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The Raman spectrum of tetraethyl silane is reported. Assignments of frequencies for this compound and for other tetraalkyls are made. An analysis of resonance between vibrations $\nu_1 + \nu_2$ and ν_3 explains the presence of extra lines which appear in the Raman spectra of each of these compounds. Resonance between frequencies $2\nu_2$ and ν_4 explains the presence of two additional lines observed in $Si(C_2H_5)_4$. Resonance between ethyl vibrations in $Si(C_2H_5)_4$ and in $Pb(C_2H_5)_4$ accounts for a split in the frequencies characteristic of the ethyl group. First-order perturbation calculations of the observed resonance effects are given in some detail.

INTRODUCTION

THE Raman spectra of a number of tetra-alkyl compounds of fourth group elements have been observed; namely, tetramethylmethane,[1, 2] tetramethyl silane,[2] tetramethyl tin,[3] tetramethyl lead[4] and tetraethyl lead.[3, 4] All exhibit an extra line in the vibration spectrum which has been ascribed to vibrational resonance within the molecule.[2] Previous authors have discussed such resonance in the case of carbon dioxide[5] and the methyl group.[6]

In this paper are presented the results of an investigation of the Raman spectrum of tetraethyl silane together with a somewhat detailed discussion of resonance between vibrational levels in the tetraalkyl molecules whose Raman spectra have been reported.

EXPERIMENTAL

The silicon tetraethyl used was prepared by Professor W. C. Johnson of the University of Chicago. After careful fractional distillation, a 10-ml portion had the following properties: b_{746} 153.3–153.8°C; $d_4{}^{25}$ 0.7635; $n_D{}^{25}$ 1.4249. The Raman spectrum of this portion was obtained by using light from a water-cooled mercury arc filtered through a solution containing quinine sulfate and rhodamine B which absorbed all but the 4300A lines of mercury.

RESULTS AND GENERAL DISCUSSION

All the lines observed for $Si(C_2H_5)_4$ were broad. The results of the measurements together with the data available for other tetraalkyls are given in Table I. The data are also presented

TABLE I. *Raman spectra of tetraalkyls.*

$C(CH_3)_4$ (cm^{-1})	$Si(CH_4)_4$ (cm^{-1})	$Si(C_2H_5)_4$ (cm^{-1})	$Sn(CH_3)_4$ (cm^{-1})	$Pb(CH_3)_4$ (cm^{-1})	$Pb(C_2H_5)_4$ (cm^{-1})
	202(20)	160(4)	152(7)	130(8)	96(4)
	239(15)	249(3)	262(4)		165(2)
332(10)	598(20)	303(6)			239(4)
415(3)	696(15)	393(2)			444(4)
731(20)	863(10)	553(10)	506(8)	460(10)	
790(2)		625(3)	526(5)	473(5)	463(3)
921(2)		736(3)		577(0)	535(1)
		865(1)		767(1)	
		978(5)	952(0)	930(0)	941(1)
		1021(5)	1046(0)	1155(5)	1013(2)
1250(20)	1264(10)	1200(7)	1200(5)	1170(4)	1165(3)
1453(15)	1427(15)	1423(7)	1262(0)		1460(1)
2711(5)		1467(8)			
2745(2)		2734(1)		2292(1)	1781(1)
2790(3)		2813(3)		2918(7)	2869(1)
2864(7)		2885(10)		2999(6)	2927(5)
2892(3)		2912(6)	2915(3)	3679(1)	
2911(10)		2950(5)	2979(2)	3755(1)	
2937(3)					
2954(7)					

Numbers in parentheses indicate relative intensities.

graphically in Fig. 1 where the assignments are indicated.

With Bennet and Meyer's notation,[6, 7] lines characteristic of the methyl group, *C*, *D*, *E*, and *F* are easily recognized from the values of the frequencies. In the case of tetramethylmethane other lines in the neighborhood of *E* and *F* are doubtless due to interactions of hydrogens on methyl groups. A double line $\nu \approx 950$, 1020 cm^{-1} is observed only in tetraethyl silane and tetraethyl lead. It is therefore ascribed to the vibrations characteristic of the ethyl group. These lines will be discussed in more detail later.

