

The InfraRed and Raman Spectra of Chlorine Monofluoride

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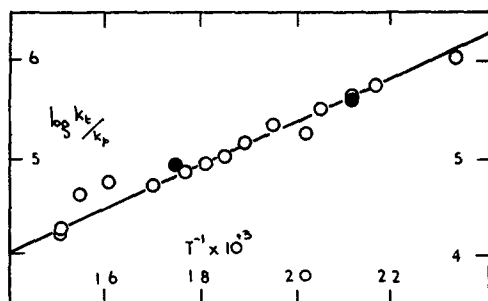


FIG. 1.

tion energy and also for deviations from the square root law at low light intensities. From their sector experiments, Haden and Rice obtain a value for the rate constant of such a chain termination, which, if used to correct the reported activation energies, not only raises the first two, but also Leermakers', to 10.4 kcal./

TABLE I.

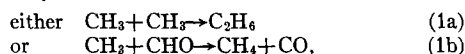
	Frequency factors (mole ⁻¹ cc sec. ⁻¹)	
	k_p	k_t
Present work	8.0×10^{12}	5.3×10^{13}
Haden and Rice	7.4×10^{12}	2.7×10^{14}
Collision numbers	8.3×10^{12}	9.0×10^{13}

mole (± 0.2). Thus, combining activation energies from the steady and the intermittent reactions, we obtain

$$E_p = 10.4 \pm 1.0 \text{ kcal./mole and } E_t = 0 \pm 2.0 \text{ kcal./mole.}$$

Using Rollefson and Grahame's absolute values of quantum yield at 200°C, and putting $k_t = 0.2$, values for the frequency factors for k_p and k_t may be obtained and compared with the collision numbers. Table I also includes Haden and Rice's stated values, they having used Gorin's⁶ $k_t = 0.7$, Rollefson and Grahame's quantum yield at 200°C, and Leermakers' activation energy.

Thus the termination reaction, which must be a bimolecular association, probably



has little or no activation energy. Furthermore, contrary to suggestions⁷ by Steacie, Darwent, and Trost, and by Bamford and Dewar, that such radical reactions having low activation energies will usually also have low collision efficiencies of the order 10^{-5} – 10^{-6} , it appears that whichever radical association is here involved has a normal frequency factor. This may well be an argument in favor of (1b), where two products are formed.

This work will be published in greater detail elsewhere when the parallel investigation of higher aldehydes is complete.

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³ G. K. Rollefson and D. C. Grahame, *J. Chem. Phys.* **8**, 98 (1940).

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The Infra-Red and Raman Spectra of Chlorine Monofluoride*

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THE infra-red spectrum of gaseous chlorine monofluoride has been observed from 2–15 μ and the Raman spectrum obtained in the liquid state. Studies were made on the material pre-

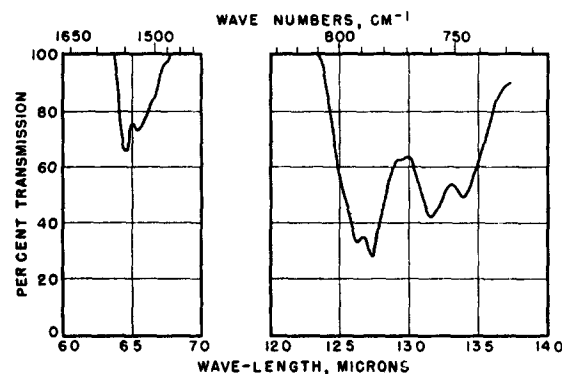


FIG. 1. Infra-red spectrum of chlorine monofluoride.

pared by three methods: (a) fractional distillation from a cylinder of commercial ClF_3 , in which appreciable quantities of ClF exist as an impurity; (b) combination of suitable quantities of ClF_3 and Cl_2 at elevated temperatures;¹ (c) direct combination of F_2 and Cl_2 .^{2,3}

The infra-red spectrum was studied using a Perkin-Elmer Model 12B spectrometer equipped with rocksalt optics. The absorption cells were 10 cm in length and were machined from fluorothene⁴ bar stock. The optical windows were sealed to the cell by means of a chemically resistant sealing wax (fluorothene-W) of the same chemical constitution as fluorothene, but of lower molecular weight. The rocksalt windows were attacked slowly by the gas at low pressures but at elevated pressures (e.g., $\frac{3}{4}$ atmos.) the reaction rate was considerably increased. This attack alters the infra-red transmission of the windows and results in several specific absorption bands associated with a corrosive film or other surface changes. No gaseous reaction products with detectable infra-red absorption were formed. Measurements on evacuated cells before and after corrosion by ClF have shown that these window bands do not fall in the region of the ClF absorption.

