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Tetramethyllead: Far Infrared Spectra, Molecular Vibrations, and

Chemical Thermodynamic Properties. Resolution of an Entropy Discrepancy

G. A. Crowder and G. Gorin

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Department of Chemistry, Oklahoma State University, Stillwater, Okla.

F. H. Kruse

Los Alamos Scientific Laboratory, University of California, Los Alamos, N. M.

D. W. Scott\*

Bartlesville Petroleum Research Center, Bureau of Mines

U. S. Department of the Interior, Bartlesville, Okla.

\* To whom reprint requests should be sent.

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LADC-6413 TETRAMETHYLLEAD: FAR INFRARED SPECTRA, MOLECULAR VIBRATIONS,  
AND CHEMICAL THERMODYNAMIC PROPERTIES. RESOLUTION OF AN  
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Proposed running head:

SPECTRA AND THERMODYNAMICS OF  $(CH_3)_4 Pb$

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Donald W. Scott  
Bureau of Mines  
P. O. Box 1321  
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## (ABSTRACT)

Far-infrared spectroscopy and a normal-coordinate analysis for tetramethyllead yielded the first vibrational assignment consistent with the observed entropy of the vapor. The apparent entropy discrepancy with previous assignments was shown to result from use of liquid-state values for the low C-Pb-C bending frequencies in calculating the vapor-state entropy. A table of the chemical thermodynamic properties of tetramethyllead at selected temperatures was prepared.

## (TEXT)

The fundamental vibrational frequencies of the tetramethyllead molecule have been the subject of several investigations (1-9). These investigations, however, did not lead to a really satisfactory vibrational assignment, for even the most recent assignments are not consistent with the observed value of the entropy in the vapor state,  $S^{\circ}_{298.15} = 100.48 \pm 0.20 \text{ cal deg}^{-1} \text{ mole}^{-1}$  (10). For example, Lippincott and Tobin (6), assuming free rotation of the methyl groups, calculated with their vibrational assignment,  $S^{\circ}_{298.15} = 99.86 \text{ cal deg}^{-1} \text{ mole}^{-1}$ ; any hindrance to the rotation of the methyl groups would make the discrepancy even greater.

Similar, but smaller, entropy discrepancies for toluene (11) and other substances have been traced to the use of liquid-state values for low frequencies when the vapor-state values actually are significantly different. A similar explanation of the entropy discrepancy for tetramethyllead seemed likely, since in all the vibrational assignments proposed, the two C-Pb-C bending frequencies have been based on the Raman spectrum of the liquid. Both C-Pb-C bending frequencies, of species  $e$  and  $f_2$  for  $T_d$  point-group symmetry, are permitted by the selection rules in the Raman effect. However, in the pertinent region of the Raman spectrum, only one very broad, asymmetric band is observed with maximum intensity at about  $132 \text{ cm}^{-1}$ . In recent assignments, this band has been assumed to be double and to include both C-Pb-C bending frequencies.

To test the proposed explanation of the entropy discrepancy for tetramethyllead, the far infrared spectrum was observed for both the liquid and vapor states with the results shown in Figures 1 and 2 and listed in Table I. Only the  $f_2$  C-Pb-C bending frequency is permitted by the selection rules in the infrared spectrum. As predicted, the wavenumber for the vapor state,  $120 \text{ cm}^{-1}$ , is significantly different from that for the liquid state,  $130 \text{ cm}^{-1}$ . In principle, a vapor-state value of the inactive  $e$  C-Pb-C bending frequency also could be obtained from the infrared spectrum by observing infrared-active binary combinations involving that frequency, but actually no band in the infrared spectrum of the vapor can be assigned definitely to such a combination.

It is evident now why earlier assignments, basing the value of the  $f_2$  frequency on liquid-state spectra, did not give a correct calculated value for the vapor-state entropy. Unfortunately, a quantitative comparison of calculated and observed entropy values still is not possible as long as an experimental vapor-state value of the  $e$  frequency is lacking. However, with the assurance that a correct value of the entropy would be calculated with correct values of the vapor-state frequencies, it now is permissible to reverse the procedure and use the observed entropy value to determine the  $e$  frequency. When the molecular structure constants and all other vibrational frequencies are assigned the values given later in this paper, vibrational anharmonicity is neglected, and rotation of the methyl groups is assumed free, the calculated wavenumber for the  $e$  C-Pb-C bending mode

TABLE I

Far Infrared Spectra of Tetramethyllead. Wavenumbers in  $\text{cm}^{-1}$ .