If the alkyl groups are considered to be units

* Contribution No. 524.
[1] Kohlrausch and Barnes, Annales Fisica y Quimica **30**, 733 (1932); Kohlrausch and Köppl, Zeits. f. physik. Chemie **B26**, 209 (1934).
[2] D. H. Rank and E. R. Bordner, J. Chem. Phys. **3**, 248 (1935).
[3] N. G. Pai, Proc. Roy. Soc. **A149**, 29 (1935).
[4] A. B. F. Duncan and J. W. Murray, J. Chem. Phys. **2**, 636 (1934).
[5] E. Fermi, Zeits. f. Physik **71**, 250 (1931); Adel and Dennison, Phys. Rev. **43**, 716 (1933); **44**, 99 (1933).
[6] Adel and Barker, J. Chem. Phys. **2**, 627 (1934).
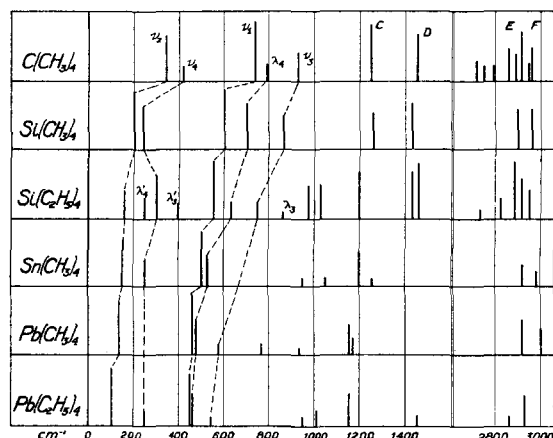[7] Bennet and Meyer, Phys. Rev. **32**, 888 (1928).

FIG. 1. Raman spectra of tetraalkyls.

at tetrahedral corners about the central atom, all lower frequencies can be ascribed to tetrahedral vibrations. In a number of cases[4] depolarization measurements have indicated that the most intense frequency in the spectra is due to ν_1, the symmetrical stretching vibration. The lowest frequency in each case is assigned to ν_2, the doubly degenerate bending vibration. The assignments of ν_3 and ν_4, the triply degenerate vibrations are indicated in Fig. 1. The presence of the remaining lines in the spectra can then be ascribed to resonance between vibrational levels having approximately equal energies.

On the basis of these assignments the infrared absorption bands observed[8] for $Sn(CH_3)_4$ and $Pb(CH_3)_4$ can be assigned to the combinations of frequencies indicated in Table II. ν_4 is not observed in the Raman spectrum of $Pb(CH_3)_4$; its value was obtained from the frequency at 777 cm^{-1}, $\nu_3 + \nu_4$. As might be expected both ν_3

TABLE II. *Infrared spectra of $Sn(CH_3)_4$ and $Pb(CH_3)_4$.*

Sn(CH₃)₄			Pb(CH₃)₄		
νobs (cm^{-1})	νcalc (cm^{-1})	COMBI-NATION	νobs (cm^{-1})	νcalc (cm^{-1})	COMBI-NATION
777(10)	768	$\nu_1 + \nu_4$	777(9)	(777)	$(\nu_3 + \nu_4)$
943(2)	922	$\nu_3 + \nu_4$	935(3)	977	$\nu_3 + 2\nu_4$
1036(2)	1034	$2\nu_4 + \nu_1$	1064(1)	1037	$\nu_1 + \nu_3$
1262(R)	1276	$2\nu_1 + \nu_4$	1170(6)	1163	C
1205(9)	1200	C	1300(3)	1284	$2\nu_3 + \nu_2$
1369(4)	1352	$C + \nu_2(?)$	1470(6)	(1470)	D
1470(7)	1468	$2\nu_3 + \nu_2$, D	1610(5)	1614	$2\nu_3 + \nu_1$
1724(3)	1706	$C + \nu_1(?)$	1890(0)	1860	$3\nu_3 + \nu_2$
2330(1)	2328	$2\nu_3 + 2\nu_1$	2174(0)	2190	$3\nu_3 + \nu_1$
2464(1)	2480	$3\nu_3 + \nu_1$	3030(9)	3024	G
3030(9)	3024	$G^{(6)}$	3704(0)	3490	$3C$
3700(1)	3600	$3C$	4348(0)	(4300)	$3D^{(6)}$
4350(1)	(4300)	$3D^{(6)}$			

[8] Kettering and Sleator, Physics **4**, 39 (1933).

and ν_4 occur frequently in the combinations. It is interesting to note that $3D$ predicted by Adel and Barker to be a split frequency appears as a single frequency.

