. Some of the electronic transitions in CH_2Cl_2 and in CCl_2F_2 were accompanied by vibrational structure, which is given a tentative interpretation. Similarities in the spectra of CH_2F_2 and CF_4 are not apparent and no general conclusions can be drawn. An approximate thermochemical calculation of the ionization potential of CF_4 gave about 14.21 e.v., which was supported by the experimental observations of absorption limit.

The electronic structure of the series of molecules which result from the substitution of the hydrogens of methane by F and Cl furnishes an interesting case for experimental and theoretical investigation. The normal state properties of the molecules are well known.[3] The major part of the electronic spectra of the molecules is in the vacuum ultraviolet region and the majority of previous investigations have been incomplete with respect to wave length region covered and pressure variation of absorbing vapor. However CH_3Cl has been investigated by Price[4] and CH_2F_2 by Wagner and Duncan[5] to the shortest wave lengths at which significant absorption occurs. CF_4 has been incompletely investigated by Moe and Duncan[6] and CCl_4 by Leifson.[7] For CCl_2F_2, CH_2Cl_2 and $CHCl_3$ only long wave limits near 2000 Å. at high pressures have been reported.[8–10] In the present paper results on the electronic absorption spectra of $CHCl_3$, CH_2Cl_2 and CF_2Cl_2 are reported in detail. In addition the spectra of CCl_4 and CF_4 were exextended to shorter wave lengths. Many apparent similarities were found in this group of molecules, especially when the results on CH_3Cl and on CH_2F_2 were included, which will be discussed.

Experimental Details

In order to accommodate other research problems which were in progress, the two vacuum grating spectrographs described in the preceding paper[5] were used at different times in the course of the present work. There was no difference in the results from the two gratings, but where vibrational structure appeared, results were always obtained with the larger spectrograph. The Lyman discharge tube was modified according to a design of Rathenau[11] to allow more precise alignment of the quartz capillary with the optical axis of the spectrograph. The capillary was held by glass wool in a larger glass tube which could be moved by tangent screws. The vapors were introduced directly into the spectrograph at accurately known pressures. The short wave length limit of observation was a little below 500 Å., where the continuous self-absorption of helium from the discharge began to be appreciable. However no significant spectra, only continuous absorption was observed below 1000 Å. in compounds containing Cl and below 800 Å. in compounds containing F. The plates were measured in the usual way, as described in the preceding paper.

Every effort was made to obtain samples which were as pure as possible, and criteria for purity were considered carefully. CCl_4, $CHCl_3$ and CH_2Cl_2 were fractionally distilled in conventional columns, and fractionated further *in vacuo* before and during use. It was necessary to remove the preservative from $CHCl_3$ (Mallinckrodt Reagent) by washing with H_2SO_4, water and drying before fractionation. The compounds CCl_2F_2 and CF_4 presented more difficulty, particularly the latter. These compounds were obtained from the Kinetic Chemicals Division of du Pont. The CF_4, which contained some CHF_3, was fractionated at low temperatures in a Podbielniak column; the middle fraction boiling at −129° was retained. This fraction was refractionated and only the middle fraction was retained for final use. In this case the infrared absorption spectrum appears to furnish a sensitive test for CHF_3, and it could not be detected in the final sample. The sample of CCl_2F_2 showed no impurities which could be detected by infrared absorption. Its boiling point was quite sharp (−29.8°) and further fractionations *in vacuo* are believed to have been effective in removing all interfering impurities.

Experimental Results

The experimental results are shown concisely in Fig. 1, where the observed energy levels are plotted as lines, in wave numbers above the normal states of the molecules. In most cases the positions of the lines correspond to intensity maxima. Vibrational levels associated with a given electronic level are bracketed. The top line in each case marks the beginning of strong continuous absorption, beyond which no transitions can be resolved. Experimental data on CH_3Cl[4] and CH_2F_2[5] have been included. Description of the spectra of individual molecules follows.

CCl_2F_2.—Preliminary results were obtained by Dr. L. H. Jones[12] and P. Wagner.[13] They found

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[2] Eastman Kodak Company Fellow, 1953–1954. Part of a dissertation presented to the Faculty of the Graduate School of the University of Rochester in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

[3] A recent summary of spectroscopic data for this series is found in NRL Report 3567. "Spectroscopic Properties of Fluorocarbons and Hydrocarbons," D. C. Smith, J. Rud Nielsen, L. H. Berryman, H. H. Claassen and R. L. Hudson, Naval Research Laboratory, Washington, D. C., September 15, 1949. See also G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945.