The Raman studies were made in a fluorothene tube which was connected to a copper transfer system. The liquid ClF was condensed into a Raman tube mounted vertically in an unsilvered Dewar and maintained at approximately -120°C by a stream of cooled nitrogen. The Raman spectrum was obtained with a Lane-Wells spectrograph and irradiation unit. The 5460 Å Hg line was used for excitation as ClF condenses to a yellow liquid which absorbs in the 4047 and 4358 Å regions. Exposure times were of the order of two hours. The filter used consisted of a combination of a solution of neodymium nitrate plus a Wratten filter 57A wrapped around the fluorothene tube.

The fundamental infra-red absorption band of ClF is shown in Fig. 1. The fundamental has its center at 772 cm^{-1} . Typical of diatomic molecules it displays *P* and *R* branches but no *Q* branch. In this case, both the *P* and *R* branches are doublets. This is attributed to the two isotopic forms, Cl^{35}F and Cl^{37}F .

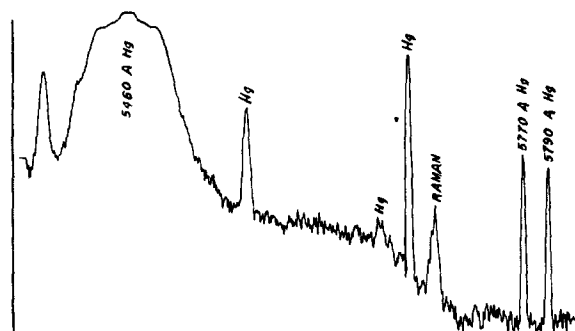


FIG. 2. Raman spectrum of chlorine monofluoride.

The electronic spectrum of chlorine monofluoride has been investigated by Wahrhaftig⁵ and Schmitz and Schumacher.⁶ From a value for ω_e and $X_{e\omega_e}$ given by these authors, the fundamental is predicted to fall at 773.4 cm⁻¹ and at 772.4 cm⁻¹, respectively. Both are in good agreement with the observed position.

The first overtone falls in a region of strong water vapor absorption at 6.26 μ , which has hampered the study of the band. Using a 10-cm cell filled to a pressure of $\frac{2}{3}$ atmos., a band centered at 1535 cm⁻¹ has been observed. This is 8 cm⁻¹ higher than the position predicted from the electronic spectrum, but is probably within the experimental error introduced by water vapor absorption.

Figure 2 shows a microphotometer tracing of the Raman spectrum of liquid ClF. A single line is observed at a shift of 758 cm⁻¹. This is to be compared to the value 772 cm⁻¹ for the fundamental of the gas. Attempts to resolve the line to show the isotope effect have been unsuccessful.

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

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⁶ See reference 1, p. 359.

Note on the Derivation of the Frequency Spectrum of a Crystal from Specific Heat Measurements

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December 5, 1949

THE portion of the specific heat of a solid which is due to lattice vibrations is given by

$$C_v(T) = 3R \int_0^\infty E(h\nu/kT) \rho(\nu) d\nu, \quad (1)$$

where $E(x) = x^2 e^x / (e^x - 1)^2$ and $\rho(\nu) d\nu$ is the number of modes of vibration in the frequency range ν to $\nu + d\nu$. Equation (1) has usually been used to calculate $C_v(T)$ on the basis of a more or less reasonable assumption concerning the frequency spectrum $\rho(\nu)$. It would be of great interest to calculate $\rho(\nu)$ from experimental values of $C_v(T)$. Montroll¹ has given a method by which this problem can be formally solved, but the solution involves gamma- and zeta-functions of a complex argument, which have not yet been tabulated, with laborious numerical integration.