Liq. or Soln.	Vapor	Interpretation
130 <sup>a</sup>	120	Fundamental $f_2$
	243	$2 \times 120 = 240 \underline{A}_1 + \underline{E} + \underline{F}_2$
	355	$476 - 120 = 356 \underline{A}_1 + \underline{E} + \underline{F}_1 + \underline{F}_2$
475	468 P 476 Q 483 R	Fundamental $f_2$
	580	$460(\underline{a}_1) + 120 = 580 \underline{F}_2$
	599 <sup>b</sup>	$476 + 120 = 596 \underline{A}_1 + \underline{E} + \underline{F}_1 + \underline{F}_2$

<sup>a</sup> Solution in cyclopentane, 129; absorbed in polyethylene, 127; liquid, 130.

<sup>b</sup> Nearly obscured by stronger neighboring bands. Probably actually more intense than the  $355 \text{ cm}^{-1}$  band, as expected for a sum- relative to a difference-combination.

is  $117 \pm 6 \text{ cm}^{-1}$ . If rotation of the methyl groups is at all hindered, a somewhat lower wavenumber would be calculated; for example, if the barrier hindering rotation of the methyl groups is assumed equal to RT at room temperature,  $592 \text{ cal mole}^{-1}$ , the calculated wavenumber would be  $104 \text{ cm}^{-1}$ . However, study of infrared band-width phenomena by Jones and Sheppard (12) suggests strongly that the barrier is considerably lower than RT. Accordingly, the value  $117 \text{ cm}^{-1}$  will be used for the e C—Pb—C bending mode in the calculations that follow, even though the evidence does not rule out the existence of a slight hindrance to rotation and a correspondingly lower wavenumber for the e mode.

For thermodynamic calculations, it was necessary to consider all the other vibrational frequencies in addition to the ones for C—Pb—C bending. To that end, a normal-coordinate analysis was made. Such a normal-coordinate analysis already had been reported by Overend and Scherer (13), but their work needed to be repeated for two reasons: (a) they used values of the C—Pb—C bending frequencies based on liquid-state spectra, and (b) they used for the e species, in following the Lippincott and Tobin assignment (6), values of  $700$  and  $1400 \text{ cm}^{-1}$  for which the spectroscopic evidence is far from conclusive. These values were obtained from Raman bands so weak that they have not been observed in most investigations of the Raman spectrum.

Table II presents the results of the present normal-coordinate analysis. These calculations were done on an IBM 7094 computer with G-Matrix Evaluation Program SD-9064-I, Z-Matrix Evaluation Program SD-9080-I, and Vibrational Secular Equation Program SD-9032-IV. The molecular structure

TABLE II

Observed and Calculated Wavenumbers of Tetramethyllead in  $\text{cm}^{-1}$  and

Final Converged Values of Force Constants with their Uncertainty.

K and F in units of  $\text{md A}^{-1}$ , H and  $\chi$  in  $10^{-11} \text{ erg radian}^{-2}$ 

Obs.	Calc.	Obs.	Calc.	Force Constant and Uncertainty	
<u><math>\underline{g}_1</math></u>					
2920	2920	----	3000	$\underline{K}_{\text{CH}}$	$4.465 \pm 0.107$
1169	1159	----	1434	$\underline{K}_{\text{CPb}}$	$0.664 \pm 0.124$
460	460	---	765	$\underline{H}_{\text{HCH}}$	$0.511 \pm 0.015$
		(117)	117	$\underline{H}_{\text{PbCH}}$	$-0.298 \pm 0.190$
<u><math>\underline{f}_2</math></u>					
3000	3000	<u><math>\underline{f}_1</math></u>		$\underline{F}_{\text{HH}}$	$0.053 \pm 0.022$
2920	2920	----	3000	$\underline{F}_{\text{HPb}}$	$0.888 \pm 0.255$
1435 <sup>a</sup>	1434	----	1433	$\underline{F}_{\text{CC}}$	$0.008 \pm 0.035$
1152 <sup>a</sup>	1164	---	763	$\underline{\chi}_{\text{Pb}}$	$0.053 \pm 0.049^b$
769 <sup>a</sup>	767			$\underline{\chi}_{\text{CH}_3}$	0.000 constrained
476	476				
120	120				

<sup>a</sup> The infrared spectrum of Jones and Sheppard (12), which became available after these calculations were finished, and which was obtained with a purer sample and higher resolution than used by earlier workers, gives

, and  $\text{cm}^{-1}$ . The differences are unimportant thermodynamically.

