

## The InfraRed and Raman Spectra of Chlorine Trifluoride

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TABLE I.

$L =$	$4p$	$4p+1$	$4p+2$	$4p+3$
$\Gamma_1$	$p+1$	$p+1$	$p+1$	$p+1$
$\Gamma_2$	$p$	$p$	$p$	$p$
$\Gamma_3$	$p$	$p$	$p+1$	$p+1$
$\Gamma_4$	$p$	$p$	$p+1$	$p+1$
$\Gamma_5$	$2p$	$2p+1$	$2p+1$	$2p+2$

In general, if the  $z$  axis is chosen normal to the surface, any state whose degeneracy in the interior is due to the equivalence of the  $z$  and  $x$  (and/or  $y$ ) axes, will be split in the surface. For example, in a hydrogen-like ion, the state  $n=2$  is split into two states in a field of cubic symmetry, namely a  $2-s$  state and a doubly degenerate  $2-p$  state.<sup>1</sup> In the surface of a cubic crystal, where the  $z$  axis is no longer equivalent to the other axes, the  $p$  state undergoes a further splitting into a single level ( $m=0$ ) and a degenerate level ( $m=\pm 1$ ). It will be true in general that all levels belonging to states for which  $m=0$  are single. Moreover, these states have the same symmetry properties in the surface, namely they are all totally symmetric with respect to all symmetry operations for the surface field. Therefore, it is possible that all these states mix; in that case, the matrix elements of the  $z$  component of the dipole moment between two states with different principal quantum number but with (apparently) the same azimuthal quantum number will not vanish and transitions with  $\Delta l=0$  become possible, in particular  $s-s$  transitions.

This can be generalized for the case of atoms and ions with any number of electrons by applying the group theoretical method developed by Bethe<sup>1</sup> to the energy levels of an ion in the surface. In the surface the highest possible symmetry is  $C_{nv}$ , where  $n=2, 3, 4$ , or  $6$ . For all values of  $L$  and all integral values of  $J$  one can show that the totally symmetric representation is contained at least once in the  $2L+1$ ,  $2J+1$ -dimensional representation of the three-dimensional rotation-reflection group. The procedure is exactly the same as Bethe's. Because Bethe does not give the characters for the classes consisting of reflections, they will be given here. Since all planes of reflection pass through the  $z$  axis, which is considered normal to the surface, the effect of a reflection in one of these planes is merely the replacement of a right-handed coordinate system by a left-handed system. Therefore,  $P_1^m(\cos\theta)e^{im\varphi}$  will go over into  $P_1^m(\cos\theta)e^{-im\varphi}$ , but  $P_1^0(\cos\theta)$  will go over into itself. Therefore, the characters of the symmetry classes which consist of these reflections are all  $+1$ . Once these characters have been obtained it is simple to reduce the  $2L+1$ , the  $2J+1$ -dimensional representations of the rotation-reflection group. If, for example, the symmetry of the crystal is cubic, the 100-plane has  $C_{4v}$ -symmetry. This group has five symmetry classes and eight elements. Therefore, there are four one-dimensional representations and one two-dimensional representation. Following Bethe<sup>1</sup> these shall be called  $\Gamma_1$ ,  $\Gamma_2$ ,  $\Gamma_3$ ,  $\Gamma_4$ , and  $\Gamma_5$ .  $\Gamma_1$  is the totally symmetric representation. In Table I the frequency of occurrence of these irreducible representations has been given. In this table,  $p$  may be any positive integer.

This result is remarkable in one respect. Although the  $C_{4v}$  and  $D_4$  groups are isomorphic, the  $2L+1$ -dimensional representations reduce differently in the two groups.

Physically it is clear that all states which have axial symmetry about the  $z$  axis, i.e., states for which  $M_L$  or  $M_J$  are zero, and which do not depend on  $\varphi$ , are symmetric with respect to all operations of the groups  $C_{nv}$ . It follows that the matrix elements connecting these states will in general not vanish. Mixing of states with different  $L$  (or  $J$ ) values will, therefore, be more pronounced for the surface than for the inside of a crystal. In this case, the matrix elements of the  $z$  components of the dipole moments between these states will in general not vanish. Consequently, a breakdown of the

selection rules for  $L$  or  $J$  in the surface will take place to a considerably higher extent than in the inside of a crystal. In particular the transition  $J=0 \rightarrow 0$  may become allowed. A quantitative investigation of the change in the absolute transition probabilities has not yet been made.

The application of this to the absorption spectra of rare earth ions in crystals is evident. It reopens the question of the cause of the additional lines observed in reflection over that found in absorption, which was originally reported by Freed and Spedding.<sup>2</sup> The explanation proposed by Spedding and Baer<sup>3</sup> that the additional lines were due to a "filter effect" has been generally accepted. Unquestionably both effects play a role. At present, it is not possible to evaluate the relative importance of each.