VIBRATIONAL RESONANCE IN TETRAALKYLS

To treat the problem of resonance between vibrational levels in a molecule we may first set down the wave equation in normal coordinates and obtain the solutions as products of the normalized orthogonal Hermite functions of the normal coordinates. To obtain interactions between the normal vibrations third-order and higher terms in the normal coordinates consistent with the symmetry of the molecule must be included in the potential energy expression. These additional terms are then considered as a perturbation H^1 on the zeroth order solutions just obtained.

The perturbation energy will be appreciable, and additional lines in the Raman spectrum may be observed if a degeneracy of the type

$$V_1\nu_1 + V_2\nu_2 + \cdots = \nu_4 \cdots \qquad (1)$$

can be considered to exist, and if the symmetry of the molecule permit such an interaction. If only third-order terms are included in the potential energy expression and none of the fundamental frequencies ν_1, ν_2, $\cdots$ ν_4 is degenerate, the first-order perturbation energies are zero and second-order perturbations must be considered. If, however, one or more of the vibrations ν_1, ν_2, $\cdots$, ν_4 is degenerate, first-order perturbation energies will not vanish. The perturbation method[9] consists in finding the correct zeroth order wave function for the perturbation H' as a linear combination of all the wave functions which correspond to the energy ν_4. In order that the equations determining the coefficients in this combination of eigenfunctions have a solution the new energies resulting from the interaction must satisfy a secular equation. One can then solve this equation for the energy levels of the perturbed system.

The presence of the lines indicated as λ_3 and λ_4 in Fig. 1 can be ascribed to resonance between the doubly degenerate level $\nu_1\{1\} + \nu_2\{2\}$ and

[9] Pauling and Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Co., 1935), p. 165.

TABLE III. *Resonance in tetraalkyls.*

COM-POUND	$\nu_1+\nu_2$ (cm^{-1})	ν_3 (cm^{-1})	$\nu_1+\nu_2-\nu_3$ (cm^{-1})	λ_4 (cm^{-1})	$\frac{1}{2}(\nu_1+\nu_2+\nu_3)$ $-\lambda_4$(cm^{-1})	$(\lambda_3$calc) (cm^{-1})	$(\lambda_3$obs) (cm^{-1})	P (cm^{-1})	B (cm$^{-5/2}\times10^{-4}$)	C (cm$^{1/2}\times10^4$)
C(CH$_3$)$_4$	1063	921	142	790	202	1194	—	77	117	51
Si(CH$_3$)$_4$	800	863	−63	696	136	968	—	54	55	53
Si(C$_2$H$_5$)$_4$	713	736	−23	625	100	825	865	41	33	51
Sn(CH$_3$)$_4$	658	(658)	(0)	526	(132)	(790)	748	(54)	(39)	(75)
Pb(CH$_3$)$_4$	590	577	13	473	111	694	656	45	26.5	(77)
Pb(C$_2$H$_5$)$_4$	540	535	5	463	75	613	—	31	14.5	(64)

the triply degenerate frequency $\nu_3\{3\}$. Numbers in braces denote degeneracies of the respective fundamental frequencies. We may assume initially that $\nu_1+\nu_2=\nu_3$. The term in the potential energy which will give rise to interactions between these levels is[10]

$$H_1' = \beta_1 Q_1 (Q_2+Q_2')(Q_3+Q_3'+Q_3'')$$

where Q_i is the normal coordinate having the frequency ν_i. Primes affixed to the Q_i's distinguish the normal coordinates having the same frequency from each other. Omitting zero-point energies, the secular equation turns out to be

$$\begin{vmatrix} \nu_1+\nu_2-\lambda & 0 & P_1 & P_1 & P_1 \\ 0 & \nu_1+\nu_2-\lambda & P_1 & P_1 & P_1 \\ P_1 & P_1 & \nu_3-\lambda & 0 & 0 \\ P_1 & P_1 & 0 & \nu_3-\lambda & 0 \\ P_1 & P_1 & 0 & 0 & \nu_3-\lambda \end{vmatrix} = 0.$$

P_1 is the perturbation integral,

$$P_1 = \beta_1 h^{\frac{3}{2}}/16\sqrt{2}\pi^3(\nu_1\nu_2\nu_3)^{\frac{1}{2}} = B_1/(\nu_1\nu_2\nu_3)^{\frac{1}{2}}.$$