<sup>b</sup> The "intermolecular tension" actually calculated was:

$$\rho_{\text{Pb}} = -81/(32\sqrt{2}) \chi_{\text{Pb}} = -0.095 \pm 0.087$$

constants used were 2.203 Å for the Pb—C distance (14), 1.10 Å for the C—H distance, and the tetrahedral value for all angles. A basic Urey-Bradley field, as described by Overend and Scherer (13), was used; the reader should consult their paper for details. The linear constants  $F_{ij}^{'}$  were constrained by the conventional relationship,  $F_{ij}^{'} = -0.1 F_{ij}$ , and the intramolecular tension of the methyl group,  $\chi_{CH_3}$  was constrained to zero. The force constants not constrained were adjusted to give the best least-squares agreement of calculated and observed wavenumbers, weighted appropriately for a constant uncertainty for each observed wavenumber.

The observed wavenumbers were selected by averaging the available molecular spectral data (1 - 9), giving greater weight to the values judged more reliable. It can be seen that there is good agreement between observed and calculated values, the maximum difference being  $12 \text{ cm}^{-1}$ . The agreement is not a critical test of the assignment, since nearly as many force constants were adjusted as there were observed wavenumbers. However, it shows that the spectrum can be interpreted on the basis that the wavenumbers for species  $e$  and  $f_2$  are so nearly the same that they are not observed separately in the Raman spectrum. Owing to the different assignments used in the two calculations, the derived force constants in Table II differ quantitatively from the ones obtained by Overend and Scherer. However, the two sets of constants are qualitatively similar in such features as the negative value of  $H_{-PbCH}$  and the large value of  $F_{-HPb}$ .

Table III, columns 2 - 6, gives the thermodynamic functions calculated

TABLE III  
The Molal Thermodynamic Properties of Tetramethyllead in the Ideal Gas State

<u>T</u> , °K	$(G^\circ - H^\circ_0)/T$ , cal deg <sup>-1</sup>	$(H^\circ - H^\circ_0)/T$ , cal deg <sup>-1</sup>	$H^\circ - H^\circ_0$ , kcal	<u>S</u> <sup>°</sup> , cal deg <sup>-1</sup>	<u>C</u> <sub>P</sub> <sup>°</sup> , cal deg <sup>-1</sup>	$\Delta H_f^\circ$ , <sup>a</sup> kcal	$\Delta G_f^\circ$ , <sup>a</sup> kcal	$\log K_f$ <sup>a</sup>
0	0	0	0	0	0	40.5	40.5	infinite
273.15	-75.4	22.2	6.06	97.6	32.3	33.1	62.0	-49.6
298.15	-77.4	23.1	6.89	100.5	34.2	32.6	64.7	-47.4
300	-77.5	23.2	6.96	100.7	34.3	32.6	64.9	-47.3
400	-84.7	26.9	10.8	111.6	41.5	30.6	76.0	-41.5
500	-91.1	30.4	15.2	121.5	47.6	28.9	87.6	-38.3
600	-96.9	33.8	20.2	130.7	52.8	27.5	99.4	-36.2
700	-102.4	36.8	25.8	139.2	57.3	25.2	111.7	-34.9
800	-107.4	39.6	31.7	147.0	61.2	24.4	124.1	-33.9
900	-112.2	42.2	38.0	154.4	64.7	23.7	136.6	-33.2
1000	-116.8	44.6	44.6	161.4	67.7	23.3	149.2	-32.6

<sup>a</sup> The standard enthalpy and Gibbs energy, and common logarithm of the equilibrium constant of formation by the reaction,  $4C(c, \text{graphite}) + 6H_2(g) + Pb(c \text{ or } l) = C_4H_{12}Pb(g)$ . The reference states for lead are the crystals above the dotted line and the liquid below.

for tetramethyllead. The calculations, based on the rigid-rotator, harmonic-oscillator, independent-internal-rotator approximation, were made with the usual formulas of statistical thermodynamics (15). Vibrational contributions were computed from the values of Table II; observed wavenumbers were used whenever possible.

Finally, the enthalpy, Gibbs energy, and logarithm of the equilibrium constant of formation of tetramethyllead from the elements were calculated. The value of  $\Delta H_f^{\circ} \text{298.15}$  was taken from reference 10, and the values of the thermodynamic functions of carbon, hydrogen, and lead were taken from the JANAF Tables (16). The results are in columns 7, 8, and 9 of Table III.

