The Raman and Ultraviolet Absorption Spectra of Some Metal Carbonyls and Alkyls

A. B. F. Duncan and John W. Murray

TABLE I. *Vibrations in* NH_3.

	Raman spectra[2]	Model
ω_1	3210 cm^{-1}	3210*
ω_2	1580	1675
ω_3	3310 } 3380 }	3400
ω_4	1580(?)	1370

TABLE II. *Vibrations in* CH_4.

	Spectra[4]	Model
ω_1	2915 cm^{-1}	2915*
ω_2	1304	1260
ω_3	1520	1575
ω_4	3022 } 3070 }	3180

agreement) to values comparable with the spectral frequencies. Only the qualitative agreement is significant.

Fig. 4 shows the vibrations observed in CH_4 and the frequencies either observed or deduced from spectra are given in Table II.

The method has been applied with considerable success in the study of some metal carbonyls and alkyls by Duncan and Murray[3]

and in the study of.the motions of the benzene ring to be discussed in a forthcoming article. It should be especially useful in unsymmetrical compounds such as hydrogen compounds consisting partly of protium and partly of deuterium where the lack of symmetry makes an analytical solution by means of determinants or group theory extremely difficult.

[2] P. Daure, Ann. de physique 12, 375 (1929).
[3] A. B. F. Duncan and J. W. Murray, J. Chem. Phys. 2, 636 (1934).

[4] The authors' interpretation of the results of D. M. Dennison, J. Astrophys. 62, 73 (1925) and Dickinson, Dillon and Rassetti, Phys. Rev. 34, 582 (1929).

The Raman and Ultraviolet Absorption Spectra of Some Metal Carbonyls and Alkyls

A. B. F. DUNCAN AND JOHN W. MURRAY, *Chemistry Laboratory, Johns Hopkins University*
(Received July 17, 1934)

The Raman spectra of nickel carbonyl, iron pentacarbonyl, lead tetramethyl, and lead tetraethyl and the ultraviolet absorption spectra of nickel carbonyl, lead tetramethyl and lead tetraethyl have been studied. The symmetry number of nickel carbonyl has been calculated. The vibrations of a mechanical model of a plane XY_4 molecule have been studied. The correlation of the observed Raman lines with modes of vibration is discussed. It is concluded, from the observed spectrum and the vibrations shown by the mechanical model, that nickel carbonyl has a plane rather than a tetrahedral structure.

THE structure of compounds containing metal-carbon homopolar bonds has received little attention. The question is of interest not only from a purely scientific standpoint, but also because these substances are noted for their "anti-knock" properties when used in small concentrations in gasoline. We have obtained new optical data on nickel carbonyl, iron pentacarbonyl, lead tetramethyl and lead tetraethyl which we wish to report here.

The Raman spectrum of nickel carbonyl has been obtained previously by Dadieu and Schneider,[1] and by Anderson.[2] The former

authors also attempted to obtain the Raman spectra of cobalt tetracarbonyl and iron pentacarbonyl without success. The lead alkyls have not been examined from this viewpoint heretofore. The ultraviolet absorption spectrum of nickel carbonyl has been examined by Thompson and Garratt[3] whose findings are confirmed by our work. The ultraviolet absorption of the other compounds treated in this work have not been investigated previously.*

[1] Dadieu and Schneider, Anzeiger der Acad. der Wiss. in Wien, Math. Naturwiss. Klasse 68, 191 (1931).
[2] J. S. Anderson, Nature 130, 1002 (1932).

[3] H. W. Thompson and A. P. Garratt, J. Chem. Soc. (1934), 524.
* H. W. Thompson (J. Chem. Soc. London, 1934, 790) has recently reported a system of discrete bands belonging to lead tetraethyl which lies on the long wave side of the continuum observed by us and by him. Although we used a slightly longer path and corresponding pressures, we

The modes of vibration of a mechanical model of a plane XY_4 molecule have been investigated in order to facilitate the interpretation of the observed spectra.

EXPERIMENTAL

The Raman spectra of $Ni(CO)_4$, $Pb(CH_3)_4$, and $Pb(C_2H_5)_4$ were obtained with the apparatus described by Murray and Andrews.[4] For iron carbonyl, which is orange colored and decomposes rapidly with light of shorter wave-length than the red, another technique had to be used. The liquids were distilled into the Raman tubes in vacuum by cooling the tubes with solid carbon dioxide, frozen out, and sealed off as they decompose at high temperatures.

