

## The InfraRed and Raman Spectra of COCIF

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explained by the positive charge on the N atom inhibiting the resonance. Hypsochromic shifts of about 10~20  $m\mu$  are noticed in the transition from diphenyl to monophenyl derivatives. However, this effect cannot be accounted for by the simple scheme indicated above.

Applying the electron gas model<sup>2</sup> as a very crude approximation to these molecules, we obtain  $\lambda_{1,calc}$  340  $m\mu$  and 430  $m\mu$  for the simple diphenyl-benzylidene and the monophenyl-cinnamylidene derivatives, respectively. The coincidence of the former value with the experimental 336  $m\mu$  is rather too good, as the electron gas model assumes complete resonance between the two extreme structures (as obtains in a symmetrical cyanine ion), which is not the case in our molecules.

<sup>1</sup>First prepared by T. Tsumaki, Bull. Chem. Soc. Japan 6, 1 (1931), *ibid.* 7, 48 (1932).

<sup>2</sup>H. Kuhn, J. Chem. Phys. 17, 1198 (1949).

## The Raman Spectra of Ethylchlorosilanes

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June 29, 1950

RECENTLY T. Shimanouchi, I. Tsuchiya, and Y. Mikawa<sup>1</sup> have observed the Raman spectra of methylchlorosilanes and calculated the normal vibrations of these tetrahedral molecules using the Urey-Bradley field. Consulting their results we have tentatively assigned the skeletal frequencies of ethylchlorosilanes, assuming ethyl groups as one particle.

The Raman spectra of tetrachlorosilane and tetraethylsilane have been reported by several investigators.<sup>2</sup> We have measured the Raman spectra of ethyltrichlorosilane, diethyldichlorosilane,

## The Infra-Red and Raman Spectra of COCIF

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June 26, 1950

THE infra-red spectrum of gaseous carbonyl chlorofluoride and the Raman spectrum of the liquid have been investigated. Table I lists the frequencies of the observed infra-red bands and Raman lines.

TABLE I. Infra-red and Raman frequencies of COCIF.

Infra-red bands (gas) $cm^{-1}$	Raman lines (liquid) $cm^{-1}$	Assignment
415	410	$\nu_6$
501	506	$\nu_2$
665	665	$\nu_2$
776	765	$\nu_1$
910		$\nu_2 + \nu_6$
1004		$2\nu_3$
1095	1085	$\nu_4$
1164		$\nu_3 + \nu_6$
1182		$\nu_1 + \nu_6$
1330		$2\nu_6$
1508		$\nu_1 + \nu_6$
1867	1832	$\nu_2$
	1858	$\nu_1 + \nu_4$
2063		$2\nu_1 + 2\nu_4$
2179		$2\nu_4$
2647		$\nu_1 + \nu_2$
3743		$2\nu_2$

COCIF is probably a planar molecule belonging to the point group  $C_s$ . This model has six non-degenerate vibrations all of which are Raman and infra-red active. Six fairly strong bands observed in the infra-red spectrum were found to be in agreement with six Raman lines and consequently have been designated as the fundamentals of the molecule. The assignments of the overtone and combination bands given in column 3 appear to be reasonable on the basis of these fundamentals. The infra-red bands at 665, 776, and 1095  $cm^{-1}$  have  $P$ ,  $Q$ , and  $R$  structure and the 501  $cm^{-1}$  band appears to be a doublet at this resolving power. The contour of the 410  $cm^{-1}$  band could not be determined because it occurs near the limit of the KBr region. Two Raman lines separated by 26  $cm^{-1}$  were observed in the  $C=O$  region at 1832 and 1858  $cm^{-1}$ . This doubling can be attributed to a Fermi resonance between  $\nu_2$  and the combination band  $\nu_1 + \nu_4$ . As the selection rules do not in this case forbid the occurrence of either of these bands in the infra-red spectrum, this region was studied under high resolution. Two bands with a separation of approximately 20  $cm^{-1}$  were observed in good agreement with the Raman lines.

A more detailed analysis of this molecule will be reported later.

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

TABLE I. Raman spectra of ethylchlorosilanes ( $cm^{-1}$ ).