### EXPERIMENTAL

The spectra of tetramethyllead were determined at room temperature with a Perkin-Elmer Model 301 far infrared spectrophotometer. The Globar source was used exclusively to avoid photochemical decomposition of the sample from exposure to ultraviolet radiation from the H4 mercury lamp of the alternate source. A cell especially made for the instrument, with path-length variable in increments of 1 meter up to 6 meters, was used in obtaining the vapor-state spectrum. The sample, supplied by Ethyl Corporation, was about 99.95 mole % pure.

### ACKNOWLEDGEMENT

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## (Captions for figures)

Fig. 1. Far infrared spectra of tetramethyllead in condensed phases;  
(a) 0.5% solution in cyclopentane, (b) absorbed in polyethylene, (c) liquid.

Cell lengths are indicated on figure.

Fig. 2. Far infrared spectrum of tetramethyllead vapor; (a) (c) pressure  
not measured but  $\leq$  1 torr, (b) 7 torr. Cell lengths are indicated on figure.

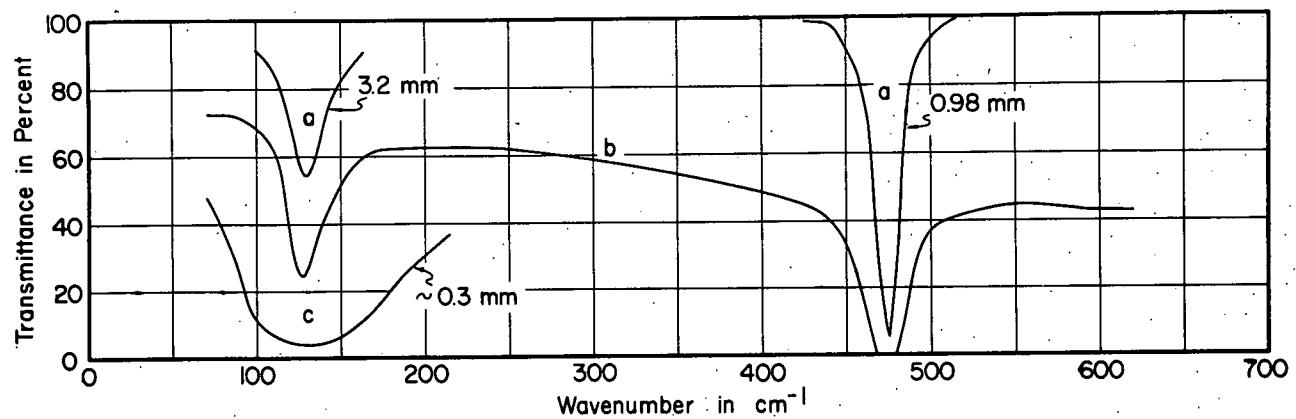


Figure 1

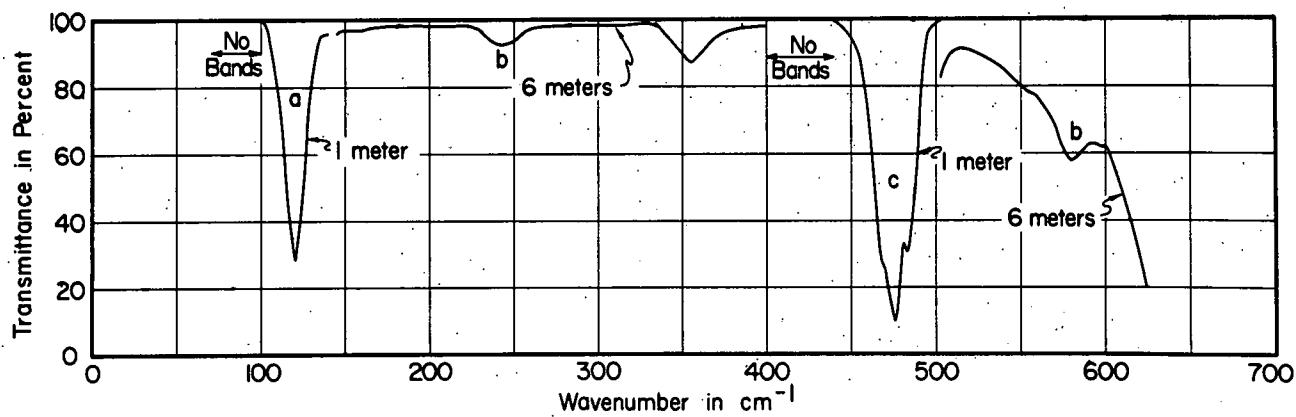


Figure 2