The nickel carbonyl was prepared by Mr. C. B. Jackson of this laboratory from carbon monoxide and finely divided nickel. Spectra of this compound were excited by the 4358 and 5461 lines of mercury using a filter of saturated sodium nitrite, nitrobenzene, and praseodymium nitrate solution. The lead tetramethyl was furnished by Professor F. O. Rice and was subjected to vacuum distillation before using. Spectra were excited with the 4358 and 5461 lines as in the case of $Ni(CO)_4$ and also by the 4047 line using a filter of dilute sodium nitrite solution and iodine in carbon tetrachloride. Slight decomposition occurred with the latter method of excitation. The lead tetraethyl was furnished by the Ethyl Gasoline Corporation. The original material, which was quite pure, was fractionated in vacuum before using. It was found to decompose rapidly with violet and blue light. With the green mercury line, decomposition was not noticeable with an eight hour exposure. A filter of copper nitrate, didymium nitrate, and potassium chromate was used to obtain monochromatic green light. Several exposures were obtained with the filter used for blue excitation but the irradiation was limited to 20 minutes with one arc by decomposition and the appearance of a white precipitate. The iron carbonyl was obtained from the General Motors Corporation in the form of a 50 percent solution in kerosene. The iron carbonyl was separated by distillation in an atmosphere of nitrogen in red light as preliminary experiments had shown that it decomposes rapidly in green light with the formation of orange crystals. The spectrum was excited by the 6439 line of cadmium. The source of illumination was a cadmium-tin quartz arc as recommended by Krishnamurti.[5] The arc was about 12 cm long with electrodes of tungsten wire sealed in with picein and cooled by water jackets. The arc was operated in the vertical position on a current of 6 amperes with continuous pumping. It was surrounded by a semi-elliptical reflector and cooled by an air jet. The Raman tube was placed in the vertical position and had its window sealed onto a smaller tube projecting into the liquid at the top in order to keep the window free from the crystals formed by decomposition. The Raman tube was surrounded by a filter jacket containing a filter of iodine and potassium iodide dissolved in water and the tube and jacket were cooled in running water. This arrangement permitted intense illumination with the cadmium red line while no lines of wave-length (less than 6300) were recorded on the plate with a 65 hour exposure. The spectrum was photographed on Eastman Spectroscopic plates, I–F and I–N which have adjacent bands of maximum sensitivity covering the spectral region between the cadmium red line and 8000A which includes all of the Raman lines to be expected for this type of substance. The plates were hypersensitized with ammonia just before using.

The apparatus used for investigating the polarization of the Raman lines of nickel carbonyl and lead tetramethyl differed from those described in the literature in a few details and will be discussed briefly. Strictly quantitative data were not necessary for our purpose so several simplifications could be made. The illumination was furnished by a quartz capillary arc focussed by reflectors. The illumination was perpendicular to the direction of observation and to the spectrograph slit and was restricted to an angle of five degrees from the principal direction by a set of parallel strips of blackened cardboard set in planes perpendicular to the axis of the Raman tube. The Raman tube was in a vertical position and the light emerging from the window at the

obtained no evidence of them. We must conclude that our dispersion and resolving power were too low (Hilger E 37 used).

[4] J. W. Murray and D. H. Andrews, J. Chem. Phys. 1, 406 (1933).

[5] P. Krishnamurti, Ind. J. Phys. 5, 587 (1930).

TABLE I. *Nickel carbonyl.*

$\bar{\nu}$	$\Delta\bar{\nu}$	Ex.	I	P	ν	$\Delta\bar{\nu}$	Ex.	I	P	$\bar{\nu}$	$\Delta\bar{\nu}$	Ex.	I	P
23532	−594	h	0		22396	599	g	1		20953	2042	g	4	
23396	−458	h	3		22337	601	h	4		20895	2043	h	30	p
23314	−376	h	10	P	22220	718	h	0		20806	2132	h	5	
22856	82	h	100	p	22105	833	h	2		20715	2223	h	1	
22658	381	f	2		22066	872	h	2		18230	78	k	100	p
22613	382	g	4		22025	913	h	2		17922	386	k	20	P
22556	382	h	20	P	21329	1609	h	0		17840	464	k	8	
22475	463	h	8	D	21001	2038	f	2						

82(100, p), 382(20, P), 463(8, D), 601(4), 718(0), 833(2), 872(2), 913(2), 1609(0), 2043(30, p), 2132(5), 2223(1).