Modes of vibration $\tau(Si-C)^*$	$SiCl_4$	$C_2H_5SiCl_3$	$(C_2H_5)_2SiCl_2$	$(C_2H_5)_3SiCl$	$(C_2H_5)_4Si$
$\delta(Si-Cl)$					
$\delta(Si-C_2H_5)$					
$\delta(C-C)$					
$\nu(Si-Cl)$					
$\nu(Si-C_2H_5)$					
$\nu(C-C)$					
$\delta(C-H)$					
$\nu(C-H)$					

\*  $\tau$  denotes the internal rotation around the axis of  $Si-C$  bond

and triethylchlorosilane. The ethyltrichlorosilane (b.p. 97.5°C) and diethyldichlorosilane (b.p. 128.9°C) used were prepared by the direct reaction of  $C_2H_5Cl$  upon silicon metal, and triethylchlorosilane (b.p. 146°C) by Grignard reagent upon diethyldichlorosilane, purified by careful fractional distillation, and confirmed by the analysis of chlorine content. The results for these compounds together with the data available for the two compounds  $SiCl_4$  and  $Si(C_2H_5)_4$  are given in Table I. Taking into account the result obtained for methylchlorosilanes, we have assigned the observed lines as shown in Table I, where  $A$  denotes totally symmetric,  $B$  antisymmetric,  $E$  twofold degenerate, and  $F$  threefold degenerate vibrations of the tetrahedral molecule, respectively. Thus it is seen that the Raman spectra of ethylchlorosilanes provide with another typical example of a sequence of  $XY_4 \rightarrow XZ_4$ .<sup>3</sup>

- <sup>1</sup> Shimanouchi, Tsuchiya, and Mikawa, *J. Chem. Phys.* **18**, 1356 (1950).  
<sup>2</sup> J. F. Anderson, *J. Chem. Phys.* **4**, 161 (1936).  
<sup>3</sup> Lecomte, Volklinger, and Tchakirian, *Comptes Rendus* **204**, 1927 (1937).

### On the Time Lag in the Precipitation of Ice by Silver Iodide Crystals

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 July 20, 1950

IN a paper by H. Reiss<sup>1</sup> the time lag in the precipitation of ice by silver iodide, as described by B. Vonnegut<sup>2</sup>, is ascribed to the time factor in precipitation on particles below the critical size. It seems to the writer that there is another possibility, not mentioned by H. Reiss or B. Vonnegut (the latter favors the deposition of silver iodide particles on the walls); this is the coagulation of the cloud of silver iodide particles, so that initially deposition occurs on the large particles and then, as coagulation proceeds, more large particles appear and act as immediate nuclei. Of course the simple Gibbs theory cannot apply to the large particles, which will probably be aggregates and not single particles; this will be true even at the start of the experiment with a polydisperse cloud. However, it might well be expected that an aggregate would be more likely to act as a nucleus the larger the size.

- <sup>1</sup> H. Reiss, *J. Chem. Phys.* **18**, 529 (1950).  
<sup>2</sup> B. Vonnegut, *Chem. Rev.* **44**, 277 (1949).

### Adsorption of Carbon Dioxide on Reduced Nickel

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 July 24, 1950

THE present author recently investigated the adsorption of carbon monoxide<sup>1</sup> on platinum catalyst statistically mechanically with special reference to its state on platinum, concluding that it was dissociated into statistically independent atoms. Developing the method further, carbon dioxide adsorption was not investigated on reduced nickel.

Adsorption isotherms of carbon dioxide are derived, introducing a set of functions,  $p$ ,  $q$ , and  $\theta$  (due to Horiuti<sup>2</sup>), respectively, for the undissociative adsorption,  $CO_2 \rightleftharpoons CO_2(a)$ , the partially dissociative one,  $CO_2 \rightleftharpoons CO(a) + O(a)$  and for the completely dissociative one into three statistically independent atoms,  $CO_2 \rightleftharpoons C(a) + O(a) + O(a)$  as

$$\frac{\theta}{1-\theta} = \frac{q^{CO_2(a)}}{p^{CO_2}} \quad (1.1)$$

$$\left(\frac{\theta}{1-2\theta}\right)^2 = \frac{q^{CO(a)}q^{O(a)}}{p^{CO_2}} \quad (1.2)$$

$$\left(\frac{\theta}{1-3\theta}\right)^3 = \frac{q^{C(a)}q^{O(a)}q^{O(a)}}{p^{CO_2}} \quad (1.3)$$

