

mercury atoms react with nitrous oxide molecules. (5) Since the final equation of the complete reaction is $\text{Hg} + \text{N}_2\text{O} = \text{HgO} + \text{N}_2$, either ozone or excited oxygen molecules finally react with the mercury to produce mercuric oxide. This is considered to be a relatively fast reaction. The possibility of nitrogen dioxide is not considered to be of importance due to the fact that the final nitrogen pressure in long runs is equal to the initial nitrous oxide pressure. Some reaction of the type $\text{NO}_2 + \text{Hg} = \text{HgO} + \text{NO}$ may, however, take place in the gas phase. With nitric oxide and oxygen present, nitrogen dioxide would result when the gases are cooled in the liquid-air trap.

Summary

1. The total reaction between excited mercury and nitrous oxide may be represented by the equation $\text{Hg} + \text{N}_2\text{O} = \text{HgO} + \text{N}_2$.

2. Definite decision as to the nature of the initial step is not possible, although certain conclusions are drawn. The effects of adding oxygen and nitric oxide make identification of some steps possible.

3. As ascertained from reaction rate experiments the effective cross section of the nitrous oxide molecule as regards its interaction with excited mercury is very large.

PROVIDENCE, RHODE ISLAND

[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE RAMAN SPECTRUM OF GERMANIUM TETRACHLORIDE

BY R. R. HAUN AND WILLIAM D. HARKINS

RECEIVED JUNE 6, 1932

PUBLISHED OCTOBER 5, 1932

The Raman spectrum of germanium tetrachloride was obtained by the method described in the next paper of this series. The frequencies of the Raman lines are given in Table I.

Considerable work, both experimental and theoretical, has been done upon the problem of the vibrational frequencies of molecules of the type

TABLE I
THE RAMAN LINES OF GERMANIUM TETRACHLORIDE

Raman	Raman lines, exciting lines and displacements in cm.^{-1}				
	Excit.	D	Raman	Excit.	D
22487 (1)	22938	451	23112 (5)	22938	174
22544 (10)	22938	394	23337 (6)	22938	399
22595 (1)	22995	400	24309 (6)	24705	396
22768 (6)	22938	170	24535 (2)	24705	171
22808 (6)	22938	130	24571 (2)	24705	134
23070 (5)	22938	132			

SUMMARY OF DISPLACEMENTS IN ORDER OF INTENSITY

397 (10), 132 (6), 171 (6), 451 (or 508) (1)

XY_4 , which contain five atoms. Table II gives a comparison of the wave numbers for the tetrachlorides of carbon, silicon, titanium and tin, with those of germanium.

TABLE II
RAMAN FREQUENCIES OF TETRAHALIDES

	$CCl_4(6)$	$SiCl_4(14)$	$TiCl_4(22)$	$GeCl_4(32)$	$SnCl_4(50)$	CBr_4	$SnBr_4$
$\omega_2(?)$	217 (8)	151 (5)	(120 (4))	132 (6)	104 (5)	123 (2)	64 (2)
$\omega_4(a)$	313 (8)	221 (5)	(144 (1))	171 (6)	134 (6)	183 (4)	88 (4)
$\omega_1(?)$	459 (8)	452 (10)	(386 (6))	397 (10)	366 (10)	265 (5)	220 (4)
$\omega_3(a)$	760 (3)	607 (2)	(497 (2))	451 (1)	404 (6)	667 (3b)	279 (3)
	791 (3)			(or 508)			
	1537 (1)						

The data for all of the substances with the exception of germanium tetrachloride are taken from the compilation by Kohlrausch.¹

In this table the chlorides are arranged in increasing order of the atomic numbers of the fourth group elements. The values for germanium tetrachloride appear to be too high in comparison with those of titanium and tin. However, this discrepancy is partly fictitious, since titanium belongs to another subdivision of group 4 of the periodic system² than germanium and tin. The normal term is 3F_2 for titanium, but 3P_0 for all of the other elements of this group.