The secular equation has the following solutions for the λ's the energy levels resulting from resonance:

$$\lambda_1\{1\} = \nu_1+\nu_2,$$
$$\lambda_2\{2\} = \nu_3,$$
$$\lambda_3\{1\} = \tfrac{1}{2}[\nu_1+\nu_2+\nu_3 + \{(\nu_1+\nu_2-\nu_3)^2+24P_1^2\}^{\frac{1}{2}}],$$
$$\lambda_4\{1\} = \tfrac{1}{2}[\nu_1+\nu_2+\nu_3 - \{(\nu_1+\nu_2-\nu_3)^2+24P_1^2\}^{\frac{1}{2}}].$$

$\lambda_1\{1\}$, a combination frequency, may be expected to be weak in the Raman effect, while $\lambda_2\{2\}$, $\lambda_3\{1\}$ and $\lambda_4\{1\}$ are permitted but not necessarily with equal intensities.

Assignments of frequencies and results of

[10] Tetrahedral symmetry does not permit H_1'. However the tetraalkyl molecules have tetrahedral symmetry only for very special orientations of the alkyl groups. For general orientations, the term H_1' is then allowed. If the assignments of frequencies, ν_2 and ν_4, were interchanged, tetrahedral symmetry would permit such a term as H_1'. However if this were done certain of the infrared combinations would not be allowed and there would be absolutely no agreement with valence force criteria (Rosenthal, Phys. Rev. **45**, 538 (1934); **46**, 730 (1934).

calculations are presented in Table III. Both λ_4 and ν_3 have been observed for all but Sn(CH$_3$)$_4$, in which case it appears that λ_4 is observed while ν_3 is not. ν_3 was obtained in this case by assuming that $\nu_1+\nu_2=\nu_3$. In each case λ_3, P_1 and B_1 were calculated from values of λ_4 and ν_3. λ_3 is observed in the Raman spectrum of Si(C$_2$H$_5$)$_4$ and in the infrared spectra of Sn(CH$_3$)$_4$ and Pb(CH$_3$)$_4$,[8] where it appears as a satellite of strong absorption lines. The agreement of observed and calculated values of λ_3 is satisfactory considering the approximations made in assuming Eq. (1).

The values of P_1 obtained are of the same order of magnitude as those for vibrational interactions in the carbon dioxide molecule and for the interactions of hydrogen vibrations in methyl groups. The magnitude of the effect is greater because of the degeneracy of the resonating levels. Inasmuch as the normal coordinates for tetrahedral molecules are not known it seems impossible at this time to relate the B's to actual displacements of the groups in the molecules.

In the last column of Table III are given values of

$$C_1 = B_1/\nu_1\nu_2\nu_3 = P_1/(\nu_1\nu_2\nu_3)^{\frac{1}{2}},$$

which, interestingly enough, turn out to be nearly constant, i.e., independent of the nature of the central atom and of the character of the alkyl group.

If the above analysis is correct, one must conclude that Raman lines resulting from resonance may be more intense than those from fundamental modes, as is the case in Si(CH$_3$)$_4$ and Pb(C$_2$H$_5$)$_4$. In an extreme case, such as apparently exists in Sn(CH$_3$)$_4$, the resonance line may appear strongly and the fundamental not at all. Without a somewhat detailed analysis of the possibility of resonance between normal

modes, extreme caution must be taken in applying the results of normal coordinate treatments to observed frequencies.

Apparently another case of resonance exists in $Si(C_2H_5)_4$, namely, that brought about by the fact that $2\nu_2(2) \approx \nu_4(3)$. The term in the potential energy expression which gives rise to resonance between these levels is:

$$H_2' = \beta_2(Q_2^2 + Q_2Q_2' + Q_2'^2)(Q_3 + Q_3' + Q_3'').$$

The secular equation in this case has the same form as in the previous case, with $2\nu_2$, ν_4, and P_2 replacing $(\nu_1 + \nu_2)$, ν_3, and P_1, respectively. In this case

$$P_2 = \frac{\beta_2 h^{\frac{3}{2}}}{16\sqrt{2}\pi^3\nu_2(\nu_4)^{\frac{3}{2}}} = \frac{B_2}{\nu_2(\nu_4)^{\frac{3}{2}}}$$

and the levels permitted by the secular equation are

$$\lambda_1'\{3\} = 2\nu_2,$$
$$\lambda_2'\{2\} = \nu_4,$$
$$\lambda_3'\{1\} = \frac{1}{2}[2\nu_2 + \nu_4 + \{(2\nu_2 - \nu_4)^2 + 24P^2\}^{\frac{1}{2}}],$$
$$\lambda_4'\{1\} = \frac{1}{2}[2\nu_2 + \nu_4 - \{(2\nu_2 - \nu_4)^2 + 24P^2\}^{\frac{1}{2}}].$$