One of us (J.P.S.) has devised a much less laborious method. Let $pkT/h = \tau$, $p\nu = t$, $C_v(T) = \gamma(\tau)$, $\rho(\nu) = g(t)$, where p is an arbitrary constant. Let also $E(x)$ be expanded in powers of e^x . Equation (1) becomes

$$\tau^2 \gamma(\tau) = (3R/p) \sum_{n=1}^{\infty} n \int_0^\infty t^2 g(t) e^{-n t / \tau} dt. \quad (2)$$

Let

$$t^2 g(t) = (2p/\pi) \sum_{m=1}^{\infty} a_m (1 - \cos mt) / m, \quad (3)$$

which is chosen because the Laplace transform has a convenient form. We then obtain

$$\gamma(\tau) = 3R \sum_{m=1}^{\infty} a_m (\coth m\pi\tau - 1/m\pi\tau). \quad (4)$$

In order that $\gamma(\tau)$ may represent the specific heat of a solid, it must satisfy the following asymptotic conditions. For large values of τ , $\gamma(\tau) \rightarrow 3R$, therefore $\sum a_m = 1$. As $\tau \rightarrow 0$ the specific heat approaches zero as $A\tau^3$, where A is an experimental constant.

Therefore $\sum m a_m = 0$ and $\sum m^3 a_m = (15A/R)(h/\pi p k)^3$. The arbitrary constant p is chosen so as to make the important values of τ lie within a tractable range. Then it is possible, using at most six terms of the series, to make the function (4) agree very well with any specific heat which is due only to lattice vibrations, and which therefore increases monotonously. Finally the frequency spectrum can be determined by means of Eq. (3).

An attempt has been made to apply this method to bismuth, which has no transitions below 300°K and has a negligible electronic specific heat,² but which evidently has a vibration spectrum very different from that of an elastic continuum. The experimental curve was constructed from measurements by Keesom and van den Ende³ below 12°K, Armstrong and Grayson-Smith⁴ from 14° to 22°K, and Anderson⁵ above 60°K. These were combined by plotting a smooth curve of the apparent Debye Θ as a function of T .

There was no difficulty in fitting the smoothed curve of C_v with a function of the form (4), and hence of deriving a function $\rho(\nu)$. The derived frequency spectrum showed a steep double maximum at frequencies which dominate in determining the specific heat around 50°K, where two sets of data join. However, the result proved to be extremely sensitive to details of the specific heat curve in the region where dC_v/dT is large. A slight change in the manner of smoothing the data made the two maxima coalesce into a single, much less marked maximum. This disappointing result is clearly intrinsic to the problem, and is not due to using only a finite number of terms, because $\rho(\nu)$ is unique for a given fitted curve $\gamma(\tau)$. Montroll's method must therefore give the same result for the same smoothed curves, with the same sensitivity to a small change in the smoothing.

The conclusion is that the mathematical problem of inverting Eq. (1) can be solved with a reasonable amount of labor, but that no physical meaning can be attached to the result unless the original experimental data have a higher degree of internal consistency than any at present available. To obtain any information on crystal vibrations in this way it will be necessary to have accurate specific heat measurements, made on the same sample by the same method, throughout the range 2° to 300°K. We have been unable to find a single suitable example.

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On the Assignment of the Triplet-Singlet Emission of Benzene

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December 7, 1949

CALCULATIONS have been made upon the triplet states of benzene in a non-empirical approximation¹ taking account of configuration interaction² between configurations based on molecular orbital wave functions. The results agree with the valence-bond theory³ and the single-configuration molecular orbital theory⁴ in making the $^3B_{1u}$ state the lowest of the triplets, lower than the $^3B_{2u}$ state by 2.5 ev in this calculation. There is thus an unusual measure of agreement between the theoretical methods on the identity of this lowest triplet state, comparable only with the agreement there is between them that the lowest singlet state is $^1A_{1g}$.

However, Shull's observation⁵ that active origins in the triplet-singlet emission of benzene are provided by b_{2g} as well as e_{2g} vibrations has been interpreted by Shull, and by McClure,⁶ to mean that the triplet state concerned (presumably the lowest triplet state) has some $^1B_{1u}$ character; and further, using selection rules analogous to those for intercombinations in diatomic molecules, McClure⁶ has deduced from this that the triplet state must