<sup>1</sup> H. Bethe, Ann. d. Physik 3, 133 (1929).

<sup>2</sup> S. Freed and F. H. Spedding, Phys. Rev. 39, 212 (1930).

<sup>3</sup> F. H. Spedding and R. S. Baer, Phys. Rev. 39, 948 (1932).

### The Infra-Red and Raman Spectra of Chlorine Trifluoride\*

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February 28, 1949

THE Raman spectrum of liquid chlorine trifluoride and the infra-red absorption spectrum of the gas in the 2 to 25  $\mu$ -region have been investigated. Material from two commercial sources was used. Purification by fractional distillation may not have been entirely successful, and it is possible that some of the infra-red bands currently listed may be due to impurities.

The infra-red data from 2 to 15  $\mu$  were obtained with a Perkin-Elmer Model 12B automatic recording spectrometer with NaCl optics. The 15 to 25  $\mu$ -region was mapped with a KBr prism in a similar spectrometer. Fluorothene<sup>1</sup> absorption cells with NaCl or KBr windows as described in another letter<sup>2</sup> were used in the infra-red investigation. A fluorothene Raman tube suitable for handling highly corrosive materials was developed for this work. Technical details on the use of fluorothene in infra-red and Raman spectroscopy are scheduled for publication in the near future.

The Raman spectrum of the liquid was obtained with a Lane Wells Spectrograph, Type 40-A, and Excitation Unit Type 60-A. Because of absorption of  $\text{ClF}_3$  in the 4047A and 4358A regions, it was necessary to use Hg 5461A as the exciting line. Exposure times were of the order of several hours. Raman tubes were supported vertically in an unsilvered Dewar flask and were cooled by a stream of nitrogen which had passed through a coil immersed in liquid nitrogen. The sample was maintained at approximately  $-60^\circ\text{C}$ . The filter used was an aqueous solution of neodymium nitrate contained in an outer jacket of the Dewar flask.

TABLE I. Infra-red and Raman frequencies in the  $\text{ClF}_3$  spectrum.

Infra-red bands (gas) $\text{cm}^{-1}$	Raman lines (liquid) $\text{cm}^{-1}$
485 m.s.	321 v.w.
540 m.s.	424 v.w.
630 m.w.	502 v.s.
710 v.s.	514 v.s.
741 m.s.	
759 m.s.	753 m.s.
848 v.w.	
888 v.w.	
952 v.w.	
1028 v.w.	
1110 m.s.	
1235 m.s.	
1265 m.s.	

The results of both Raman and infra-red measurements are given in Table I. Intensities are specified as v.s., s., m.s., w., and v.w., representing very strong, strong, medium, weak, or very weak, respectively. The presence of five Raman frequencies is surprising since the expected pyramidal or planar models should have four and three Raman active frequencies, respectively. These considerations suggest either an unsymmetrical form or more probably association in the liquid state. Studies of  $\text{ClF}_3$  in the gaseous phase are planned for the near future. A more complete account of the experimental details and an analysis of the results will be published later.

We wish to express appreciation to Professor A. H. Nielsen of the University of Tennessee, and Dr. J. S. Kirby-Smith of the K-25 Research Laboratories for assistance and direction in this investigation, and to the Department of Physics at the University of Tennessee for the use of the infra-red spectrometer which made possible the study of the 15 to 25  $\mu$ -region.

\* This document is based on work performed for the AEC by Carbide and Carbon Chemicals Corporation, Oak Ridge, Tennessee.

\*\* Now at the Ohio State University, Columbus, Ohio.

<sup>1</sup> Polytrifluorochloroethylene.

<sup>2</sup> P. J. H. Woltz and E. A. Jones, *J. Chem. Phys.* 17, 502 (1949).

### The Infra-Red and Raman Spectra of Carbonyl Fluoride\*

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February 28, 1949

THIS letter is a preliminary report on the investigation of the infra-red and Raman spectra of carbonyl fluoride. The samples thus far studied were prepared in this laboratory and may contain some impurities. Further samples are being prepared, and investigation of possible impurity or decomposition product content is being made.