[4] W. C. Price, *J. Chem. Phys.*, **4**, 539 (1936).

[5] P. Wagner and A. B. F. Duncan, THIS JOURNAL, **77**, 2609 (1955).

[6] G. Moe and A. B. F. Duncan, *ibid.*, **74**, 3140 (1952).

[7] S. Leifson, *Astrophysical J.*, **63**, 73 (1926).

[8] A. Henrici, *Z. Physik*, **77**, 35 (1932). Long wave limits for CCl_4, CH_2Cl_2, $CHCl_3$.

[9] Y. P. Parti and R. Samuel, *Proc. Phys. Soc. London*, **49**, 568 (1937). Long wave limits for $CHCl_3$ and CCl_4.

[10] J. R. Lacher, L. E. Hummel, E. F. Bohnfalk and J. D. Park, THIS JOURNAL, **72**, 5486 (1950). Limits CCl_4, $CHCl_3$, CH_2Cl_2, CF_2Cl_2.

[11] G. Rathenau, *Z. Physik*, **87**, 32 (1933).

[12] Postdoctoral Fellow, University of Rochester, 1951–1952.

[13] Paul Wagner, Thesis, University of Rochester, 1952.

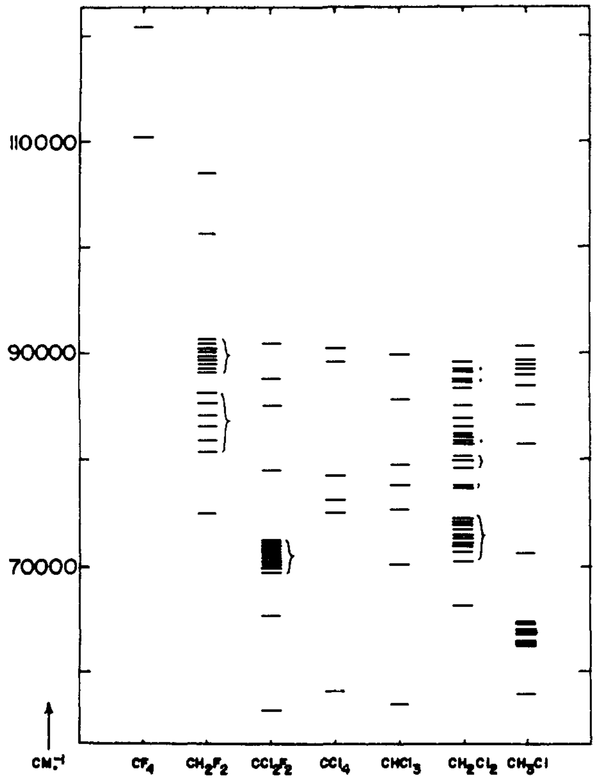


Fig. 1.—Energy level diagram of substituted methanes.

two regions of continuous absorption, with intensity maxima at about 79082 and at 57000 cm.$^{-1}$, and a transition at about 70000 cm.$^{-1}$ with vibrational structure, which was interpreted as excitation of the Cl–C–Cl bending frequency in the upper electronic state. The present measurements extend the above results in several ways. The longest wave length region was resolved into two transitions with maxima at 56465 and at 65402 cm.$^{-1}$. The origin of the transition with vibrational structure was located more precisely at 69443 cm.$^{-1}$. A single progression of fourteen vibrational bands was found. At higher frequencies three transitions with maxima at 79189, 84631 and 87207 cm.$^{-1}$ were found, the last two for the first time. At 0.008 mm. pressure the long wave length limit of continuous absorption is at about 1105 Å. With increasing pressure the limit moves toward the red until at 0.4 mm. (2 meter column) the limit is at 1970 Å. (50760 cm.$^{-1}$).

CF_4.—The spectrum was investigated over the pressure range 0.001–0.370 mm. in the one meter spectrograph and 0.001–0.500 mm. in the two meter spectrograph. Only one electronic transition, with an intensity maximum at 110500 cm.$^{-1}$ was found. This transition was observed first at 0.002 mm. pressure in a four meter column. At 0.015 mm. it extended from 106400 to 118300 cm.$^{-1}$, and was separated from the high frequency limit at 119200 cm.$^{-1}$ by a short region of transparency. At 0.500 mm. pressure, absorption is continuous to 1050 Å. (95200 cm.$^{-1}$). No indication would be obtained at the highest pressures of the absorption previously reported[6] at longer wave lengths. In view of improved methods of purification used in the present work, it is probable that the longer wave length absorption is due to an impurity.