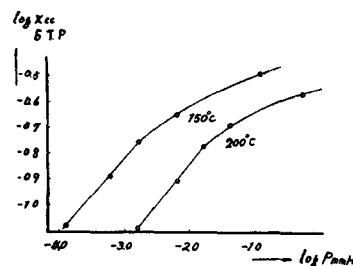


FIG. 1. Plot of log volume adsorbed against log pressure.

where  $q^{CO_2(a)}$ ,  $q^{CO(a)}$ ,  $q^{C(a)}$ , and  $q^{O(a)}$  are the partition functions of the adsorbed states of  $CO_2(a)$ ,  $CO(a)$ ,  $C(a)$ , and  $O(a)$  expressed as

$$q^{CO_2(a)} = \prod_i (1 - \exp(-h\nu_i/kT))^{-1} \exp(-\epsilon_0 + \frac{1}{2}h\nu_1/kT), \text{ etc.,}$$

and  $p^{CO_2}$  is related with the ordinary partition function,  $Q$ , of gaseous carbon dioxide and its concentration  $N$ , as

$$p^{CO_2} = Q/N.$$

Equations (1.1), (1.2), and (1.3) are expressed for the case  $\theta \ll 1$  as

$$\theta = \frac{q^{CO_2(a)} \exp[T\partial \log q^{CO_2(a)}/\partial T]}{Q_0} P e^{\Delta\epsilon/RT} \quad (2.1)$$

$$\theta^2 = \frac{q^{CO(a)}q^{O(a)} \exp[T\partial \log q^{CO(a)}q^{O(a)}/\partial T]}{Q_0} P e^{\Delta\epsilon/RT} \quad (2.2)$$

$$\theta^3 = \frac{q^{C(a)}q^{O(a)}q^{O(a)} \exp[T\partial \log q^{C(a)}q^{O(a)}q^{O(a)}/\partial T]}{Q_0} P e^{\Delta\epsilon/RT} \quad (2.3)$$

where

$$Q_0 = kT \frac{(2\pi mkT)^{3/2}}{h^3} \frac{8\pi^2 I kT}{s^2} \prod_i (1 - e^{-h\nu_i/kT})^{-1} e^{7/2}$$

$\Delta\epsilon$ : differential heat of adsorption per gram mole  
 $P$ : equilibrium pressure.

The investigation of the factors,  $q^{CO_2(a)} \exp[T\partial \log q^{CO_2(a)}/\partial T]$  etc., in the above equations shows that every one of them is generally greater than 1 and approaches 1 as  $h\nu_i \gg kT$ . Assuming that the latter condition is fulfilled, we have

$$\theta = P e^{\Delta\epsilon/RT} \quad (3.1)$$

$$\theta^2 = \frac{P e^{\Delta\epsilon/RT}}{Q_0} \quad (3.2)$$

$$\theta^3 = \frac{P e^{\Delta\epsilon/RT}}{Q_0} \quad (3.3)$$

The above equations give relations between  $\theta$  and  $P$ , respectively, appropriate to the three different adsorbed states affording a method of experimental determination of them.

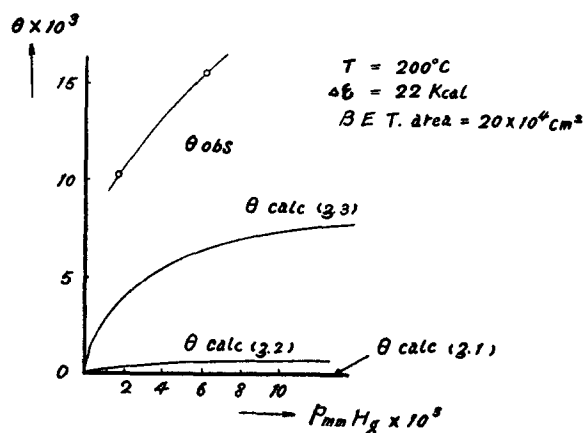


FIG. 2. Plot of  $\theta$  against pressure.