TABLE II. *Lead tetramethyl.*

$\bar{\nu}$	$\Delta\bar{\nu}$	Ex.	I	P	$\bar{\nu}$	$\Delta\nu$	Ex.	I	P	ν	$\Delta\bar{\nu}$	Ex.	I	P
24235	470	d	3b		22463	475	h	20	D	21517	2999	e	7	
24054	462	e	0		22413	2292	d	1		21418	2917	v_3	1	
23543	1162	d	4		22361	577	h	0		21026	3679	d	1b	
23531	1174	d	4		22171	767	h	1		20950	3755	d	1b	
23455	−460	g	0		22008	930	h	0		20022	2916	h	5	P
23410	−472	h	2		21882	1157	f	1		19945	2993	h	1	
23398	−460	h	5		21829	1166	g	4		18444	−136	k	8	D
23343	1173	e	1		21786	2919	d	50		18182	126	k	20	D
22804	134	h	80b	D	21783	1155	h	20	D	17840	468	k	10	p
22572	467	f	4	p	21768	1170	h	10	p	17161	1147	k	2	
22529	466	g	10	p	21705	3000	d	30		17147	1161	k	1	
22478	460	h	100	p	21597	2919	e	10						

130(80, D), 460(100, p), 473(20, D), 577(0), 767(1), 930(0), 1155(20, D), 1170(10, p), 2292(1), 2918(50, P), 2999(30), 3679(1), 3755(1).

TABLE III. *Lead tetraethyl.*

$\bar{\nu}$	$\Delta\bar{\nu}$	Ex.	I	$\bar{\nu}$	$\Delta\bar{\nu}$	Ex.	I	$\bar{\nu}$	$\Delta\bar{\nu}$	Ex.	I
23377	−439	h	1	20072	2866	h	1	17839	469	k	5
22696	242	h	2	20022	2916	h	2	17773	535	k	1
22496	442	h	10	18751	−443	k	1	17299	1009	k	2
22476	462	h	5	18549	−241	k	1	17155	1153	k	5
21924	1014	h	2	(18212)	96	k	10b	16848	1460	k	1
21775	1163	h	5	18069	239	k	2	15436	2872	k	1
21479	1459	h	1	17862	446	k	10	15381	2927	k	5

(96(20bb)), 241(2), 443(10), 464(5), 535(1), 1012(2), 1159(5), 1460(1), 2869(1), 2927(5).

bottom was reflected to the spectrograph by a right-angled prism. It was focussed on the slit by a lens of 18 cm focal length and passed through a Wollaston prism. This apparatus gave satisfactory results in a check experiment with carbon tetrachloride, the polarization of whose Raman lines is well known.

The technique for the study of the mechanical model of the plane XY_4 molecule was the same as that described by Andrews *et al.*[6]
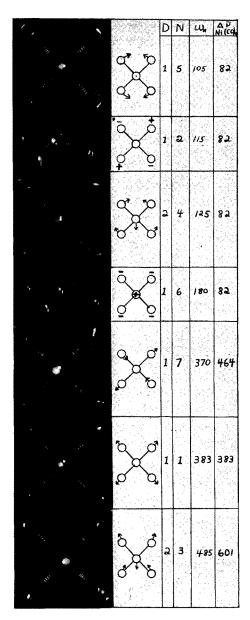
[6] D. H. Andrews and J. W. Murray, J. Chem. Phys. **2**, 634 (1934).