CCl_4.—The spectrum was studied over the pressure range 0.001 to 0.500 mm. in the one meter spectrograph. Five electronic transitions were found, all of which were regions of continuous absorption. The strongest absorption occurred at about 76900 cm.$^{-1}$ at 0.006 mm. pressure. At higher pressures two transitions appeared in this region with maxima at 76900 and at 78490 cm.$^{-1}$, and another maximum at 70390 cm.$^{-1}$. These three transitions partly overlapped. Another strong maximum at 89130 cm.$^{-1}$ appeared first at 0.006 mm. At longer wave lengths a very broad, weak band with a center apparently at about 57000 cm.$^{-1}$ was found, which corresponds probably to the transition reported by Leifson.[7] At the lowest pressure the limit of continuous absorption was at about 1106 Å., while at the highest pressure continuous absorption extended up to about 1964 Å.

$CHCl_3$.—The spectrum was investigated in the one meter spectrograph throughout the pressure range 0.001 to 0.100 mm. The strongest transition with a maximum at 85616 cm.$^{-1}$ appeared first at 0.008 mm. pressure. At 0.014 mm. four additional intensity maxima at 79491, 77640, 75245 and 70182 cm.$^{-1}$ appeared, with some overlapping between the first three of these absorption regions. Finally a weak region of absorption, with an intensity maximum at about 57140 cm.$^{-1}$ appears at about 0.075 mm. At the lowest pressure the long wave length limit of continuous absorption is at about 1112 Å. (89936 cm.$^{-1}$). At 0.100 mm. the limit cannot be located because of the broad, weak absorption, but appears to lie just below 2000 Å. In view of the similarity of the spectra of $CHCl_3$ and other molecules of this series, it is considered very doubtful that an additional electronic transition at longer wave lengths would appear at higher pressures.

There appears to be no doubt that the maxima at 57140, 75245 and 85616 cm.$^{-1}$ represent separate electronic transitions. There is some doubt, however, whether 77640 and 79491 cm.$^{-1}$ are separate electronic transitions or are vibrational members associated with the 75245 cm.$^{-1}$ transition. If the latter interpretation is the correct one, then the excited vibration can be only $\nu_1(a_1)$, C–H stretching, since the separation of the maxima are 2397 and 1851 cm.$^{-1}$, respectively. The large second difference indicates a large anharmonic factor, which may be an argument against the interpretation in terms of vibrational structure.

CH_2Cl_2.—The spectrum of this molecule was investigated throughout the pressure range of 0.001 to 0.100 on the two meter spectrograph and of 0.001 to 0.725 mm. on the one meter spectrograph. Eleven electronic transitions were found, and several of these contained vibrational structure. With the exception of the broad maximum at 66270 cm.$^{-1}$ the absorption regions were fairly sharp and well defined. The strongest maxima at 83020, 82444 and 77294 cm.$^{-1}$ became apparent at 0.006 mm. pressure. At a slightly higher pressure a transition with vibrational structure appeared with an origin at 70593 cm.$^{-1}$. At a pressure of 0.010 all of the complicated absorption shown in Fig. 2 appeared.

At higher pressures the longer wave length diffuse regions appeared and at the highest pressure of 0.725 mm. the long wave limit extended to 2065 Å. (48426 cm.$^{-1}$). At the lowest pressure of 0.004 mm. this limit was situated at about 1129 Å. (88573 cm.$^{-1}$). A detailed discussion of these transitions will be given in the following section.

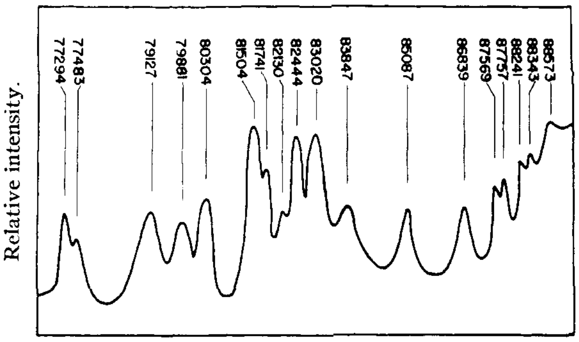
Discussion of Electronic Transitions.—Consideration of the spectra of all the molecules studied shows that similarities are most apparent in the spectra of the molecules which contain chlorine. These similarities will be discussed first. To make the discussion more nearly complete, it will be necessary to include the spectrum of CH_3Cl,[4] which was not reinvestigated in the present work.