The infra-red spectrum of gaseous  $\text{F}_2\text{CO}$  was recorded on a Perkin-Elmer Model 12B infra-red spectrometer. A NaCl prism was used to scan the 2 to 15  $\mu$ -region. The measurements from 15 to 25  $\mu$  were made with a similar spectrometer having KBr optics. Considerable difficulty was encountered in handling the  $\text{F}_2\text{CO}$  because of its great instability. An absorption cell 10 cm long and 4 cm inside diameter was constructed of fluorothene<sup>1</sup> plastic and found satisfactory. Windows of NaCl and KBr were sealed to this cell with fluorothene-W. A transfer system for filling the cell was constructed of copper and fluorothene. Observations were made with a variety of gas pressures ranging from 2 mm for the most intense absorption to 760 mm for the weakest. A number of different slit widths was used for each band in order to get the optimum resolution. Sixteen absorption bands were observed, six of which were considerably more intense than the rest. These have been named the fundamentals, though definite assignment of the normal modes has not yet been made.

For the Raman spectrum measurements on liquid  $\text{F}_2\text{CO}$ , a specially designed Raman tube<sup>2</sup> of fluorothene was used to contain the sample. The  $\text{F}_2\text{CO}$  was maintained in the liquid state by blowing a stream of nitrogen, which had been passed through a coil immersed in liquid nitrogen, over the Raman tube. A Lane-Wells Spectrograph No. 40-A was employed for these measurements. The exciting radiation was the 4358Å line of Hg filtered through a jacket containing DuPont Rhodamine 5 GDN Extra plus *p*-nitrotoluene in ethyl alcohol. The exposure times ranged up to three hours.

Table I lists the infra-red bands and Raman lines observed up to the present time. The molecule is taken to be planar, of the same type as  $\text{H}_2\text{CO}$  and  $\text{Cl}_2\text{CO}$ . This model has six fundamental modes, all of which are Raman and infra-red

TABLE I. Infra-red and Raman frequencies in the spectrum of carbonyl fluoride.

Infra-red bands (gas) cm <sup>-1</sup>		Raman lines (liquid) cm <sup>-1</sup>
4120 v.w.	1941* v.s.	1944 v.w.
3882 w.		1909 m.
3696 v.w.		
3403 v.w.	1249* v.s.	1238 v.w.
3163 v.w.	965* s.	965 s.
2887 w.	775* s.	771 v.w.
2682 v.w.	626* m.s.	620 m.
2472 w.	584* m.s.	571 w.

active. Those bands marked with an asterisk are believed to be the fundamental vibrations. An estimate of the intensities designated by v.s., s., m.s., w., v.w., meaning very strong, strong, moderately strong, weak, very weak, respectively, is also given in the table. With the exception of the band at 626 cm<sup>-1</sup>, which appears to have doublet structure, the fundamental bands have well defined *P*, *Q*, and *R* branches. An attempt to make vibrational analysis of these data is in progress.

We are indebted to the Physics Department at the University of Tennessee for the use of the infra-red spectrometer with KBr optics and to Mr. Wilbur Simon for the preparation of the samples used in this investigation. A detailed report on the preparation and handling of carbonyl fluoride will be published elsewhere. Grateful acknowledgment is made of the assistance and direction given by Professor A. H. Nielsen of the University of Tennessee and by Dr. J. S. Kirby-Smith of the K-25 Research Laboratories.

\* This document is based on work performed for the AEC by Carbide and Carbon Chemicals Corporation, Oak Ridge, Tennessee.

<sup>1</sup> Polytrifluorochloroethylene.

<sup>2</sup> Jones, Parkinson, and Murray, *J. Chem. Phys.* 17, 501 (1949).

### The Exchange of $\text{Ag}^+$ Ions between Aqueous Solutions and Surfaces of Metallic Silver

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March 2, 1949

THE exchange of  $\text{Ag}^+$  ions between solutions of silver nitrate and surfaces of metallic silver is being studied with a radioactive isotope ( $\text{Ag}^{110}$ , half-life 225 days). On the basis of measured areas, etched and polished surfaces of annealed silver foil exchange with 0.1N  $\text{AgNO}_3$  solutions to depths of about 10 and 100 atomic layers, respectively. Inactive crystalline (etched) surfaces pick up their maximum activity from stirred oxygen-free active (40,000 counts per minute per ml) solutions in a matter of seconds; under the same conditions polished surfaces acquire about 90 percent of their final equilibrium activity in 24 hours. Polished surfaces made active in this way, and immersed in non-active solutions, lose about 25 percent of their activity at roughly the same rate as they had acquired it. No decrease in the remaining activity occurs during a week's stirring in the non-active solution. Under similar conditions, crystalline surfaces appear to retain their entire activity which, however, is so low (10–20 counts above background) that the experimental results are highly uncertain.

Etched surfaces of unannealed foil, or of annealed foil that has been cold-worked in various ways, show visually distinct patterns of crystalline and "non-crystalline" metal. The latter appears as light smooth streaks or patches (depending on how the specimen was cold-worked) on the uniformly dark gray crystalline metal. (The term non-crystalline is used here to designate the condition sometimes referred to as the Beilby