RESULTS

The results obtained on the Raman spectra of $Ni(CO)_4$, $Pb(CH_3)_4$, and $Pb(C_2H_5)_4$ are presented in Tables I to III. The first column gives the wave numbers of observed Raman lines in cm^{-1}, the second column, the displacement from the exciting line or Raman frequency, the third column, the mercury line which excited the Raman line, the fourth column, the relative intensity, and the fifth column, the state of polarization, if determined. The accuracy of the wave number values is believed to be about 3

cm^{-1} for lines of average intensity and sharpness. The symbols used for the mercury lines are: d 24,705 cm^{-1}, e 24,516, v_3 24,335, f 23,039, g 22,995, h 22,938 and k 18,308. The reported intensities are estimated visually, series of graded exposures being used for the stronger lines. The symbols for the state of polarization are: P, strongly polarized; D, largely depolarized; and p, intermediate. The results for $Ni(CO)_4$ are taken from four plates with blue and green excitation, those for $Pb(CH_3)_4$ from four plates with blue and green excitation and two with violet excitation, and those for $Pb(C_2H_5)_4$ are taken from two plates with green excitation and one with blue excitation. In the case of the iron pentacarbonyl, the plates taken on I–N spectroscopic plates showed no Raman lines even with an exposure of 65 hours. In exposures of this length, crystals of the orange decomposition product formed in the tube even with red light and hence the cadmium spectrum was very strong due to the reflected light. With a I–F plate, two faint diffuse lines were observed at 15,211 and 15,033 cm^{-1} which correspond to displacements of 320 and 498 cm^{-1}, respectively. Due to the low intensity of these lines and the presence of considerable fog on the plate which was hypersensitized in ammonia, these lines must be regarded as of doubtful authenticity.

The motions observed in the mechanical model of the plane XY_4 molecule are represented in Fig. 1 by photographs and drawings together with the number of degrees of freedom corresponding to each motion, a number designating the type of motion, its frequency relative to that of ω_1 set equal to the Raman frequency assigned to it, and the frequencies of the Raman lines assigned to these motions. This method of investigating the vibrations of molecules has several limitations which must be considered in interpreting the results. The actual values of the observed frequencies have no significance and hence are not given here. The motions observed may be distorted by the effects of the angular moments of inertia of the balls representing the atoms, the mass of the spring, resistance to rotation around the bond, and inequalities in the masses of the balls and springs and the force constants of the springs. The photographs show the directions and amplitudes of the motions of the balls by the

D	N	ω_k	Δp $Ni(CO)_4$
1	5	105	82
1	2	115	82
2	4	125	82
1	6	180	82
1	7	370	464
1	1	383	383
2	3	485	601

FIG. 1.

traces of white dots painted on the balls. The phase relations are indicated by cutting off the light at one end of the vibration. Rotation of the balls caused slight variations in the apparent directions of the ball motions, especially in ω_1 and ω_7.

Ultraviolet absorption spectra

The absorption spectra of the vapors of nickel carbonyl, lead tatramethyl and lead tetraethyl were photographed with a small Hilger quartz

spectrograph. The light source was an hydrogen discharge operated at 0.05 ampere and 10,000 volts a.c. Hydrogen from a palladium tube flowed through the discharge during the exposures and the continuum was entirely free from bands. The absorption tube was about 30 cm long, of fused quartz with plane ends sealed on. The liquids were contained in a small bulb joined to the tube by a graded seal and the pressure in the absorbing column was adjusted by varying the temperature of the liquid.

The spectra were perfectly continuous at all pressures tried and gave no indication of bands at the lowest pressures. It is possible that, at still lower pressures in correspondingly longer columns, these might appear but it seems unlikely in view of the complexity of the molecules. We give, therefore, the limits of absorption observed at the corresponding temperatures of the liquid or solid in the side tube. Vapor pressures are known only in the case of nickel carbonyl. The exact measurement of the limits seemed unnecessary. The results are of interest in the possible photochemical decomposition of these substances in the gaseous state, and in the reactions which may be induced by the radicals formed by these decompositions, at low temperatures. (Table IV.)

TABLE IV.

Compound	Temperature	Limits of absorption
$Ni(CO)_4$	$-78°C$ ($p=0.7$ mm)	All light absorbed below 3350
	$25°C$ ($p=398$ mm)	3600
$Pb(CH_3)_4$	-78	no absorption
	-25	2650
	0	2700
	25	2750
$Pb(C_2H_5)_4$	-78 pressure very low	2300
	25 pressure very low	2550

DISCUSSION

As the molecules under consideration show great dissimilarities in their spectra and are rather different mechanically, it appears best to discuss each compound separately.