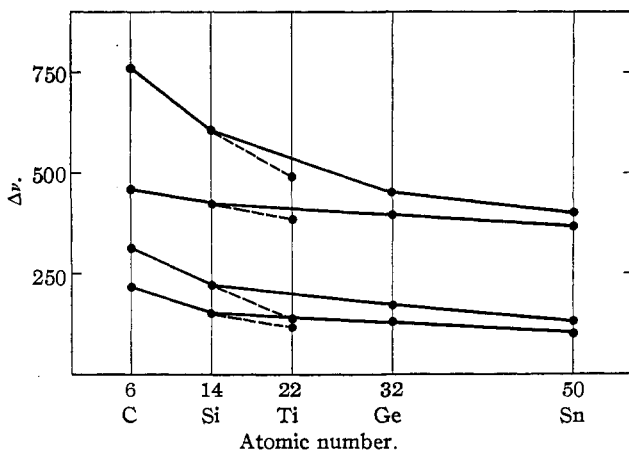


Fig. 1.—Raman frequencies for tetrachlorides (in cm^{-1}). The highest frequency for germanium may be 508 cm^{-1} instead of the value plotted. If this is true the uppermost line is also linear from Si to Sn.

Figure 1 exhibits the following interesting relations: the wave numbers for any one of the types of frequencies (ω_1 , ω_2 , ω_3 or ω_4) are nearly linear

¹ Kohlrausch, "Der Smekal-Raman-Effekt," Berlin, 1931.

² Harkins and Hall, THIS JOURNAL, 38, 169 (1916).

with respect to atomic number (1) for carbon, silicon and titanium, and (2) (except for W_3) for silicon, for germanium and tin.

The theory of the spectra of molecules of the type XY_4 has been developed for methane by Dennison³ and for tetrahalides by Schaeffer⁴ on the assumption of central forces. Trumpy⁵ has shown that the three constants of the theory can be adjusted in such a way as to give a moderately good agreement with the observed data. Urey and Bradley⁶ use a more accurate theory which considers forces which act along the "valence bonds," perpendicular to them, and also repulsive forces between the halogen atoms. Both Trumpy, and Urey and Bradley, obtain the poorest agreement in the case of titanium tetrachloride.

The frequencies ω_1 and ω_2 correspond to optically inactive vibrations which do not affect the electrical moment. The vibration for ω_1 is along the valence directions of the tetrahedron, and all the halogen atoms are supposed to move outward (or inward) simultaneously in such a way as to keep the resultant force upon the central atom equal to zero. In the vibration for ω_2 the halogen atoms are supposed to move on the surface of a sphere for which the atom X is the center. The frequencies ω_3 and ω_4 correspond to vibrations in which the symmetry of the molecule is not preserved, so the electrical moment is affected and ω_3 and ω_4 are optically active.

The writers are indebted to Professor Warren C. Johnson for the germanium tetrachloride, and to a Grant-in-Aid of the National Research Council for the spectrograph used in this investigation.

Summary

1. The Raman spectrum of germanium tetrachloride is found to correspond to four displacements of wave number with values as follows

$$\omega_2 = 132 (6), \omega_4 = 171 (6), \omega_1 = 397 (10) \text{ and } \omega_3 = 451 (1)$$

(with a possibility that ω_3 is 508). The numbers in parentheses denote the relative intensities, and ω_1 and ω_2 designate, according to the theory, optically inactive and ω_3 and ω_4 , optically active frequencies.

CHICAGO, ILLINOIS

³ Dennison, *Astrophys. J.*, **62**, 84 (1925).

⁴ Schaeffer, *Z. Physik*, **60**, 586 (1930).

⁵ Trumpy, *ibid.*, **66**, 790 (1930).

⁶ Urey and Bradley, *Phys. Rev.*, **38**, 1969 (1931).