The lowest energy transition in CH_3Cl, $CHCl_3$, CCl_4 and CF_2Cl_2 is a broad region of continuous absorption. The maxima for the four molecules are, respectively, at about 57900, 57143, 57000 and 56465 cm.$^{-1}$. There is very probably a weak transition in CH_2F_2 at about the same frequency which is hidden by the rapid decrease of frequency of the red edge of the 66269 cm.$^{-1}$ transition with pressure. In the methyl halides this transition is known generally as the A band, and it has been attributed by Mulliken[14] to excitation from a nonbonding halogen orbital to an anti-bonding carbon–halogen orbital. The similarity in appearance and in position of this transition in the other molecules suggests strongly that the same type of excitation is involved.

Other similarities occur in the high energy transitions of these molecules, although some differences in detail appear. The spectrum of CH_3Cl in the high energy region consists of a series of sharp bands converging to two ionization potentials at 11.17 and 11.25 e.v. The series fit the formula

$$\nu_n = \left\{\begin{matrix} 90500 \\ 91180 \end{matrix}\right\} - R/(n + 0.50)^2 \qquad n = 2, 3, \ldots \qquad (1)$$

The higher members of the series overlap and are obscured somewhat by continuous absorption of other transitions. There is thus a high frequency limit of continuous absorption, at or a little below the ionization potentials. In the other molecules, where Rydberg series cannot be established so definitely, the high frequency limit provides a lower limit for the ionization potential. The small variation in this limit among the molecules studied here gives some indication. Electron impact values have been reported for CH_3Cl (11.46 ± 0.04 e.v.),[15] (11.3 ± 0.3 e.v.)[16]; CCl_4 (11.0 ± 1.0 e.v.)[17]; CF_2Cl_2 (11.7 ± 0.5 e.v.).[17] The yield of positive molecular ions is usually very low for the above molecules; other processes of dissociation or electron absorption appear to be more probable. No data could be found for CH_2Cl_2 and $CHCl_3$.



Frequency (cm)$^{1-}$. →.

Fig. 2.—High energy transitions in CH_2Cl_2.

Some conclusions may be drawn from the spectrum of CH_2Cl_2 relative to its ionization potential. The levels of CH_2Cl_2, apart from details, are practically coincident with the levels of CH_3Cl. A detailed comparison is given in Table I (see also Fig. 1), where R_n refers to the frequency ν_n in equation 1, of Price's first series in CH_3Cl with our results with CH_2Cl_2 and other molecules. A tracing of the high energy part of the CH_2Cl_2 spectrum is shown in Fig. 2. Except at R_6 there are levels in CH_2Cl_2 which correspond everywhere to levels of CH_3Cl. There appear to be two transitions in CH_2Cl_2 in the expected region of R_6 at 87569 and 88241 cm.$^{-1}$, each accompanied by a vibrational transition. The average of the above frequencies corresponds exactly to R_6 in CH_3Cl. R_8 and R_9 are very weak but are fairly sharp in CH_2Cl_2. They are not shown in Fig. 2, but were measured easily on the plates. R_2 is followed by a series of vibrational transitions which will be discussed in the following section. R_3 is also accompanied by two vibrational transitions. It may be noted that Price's diagram[18] shows some transitions in CH_3Cl at energies higher than R_3, which may be vibrational transitions associated with lower Rydberg series members, or separate electronic transitions. No measurements of these transitions were given by Price. In addition to the Rydberg transitions in CH_2Cl_2, which are represented adequately by

TABLE I

ELECTRONIC TRANSITIONS (IN CM.$^{-1}$) IN SUBSTITUTED METHANES

Designation of transition	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4	CF_2Cl_2
A	57900	. . .	57140	57000	56465
B,C	62500				
	65360	66269	. . .	. . .	65402
R_2	71110	70593	70182	70390	69443
X_1			75245		
X_2		77294	77640	76900	
X_2				78490	
X_3		79127	79491		79189
R_3	81480	81504	. . .	. . .	. . .
X_4		82444	Undesignated transitions		
R_4	85110	85087	85616		84631
R_5	86870	86839			87207
		87569			
R_6	87900	(Av. 87905)			
		88241			
R_7	88550	88573			
R_8	88970	89009			
R_9	89300	89292		89130	

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[14] R. S. Mulliken, *Phys. Rev.*, **47**, 413 (1935); **61**, 277 (1942).