Nickel carbonyl

The results obtained for this substance confirm all of the lines reported by previous investigators.

New lines have been found at: 718, 833, 872, 1609 and 2223 cm^{-1}.

The structure of this molecule has been considered to be a ring in which the nickel atom is joined to only two carbon atoms.[7, 8] Sutton and Bentley[9] have determined the dipole moment of nickel carbonyl and find it to be very low, probably zero, which indicates a high degree of symmetry more in accord with a plane square or a tetrahedral structure than with a ring. Blanchard and Gilliland[10] proposed an electronic configuration in which each of the CO groups shared two pairs of electrons with the central nickel atom. Pauling[11] suggests that four nickel-carbon bonds are present and are directed toward the corners of a square, all lying in one plane.

Dadieu and Schneider[1] assumed that the structure was tetrahedral and interpreted their results on that basis, assigning to ω_1 463, ω_2 82, ω_3 601, and to ω_4 382. 913 was assigned to the harmonic of ω_1 and the higher frequencies were assigned to the stretching motions of the CO bonds. These authors, as well as Anderson,[2] pointed out that the proximity of the frequencies of the carbonyl groups to that of the CO molecule indicates that the binding in nickel carbonyl is like that in carbon monoxide rather than like that in the organic carbonyl group. This fact supports the symmetric structures rather than a ring and suggests that the Ni−CO bond is formed by a single pair of electrons.

Consideration of the more complete Raman data now available, which include measurements of the polarization of the lines, indicates that the assignments made by Dadieu and Schneider are incorrect and that the molecule is probably plane as suggested by Pauling. This conclusion is supported by a calculation of the symmetry number. Nickel carbonyl should have 21 vibrational degrees of freedom. In view of the fact that the frequencies of vibration of the CO bond are much higher than those for the motions of the Ni−CO bonds, we may consider the molecule as a pentatomic molecule with nine degrees of freedom for the vibrations of low frequency. The

[7] J. W. Mellor, A Comprehensive Treatise of Inorganic and Theoretical Chemistry, Vol. 5, p. 954.
[8] Sugden, The Parachor and Valency, p. 189.
[9] Sutton and Bentley, Nature 130, 314 (1933).
[10] A. A. Blanchard, and Gilliland, J. Am. Chem. Soc. 48, 872 (1926).
[11] L. Pauling, J. Am. Chem. Soc. 53, 1398 (1931).

remaining 12 are associated with the internal motions of the CO groups and motions involving partial rotations of the CO groups about axes perpendicular to the Ni—CO bond axes, or twisting motions. The lines at 2043, 2132 and 2223 are associated with the internal motions, the lowest value being assigned to the symmetrical type on account of its polarization and intensity.

If the tetrahedral pentatomic structure is considered, we should expect the 9 degrees of freedom to be divided among four motions: a nondegenerate symmetrical stretching motion, ω_1; a doubly degenerate bending motion in which two pairs of Ni—CO bonds bend in scissor fashion, ω_2; a triply degenerate unsymmetrical stretching motion, ω_3; and a triply degenerate unsymmetrical bending motion, ω_4; as in the case of carbon tetrachlorode.

ω_1 must be assigned to the 382 line on account of the strong polarization. ω_2 must be assigned to the 82 line on account of the low frequency. ω_4 might be assigned to 463 and ω_3 to 601. This would make one bending motion, ω_4, greater that the other, ω_2, by a factor of nearly six and hence this assignment appears very improbable. We may assign both ω_2 and ω_4 to the 82 line as it is very broad, unsymmetrical, and of unusually great intensity which suggests that it is complex. ω_3 would then be assigned to 463 leaving 601, which is fairly intense, unexplained.