Taking $2\nu_2 = 320$, $\nu_4 = 303$, and $\lambda_4' = 249$ cm^{-1}, one obtains 63 cm^{-1} for $\frac{1}{2}(2\nu_2 + \nu_4) - \lambda_4$, 12.4 cm^{-1} for P_2, 3.4×10^4 cm$^{-5/2}$ for B_2 and 44×10^{-4} cm$^{\frac{3}{2}}$ for C_2. The value for C_2 is very nearly equal to that for C_1. The calculated value, 375 cm^{-1} for λ_3' is in good agreement with the observed value, 393 cm^{-1}.

The double lines observed at 980 cm^{-1} in $Si(C_2H_5)_4$ and $Pb(C_2H_5)_4$ may be ascribed to $C-C$ vibrations in the ethyl groups. Its frequency is equal to the $C-C$ frequencies in ethane (990 cm^{-1}), ethyl chloride (966), bromide (960), iodide (950), which have been discussed in some detail by Cross and Van Vleck.[11] If there were no interactions between ethyl groups there would be a single fourfold degenerate level ω_0 with this frequency. The splitting of the level may be due to interactions between the ethyl groups represented by a term in the potential energy expression

$$H'_{C_2H_5} = \beta_{C_2H_5}(q_1q_2 + q_1q_3 + q_1q_4 + q_2q_3 + q_2q_4 + q_3q_4),$$

where q_i is the normal coordinate for the $C-C$

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[11] Cross and Van Vleck, J. Chem. Phys. **1**, 350 (1933).

vibration for the ith ethyl group. The secular equation for this interaction is

$$\begin{vmatrix} \omega_0 - \lambda & P & P & P \\ P & \omega_0 - \lambda & P & P \\ P & P & \omega_0 - \lambda & P \\ P & P & P & \omega_0 - \lambda \end{vmatrix} = 0,$$

where $P = \beta_{C_2H_5}h/8\pi^2\omega_0 = B_{C_2H_5}/\omega_0$. The solutions of the secular equation are

$$\lambda_1''\{3\} = \omega_0 - P,$$
$$\lambda_2''\{1\} = \omega_0 + 3P.$$

In Table IV are given values of λ_1'', λ_2'', ω_0 and

TABLE IV. *Vibrational resonance between ethyl groups.*

COM-POUND	λ_1'' (cm^{-1})	λ_2'' (cm^{-1})	ω_0 (cm^{-1})	P (cm^{-1})	$B_{C_2H_5} \times 10^{-4}$ (cm^{-2})
$Si(C_2H_5)_4$	978	1021	989	11	11
$Pb(C_2H_5)_4$	941	1013	959	18	17.3

P for the two compounds for which data are available. Here again it is difficult to relate the P's directly to physical quantities since the q's are not known; moreover, $H'_{C_2H_5}$ is difficult to interpret since the ethyl groups may rotate and consequently may be oriented in many ways with respect to one another. One might have predicted, however, that the interaction, P, would be greater in $Pb(C_2H_5)_4$ than in $Si(C_2H_5)_4$. Because both have a smaller electronegativity than carbon, the central atom will in each case have a slight positive charge; Pb would have a greater positive charge than Si since it has a smaller electronegativity than Si. As a result, the methylene groups in $Pb(C_2H_5)_4$ have greater negative charges than those in $Si(C_2H_5)_4$. Consequently the interaction between methylene groups might well be greater in $Pb(C_2H_5)_4$. Apparently this effect overcomes the opposing effect of the distance between methylene groups, which distance is greater in $Pb(C_2H_5)_4$. A study of tetraethyl methane, in which electronegativities play no part, would greatly clarify the situation.

In conclusion I should like to express my appreciation to Professor Don M. Yost for helpful advice and criticism, and to Dr. G. W. Wheland for his kindness in working out the combination selection rules for tetrahedral molecules from group theory considerations.