[15] J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952).

[16] H. Branson and C. Smith, THIS JOURNAL, **75**, 4133 (1953).

[17] J. T. Tate and R. F. Baker, *Phys. Rev.*, **53**, 683 (1938).

[18] W. C. Price, *J. Chem. Phys.*, **4**, **547** (1936); Fig. 2, p. 550.

Price's formula (equation 1) for CH_3Cl, there are additional transitions X_2, X_3, X_4 for which no interpretation can be offered at the present time. No two of these transitions can belong to the same Rydberg series, for any such series would converge far below the other observed series. Also the X_n transitions have a relatively high intensity and the high members of series to which they belonged must be observed. X_2 is accompanied by one, and X_3 and X_4 are accompanied each by two vibrational transitions.

While the lowest state of CH_3Cl^+ is ^2E in C_{3v} symmetry, the lowest states of $CH_2Cl_2^+$ formed by the removal of the same non-bonding electron will be $^2A_1$, $^2B_1$ or $^2B_2$ in C_{2v} symmetry, with $^2A_1$ probably the lowest. The separation between these terms may be considerably greater than between the doublet components of ^2E, and only one Rydberg series is expected to be observed which is analogous to the CH_3Cl series.

The only similarities in the spectra of $CHCl_3$, CH_4 and CF_2Cl_2 to CH_2Cl_2 and CH_3Cl are the appearance at about the same wave lengths of A and R_2 transitions, and a B,C transition in CF_2Cl_2. Several transitions in the 71000–80000 cm.$^{-1}$ region may be analogous to transitions in CH_2Cl_2. Above 80000 cm.$^{-1}$ transitions in $CHCl_3$, CCl_4 and CF_2Cl_2 occur at irregular positions and cannot be identified with Rydberg series members. The transition at 89127 cm.$^{-1}$ in CCl_4 is particularly difficult to understand in view of the broad region of high transparency below this level. It cannot be a high Rydberg series member, say R_9, since no lower members R_3 . . . R_8 are found, and the other transitions could not conceal them.

Discussion of Vibrational Structure.—The R_2 transitions in CF_2Cl_2 and in CH_2Cl_2 are accompanied by considerable vibrational structure. In CF_2Cl_2 this structure consists of a single progression of fourteen evenly spaced bands, separated by approximately 256 cm.$^{-1}$. This frequency is interpreted as the excited state value of $\nu_4(a_1)$, the symmetrical Cl–C–Cl deformation vibration which has a normal state value of 260 cm.$^{-1}$. As judged from pressure appearance measurements, the intensity maximum lies toward the high frequency end of the transition near 71780 cm.$^{-1}$. The vibrational members and assignments are given in Table II.

TABLE II

VIBRATIONAL STRUCTURE OF THE 69443 CM.$^{-1}$ ELECTRONIC TRANSITION IN CF_2Cl_2

Transition (in cm.$^{-1}$)	Assignment	Transition (in cm.$^{-1}$)	Assignment
69443	R_2	71245	$R_2 + 7\nu_4$
69700	$R_2 + \nu_4$	71511	$R_2 + 8\nu_4$
69970	$R_2 + 2\nu_4$	71780	$R_2 + 9\nu_4$
70232	$R_2 + 3\nu_4$	72006	$R_2 + 10\nu_4$
70482	$R_2 + 4\nu_4$	72262	$R_2 + 11\nu_4$
70742	$R_2 + 5\nu_4$	72515	$R_2 + 12\nu_4$
71006	$R_2 + 6\nu_4$	72787	$R_2 + 13\nu_4$

The vibrational structure of the R_2 transition at 70593 cm.$^{-1}$ in CH_2Cl_2 is somewhat more complicated, but the principal excited state frequency appears to have an average value of about 670 cm.$^{-1}$. This frequency is interpreted as $\nu_3(a_1)$, which is probably C–Cl stretching. The corresponding normal state frequency is 704 cm.$^{-1}$. In addition there appears one quantum of an excited state frequency 1617 cm.$^{-1}$, which is tentatively interpreted as $\nu_2(a_1)$ which has a normal state value of 1429 cm.$^{-1}$ and probably represents –C–H bending. The details of the structure are shown in Table III.