If we consider the transition from the tetrahedral structure to a plane square structure, whose motions are shown in Fig. 1, ω_1 remains essentially the same; ω_2 gives two non-degenerate motions, ω_2 and ω_5; ω_3 gives one non-degenerate motion, ω_7, and one doubly degenerate motion, ω_3; and ω_4 gives one non-degenerate motion, ω_6, and one doubly degenerate motion, ω_4. We assign the four bending motions to the broad 82 line, ω_1 to the 382 line, ω_7 to the 463 line, and ω_3 to the 601 line. This permits us to make what appears to be a rational assignment to all of the strong lines in the low region. As seen in Fig. 1, the frequencies observed in the model are in fair agreement with our assignment. As pointed out above, however, this should not carry much weight for the relative stretching and bending constants of the springs may not correspond well to those in the molecule. The separation of ω_1 and ω_7 in the molecular spectrum is explained by the

difference in the effects of the repulsion of the CO groups for each other in the two types of motion. This effect is not present in the model so the reversal of the order of the two motions in the spectrum has no significance. It is indeed difficult to see why they should have different frequencies in the model at all.

There remain lines at 718, 833, 872, 913 and 1609 to be explained. Dadieu and Schneider[1] have attributed the 913 line to a harmonic of the 463 line. Some of these lines are probably due to the twisting motions of the CO group but it does not seem probable that such a wide range of frequencies can all be due to this type of motion. The line at 1609 is extremely feeble and is of doubtful origin so no assignment can be made of it at this time. We assign 718, 833, 872 and possibly 913 to this type of motion. In the vibration type ω_1, the central atom is considered to be stationary. If this is the case, the frequency should be that of a diatomic oscillator in which the CO group vibrates against an infinite mass. We have calculated the force constant of the Ni—CO bond on this assumption and obtain the value, 2.4×10^5 dynes per cm which is about the value expected for a single electron pair bond.

The symmetry number of nickel carbonyl

Space will not permit a detailed account of these calculations which were made by the method described by Deitz and Andrews.[12] The vapor pressures were taken from the work of Anderson,[13] and the Raman frequencies observed by us, together with our assignments of degrees of freedom, were used as the basis for the calculation of the necessary thermal data. λ_0 was estimated from the data given in the above work and the difference $\int Cp_{\mathrm{vap}}.dT - \int Cp_{\mathrm{sol}}.dT$. The temperature used was 243°K. The specific heats calculated are shown in Table V. The only value found in the literature[14] is an average over the interval −78 to −188°C and is in fair agreement with our calculations. Preliminary measurements by Dr. S. L. Goldheim and D. Stull in this laboratory have indicated somewhat higher values over the higher part of the temperature range but the method used has not been

[12] V. Deitz and D. H. Andrews, J. Chem. Phys. 1, 62 (1933).
[13] J. S. Anderson, J. Chem. Soc. 132, 1653 (1930).
[14] Dewar, Proc. Roy. Soc., London A89, 158 (1913).

TABLE V. *The specific heat of nickel carbonyl (solid).*

Temp. °K	Cv (Debye) $\theta = 38.2$	Cp − Cv	Cv (total)	Cp (solid)
10	6.32	0.003	6.33	6.33
20	10.02	0.179	10.81	10.99
30	11.00	0.312	14.05	14.36
40	11.40	0.45	16.40	16.85
50	11.58	0.58	18.02	18.60
60	11.68	0.71	19.09	19.80
70	11.74	0.83	19.68	20.51
80	11.76	0.96	20.23	21.19
90	11.80	1.07	21.20	22.27
100	11.82	1.21	21.56	22.77
120	11.84	1.47	22.40	23.87
140	11.90	1.72	23.67	25.39
160	11.92	1.96	24.83	26.79
180	11.92	2.20	26.23	28.43
200	11.92	2.44	27.56	30.00
220	11.92	2.73	28.56	31.29
240	11.92	2.94	30.02	32.96

adequately calibrated as yet and considerable decomposition took place so that the results cannot be relied on at this time. The Debye frequency was calculated, as usual, from the melting point formula of Lindemann, the molecular volume of $Co(CO)_4$ being used. The moments of inertia were considered for the two cases of a square and a tetrahedron. Distances were derived independently from several different sources, mainly x-ray measurements on analogous compounds, and no serious differences were found. The values of the product ABC for the cases of the square and the tetrahedron were respectively, 7.62×10^{-112} and 8.84×10^{-112}.

If this molecule has a plane square configuration, the symmetry number should be 8, while if it is tetrahedral, the number should be 12. The value obtained was 6.3 and we believe that, unless some large unknown error is present in the data used, the number would not rise much above this value. This may be taken as some indication that the plane square model is correct or at least more probable than the tetrahedron.

