

The InfraRed and Raman Spectra of Carbonyl Fluoride

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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 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 μ -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.

¹ Polytrifluorochloroethylene.

² 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 F_2CO was recorded on a Perkin-Elmer Model 12B infra-red spectrometer. A NaCl prism was used to scan the 2 to 15 μ -region. The measurements from 15 to 25 μ were made with a similar spectrometer having KBr optics. Considerable difficulty was encountered in handling the F_2CO because of its great instability. An absorption cell 10 cm long and 4 cm inside diameter was constructed of fluorothene¹ 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 F_2CO , a specially designed Raman tube² of fluorothene was used to contain the sample. The F_2CO 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 4358 Å 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 H_2CO and Cl_2CO . 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 ⁻¹ | | Raman lines (liquid) cm ⁻¹ |
|---|------------|--|
| 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⁻¹, 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.

¹ Polytrifluorochloroethylene.

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

The Exchange of Ag⁺ Ions between Aqueous Solutions and Surfaces of Metallic Silver

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March 2, 1949

THE exchange of Ag⁺ ions between solutions of silver nitrate and surfaces of metallic silver is being studied with a radioactive isotope (Ag¹¹⁰, half-life 225 days). On the basis of measured areas, etched and polished surfaces of annealed silver foil exchange with 0.1N AgNO₃ 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

or polish layer, the vitreous, amorphous, or cold-worked state, etc.) Such "mixed" surfaces, although they may be largely crystalline, pick up activities commensurate with those acquired by highly polished surfaces (100–200 counts per min. per cm²), and give autoradiographs showing that this activity is largely confined to the crystalline areas. This means that crystalline silver, which by itself shows little tendency to exchange with ions in solution, receives a deposit of metal when it is mixed with non-crystalline silver. This must be the result of an electrolytic action in which ions enter the solution from the anodic worked areas and deposit from solution on the cathodic crystalline surface. However, many attempts to increase the activity take-up of an etched annealed foil by connecting it electrically with a polished foil in the same solution have been fruitless. It would seem that the potential differences involved are so small that they are effectively short-circuited by imperfections in the polish layer.

The fact that polished surfaces slowly acquire a partially removable activity and that considerable activity is picked up by the smooth anodic areas of a mixed surface suggests to the writers that two exchange mechanisms are involved. One of these, the electrochemical, discussed above, accounts for the greater part of the activity acquired by the crystalline areas of a mixed surface. The other, kinetic in nature, is responsible for the activity taken up by polished surfaces and the anodic non-crystalline areas of cold-worked specimens. The enhanced reactivity and solvent properties of metals brought about by polishing and cold-working are well known, and it is probable that such surfaces would take part in exchanges that are impossible for crystals. Preliminary experiments on the pre-treatment of surfaces in non-active solutions indicate that it is possible to separate these two effects. Other tracer experiments on corrosion of metals, the autoradiographic measurement of small potentials, and the phenomena of cold-working are in progress. Details are being published in the Canadian Journal of Research.

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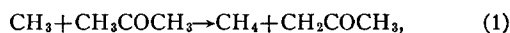
Note on Steric Factors for Some Reactions Involving Free Radicals*

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March 21, 1949

FOR purposes of possible comparison with experimental results from this Laboratory to be reported later, we have calculated steric factors for several reactions involving free radicals, using the theory of absolute reaction rates of Eyring and others.