TABLE III

VIBRATIONAL STRUCTURE OF THE 70593 CM.$^{-1}$ ELECTRONIC TRANSITION IN CH_2Cl_2

Transition (in cm.$^{-1}$)	Assignment	Transition (in cm.$^{-1}$)	Assignment
70593	R_2	73256	$R_2 + 4\nu_3$
71223	$R_2 + \nu_3$	73591	$R_2 + \nu_2 + 2\nu_3$
71877	$R_2 + 2\nu_3$	73922	$R_2 + 5\nu_3$
72210	$R_2 + \nu_2$	74239	$R_2 + \nu_2 + 3\nu_3$
72619	$R_2 + 3\nu_3$	74590	$R_2 + 6\nu_3$
72927	$R_2 + \nu_2 + \nu_3$		

Although the detailed assignment of the vibrational transitions may be in error, it is clear nevertheless that vibrations confined largely to the Cl–C–Cl part of both molecules tend to be set up in analogous electronic transitions. As was pointed out in the preceding paper on CH_2F_2, an analogous transition in that molecule at 80856 cm.$^{-1}$ showed mainly excited state vibrations which were confined to the F–C–F part of the molecule. It may be significant that this is the lowest energy transition in CH_2F_2 which shows structure and may actually be the R_2 transition in this molecule.

The vibrational structure of the transitions in CH_2Cl_2 and in CF_2Cl_2 suggests strongly that the electronic excitation is partly localized in the CCl_2 part of the molecule. This is in harmony with other evidence for excitation of a non-bonding $3p\pi$(Cl) electron.

The vibrational excitation connected with the X_2, X_3 and X_4 and R_3 levels of CH_2Cl_2 may be mentioned briefly. The excited state vibrations appear to be ν_2, ν_3 and ν_4, all of which appear with only one quantum at most. A tentative interpretation of this structure is given in Table IV.

TABLE IV

VIBRATIONAL TRANSITIONS ASSOCIATED WITH HIGH ENERGY ELECTRONIC TRANSITIONS IN CH_2Cl_2

Transition (in cm.$^{-1}$)	Designation	Transition (in cm.$^{-1}$)	Designation
77294	X_2	82130	$R_3 + \nu_3$
77483	$X_2 + \nu_4$	82444	X_4
79127	X_3	83020	$X_4 + \nu_3$
79881	$X_3 + \nu_3$	83847	$X_4 + \nu_2$
80304	$X_3 + \nu_2$	87757	$87569 + \nu_4$
81504	R_3	88343	$88241 + \nu_4$
81741	$R_3 + \nu_4$		

Discussion of CF_4.—The spectrum of CF_4 shows only one resolved transition with a maximum at about 110500 cm.$^{-1}$, which is only slightly below the limit of continuous absorption at about 120900 cm.$^{-1}$. The reported electron impact value for the ionization potential is reported to be 17.8 e.v.[19] (143700 cm.$^{-1}$). Since the limit of continuous absorption in most other cases is not so far below the ionization potential, and the ion yield of CF_4^+ is

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(19) L. Goldstein, *Ann. Phys.*, **9**, 723 (1938).

very low,[20] it is possible that the impact value is in error. We have made an independent estimation of the ionization potential from thermochemical data. The method follows essentially the calculation made for SF_6.[21] The beginning of continuous absorption (14.99 e.v.) is interpreted as dissociation into $CF_3^+ + F^-$. Adding the electron affinity (EA_F) of F, we have

$$CF_4(g) = CF_3^+(g) + F(g) + e^- - (14.99 + EA_F) \quad (2)$$

The energy of dissociation of CF_4 into its elements is[22,23]

$$CF_4(g) = C(g) + 4F(g) - (14.65 \text{ e.v.} + 2D_{F_2}) \quad (3)$$

where D_{F_2} is the heat of dissociation of F_2. For breaking a single bond it is assumed that

$$CF_4(g) = CF_3(g) + F(g) - (14.65 \text{ e.v.} + 2D_{F_2})/4 \quad (4)$$

It is also assumed that the energy of the process

$$CF_4^+(g) = CF_3^+(g) + F(g) - (14.65 \text{ e.v.} + 2D_{F_2})/4 \quad (5)$$

is the same as in process (4). On subtracting (5) from (2) we obtain for the desired ionization potential

$$CF_4(g) = CF_4^+ + e^- - 11.33 - (EA_F - D_{F_2}/2) \quad (6)$$

The difference ($EA_F - D_{F_2}/2$) is obtained from a cycle which involves theoretically computed crystal energies and other thermochemical data.[23] Using a value of 2.88 e.v. for this difference[21] the ionization potential is about equal to 14.21 e.v., which is in more satisfactory agreement with the limit of continuous absorption.