Lead tetramethyl

Since the publication of a recent note,[15] new Raman lines have been found for this compound at 577, 2292, 3679 and 3755, all of which are very weak. The complete data are presented in Table II. We are now able to give a more definite assignment to the lines of this compound which

differs, in some respects, from that suggested in our previous note. It appears probable that this compound has a tetrahedral structure although there is no direct evidence on this point from other sources. Lead tetraphenyl has been shown to have this structure by x-ray analysis.[16] By analogy to compounds of other elements in the same group in the periodic system, such a structure should be expected.

On this assumption, we assign ω_2 and ω_4 to the line at 130 which is broad and appears to be double in the microphotometer curves. The 460 line, which is strong and partially polarized, is assigned to ω_1, while the line at 473, which is weaker and largely depolarized is assigned to ω_3. This accounts for the low motions expected in a pentatomic tetrahedral molecule. The line at 930 is attributed to a harmonic of 460 and the line at 2292 to a harmonic of 1155. The lines at 577 and 767, which are very weak, cannot be assigned on the basis of our present ideas. The 767 line is also found in the infrared absorption spectrum which has been examined by Kettering and Sleator.[17] The lines at 1155 and 1170 are assigned to bending motions of the C − H bonds. The line at 2918 is strongly polarized and is assigned to the symmetrical stretching motion of the C − H bonds while the weaker line at 2999 is assigned to an unsymmetrical motion of these bonds. We can offer no good explanation for the weak lines at 3679 and 3755 although they appear on several plates. It seems improbable that they are due to water which has a complex band in this region as they do not coincide with the maxima of this band.

Lead tetraethyl

The experimental data for this compound are probably not as complete as those for lead tetramethyl. This is due to the low dispersion obtained when working in the region of the mercury green line and the difficulties arising from decomposition when working with the blue line. We are confident that a low frequency Raman line of considerable intensity exists. This appears as a broad band not clearly separated from the exciting line and the measurement of its

[15] A. B. F. Duncan, and J. W. Murray, J. Chem. Phys. 2, 146 (1934).

[16] W. K. George, Proc. Roy. Soc., London A113, 585 (1926).
[17] Kettering and Sleator, Physics 4, 39 (1933).

position is therefore only an approximation.

It may be doubted that a treatment of lead tetraethyl as a pentatomic molecule is completely justified. In view of the apparent similarity of the spectra, however, we have assigned the lower lines on this basis. We should expect deviations from the mechanical behavior of a pentatomic tetrahedral molecule due to the interaction between the internal and twisting motions of the ethyl groups with the motions of the $Pb-(C_2H_5)$ bonds. The data for this compound are given in Table III.

It seems best to assign ω_2 and ω_4 to the broad low frequency line at about 96. By analogy to the case of lead tetramethyl, we assign ω_1 to 443 and ω_3 to 464. The 1012 line is attributed to a stretching motion of the $C-C$ bonds in the ethyl groups. The 1159 line is assigned to a bending motion of the $C-H$ bonds in the methyl groups as it appears in almost exactly the same place in the spectra of lead tetramethyl and the zinc alkyls. The line at 1460 is also attributed to this type of motion as it occupies the position generally attributed to this type of motion. The lines at 2869 and 2927 are attributed to stretching motions of the $C-H$ bonds. No assignment of the line at 241 can be made at this time.

Dadieu and Schneider[1] have stated that nickel carbonyl gave an exceptionally intense Raman spectrum. We have also noticed this in our work. In estimating the relative intensities of the Raman lines, we have made series of short exposures varying the exposure times between one second and 500 or 1000 seconds which permits an approximate measure of the intensity of the Raman line relative to that of the exciting line. The ratio of the intensity of the exciting line to that of the Raman line was found to be between 50 and 100 for the 82 line in $Ni(CO)_4$ and about 100 for the 460 line of lead tetramethyl. A similar experiment with the 992 line of benzene, which is generally considered to be quite intense, gave a ratio of about 200. While the method used yields only a rough approximation and is influenced by the magnitude of displacement of the Raman line from the exciting line, it appears certain that these lines have unusually high intensities. This may be due, in the case of the line of nickel carbonyl, to the superposition of several lines as assumed in our assignment of the frequencies to modes of vibration.