I. An approximate calculation for the reaction,



leads to $P = 2 \times 10^{-4}$ (the accuracy is such that the possible range is about $6 \times 10^{-4} - 6 \times 10^{-5}$). It is probably not worth while to give the details of the calculation, but we might indicate the general features. We write, in the usual notation,

$$k = \kappa(kT/h)(F^\ddagger/F_A F_B) \exp(-E_0/kT), \quad (2)$$

$$= f(T) \exp(-E_0/kT). \quad (3)$$

We define the experimental activation energy E_{exp} by

$$E_{\text{exp}} = kT^2(d \ln k/dT) \quad (4a)$$

$$= E_0 + kT^2(d \ln f/dT). \quad (4b)$$

The steric factor P is not a fundamental quantity in the theory of absolute reaction rates. However, one can obtain a value

for P by comparing the collision theory expression

$$k = PZ \exp(-E/kT), \quad E = E_{\text{exp}} - \frac{1}{2}kT, \quad (5)$$

with Eq. (3), using Eq. (4b) for E_{exp} . This gives

$$P = \frac{f(T)e^{-1}}{Z \exp[-T(d \ln f/dT)]}. \quad (6)$$

Z is the collision number.

Thus P can be calculated, without knowing the activation energy (either E_0 or E), by an approximate treatment of the geometry, vibrational frequencies, moments of inertia, and internal rotations of the activated complex and the reactants. Because the individual factors in the vibrational partition functions are not much greater than unity, the calculation is fortunately not very sensitive to the vibrational assignment. We took $\kappa = \frac{1}{2}$ here because of the probability of the existence of a potential basin. Whether the mean molecular diameter in Z is taken from the estimated geometry of the activated complex or from an estimate of the kinetic theory, collision diameter turns out to make no appreciable difference in this case.

This type of calculation was suggested by the discussions of Glasstone, Laidler, and Eyring¹ (pp. 16–25) and Kistiakowsky and Ransom.²

II. Eyring, Gorin, and co-workers have given a treatment³ of free radical and atomic association reactions (e.g., $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$) in which a crucial role is played by the rotational energy in determining the activated complex. In this treatment the activated complex turns out to correspond to relatively large interatomic or inter-radical distances. This allows, to a good approximation, considerable cancellation in and simplification of the expression for the absolute reaction rate. The rather general results for any reaction of this type is

$$k = \frac{\kappa 2^{11/6} \pi^{\frac{1}{2}} \Gamma(\frac{3}{2}) \beta^{\frac{1}{2}} (kT)^{1/6}}{\sigma \mu^{\frac{1}{2}}}, \quad (7)$$

where σ is the symmetry number, and μ is the reduced mass of the activated complex considered as a diatomic molecule. The potential of intermolecular force is assumed to have the form $-\beta/r^6$, which should be adequate for the large values of r of interest here.

One way to test Eq. (7) is to deduce a steric factor for comparison with experiment. Using Eqs. (4a), (5), and (7), together with

$$Z = D^2/\sigma(8\pi kT/\mu)^{\frac{1}{2}}, \quad (8)$$

where D is the mean molecular diameter, one finds

$$P = \frac{\kappa \Gamma(\frac{3}{2}) \left(\frac{2\beta}{ekT}\right)^{\frac{1}{2}}}{D^2}. \quad (9)$$

In comparing P from Eq. (9) with P deduced from experimental data, one should use the same value of D in both cases.⁴

For the association of two methyl radicals, we estimate⁵ $\beta = 1.475 \times 10^{-23}$ erg-cm,⁶ and for the kinetic theory collision diameter,⁶ $D = 3.5\text{\AA}$ (at 120°C). At 120°C, this gives, from Eq. (9), $P = 1.39\kappa$.

As has been pointed out,³ the neglected hindered rotation of the two methyl radicals in the activated complex, owing to their interaction, will reduce the above values of P by a factor of perhaps two or three.

In the expression $P = 1.39\kappa$, it is quite possible that κ is much less than unity. If deactivation of the associated molecule by collision occurs in every case before redissociation, $\kappa = 1$. A high foreign gas pressure and a long lifetime of the associated molecule tend to make $\kappa \rightarrow 1$. There has already been some discussion (but no definite conclusions) using classical mechanics,^{7,8} of the increase in lifetime to be expected as a result of the possibility of distributing the energy originally belonging to the reaction coordinate among the various vibrational modes. This effect might well lead to $\kappa \approx 1$ for sufficiently complicated cases (e.g., $\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5$), but of