ROCHESTER, N. Y.

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[20] V. H. Dibeler and F. L. Mohler, *J. Research Natl. Bur. Standards*, **40**, 25 (1948).

[21] Ta-Kong Liu, G. Moe and A. B. F. Duncan, *J. Chem. Phys.*, **19**, 71 (1951).

[22] H. von Wartenberg, *Nachr. Akad. Wiss. Goettingen, Math.-phys. Klasse*, 57 (1946); W. A. Chupka and M. G. Inghram, *J. Chem. Phys.*, **22**, 1472 (1954).

[23] J. E. Mayer and L. Helmholz, *Z. Physik*, **75**, 19 (1932).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Free Energy, Enthalpy and Entropy of Dissociation of Some Perchlorates in Ethylene Chloride and Ethylidene Chloride

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From electrolytic conductance measurements at each of the four temperatures, 20, 25, 30 and 35° the values of $\widetilde{\Delta F}^\circ$, $\widetilde{\Delta H}^\circ$ and $\widetilde{\Delta S}^\circ$, accompanying the dissociation (at 25°) of nine systematically substituted phenyltrimethylammonium perchlorates in ethylene chloride and of six of these in ethylidene chloride, have been determined. The dielectric constant of ethylidene chloride at each of these four temperatures has been determined. Values of ΔH° and ΔS° have been calculated from relations derived (1) from the Bjerrum–Fuoss expression for the dissociation constant, K, and (2) from an expression for K obtained by assuming that only those oppositely charged ions which are in contact constitute associated ion-pairs. The latter simplified treatment is shown to give values of $\widetilde{\Delta H}^\circ$ and $\widetilde{\Delta S}^\circ$ in better agreement with the experimental values. Interpretations (1) of the uniformly negative values of ΔH° and ΔS° in both solvents, and (2) of the uniformly greater K values in ethylene chloride are presented.

In an investigation[2] of the effect of systematically varying the electrical asymmetry of the cations of nine substituted phenyltrimethylammonium perchlorates on the dissociation constant (K value at 25°) in ethylene chloride, the dissociation constant of one of the salts, namely, *o*-chlorophenyltrimethylammonium perchlorate was determined in ethylidene chloride. The K value of this salt in ethylidene chloride was found to be much less than (about one-tenth) its value in ethylene chloride. This was unexpected since the difference in the accepted values of the dielectric constants of these two liquids is not great enough to cause such a large difference in the K values (D_{25° of ethylene chloride, 10.23, and of ethylidene chloride, 10.00[3]).

In 1950 preliminary K values of two other of the nine salts (the *o*- and the *p*-methoxyphenyl salts) were determined[4] and found to be from one-seventh to one-tenth their respective values in ethylene chloride. An interpretation of these results was proposed. More recently Healey and Martell[5] found that a number of tetraalkylammonium picrates and a perchlorate have considerably lower K values in ethylidene chloride (from one-fifth to one-tenth less) than in ethylene chloride.

Additional information regarding the thermodynamic behavior of salts in these two solvents seems desirable. In this investigation the K values of the nine perchlorates, previously used,[2] were determined from conductance measurements in ethylene chloride at 20, 25, 30 and 35°, and those of six of the perchlorates (which were sufficiently soluble) in ethylidene chloride. The standard changes in enthalpy and entropy (at 25°) accompanying dissociation in each of the solvents were derived therefrom. The values of $\widetilde{\Delta H}^\circ$ and $\widetilde{\Delta S}^\circ$ are calculated (a) from the theoretical expression for K obtained by Bjerrum[6] and Fuoss and Kraus,[7] and (b) from an expression for K obtained from a simpler model. An interpretation of the sign of the values of ΔH° and ΔS° is given.

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[1] Polychemicals Dept., E. I. du Pont de Nemours and Co., Wilmington, Del.

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