

## Bond Force Constants and Vibrations of Tetramethylmethane and Tetramethylsilicon

F. T. Wall and C. R. Eddy

Citation: [The Journal of Chemical Physics](#) **6**, 107 (1938); doi: 10.1063/1.1750196

View online: <http://dx.doi.org/10.1063/1.1750196>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/6/2?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[The Normal Vibrations of Molecules of the Tetramethylmethane Type](#)

J. Chem. Phys. **8**, 919 (1940); 10.1063/1.1750606

[Inertial Effects in the Skeletal Vibrations of Tetramethylmethane and Tetramethylsilicon](#)

J. Chem. Phys. **7**, 1113 (1939); 10.1063/1.1750381

[Bond Force Constants and Vibrational Frequencies of Some Hydrocarbons](#)

J. Chem. Phys. **5**, 813 (1937); 10.1063/1.1749945

[Vibration Spectra and Molecular Structure II. The Force Constants of the C–C and C–O Bonds in Organic Molecules](#)

J. Chem. Phys. **5**, 293 (1937); 10.1063/1.1750026

[A Relation Between Internuclear Distances and Bond Force Constants](#)

J. Chem. Phys. **2**, 128 (1934); 10.1063/1.1749433

---



## LETTERS TO THE EDITOR

*This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor*

*not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$3.00 per page) will not be made and no reprints will be furnished free.*

### Bond Force Constants and Vibrations of Tetramethylmethane and Tetramethylsilicon

In order to get information regarding the bond force constants of the molecules tetramethylmethane and tetramethylsilicon, we have treated some of the vibrations of these molecules by the normal coordinate method. These molecules possess a large number of frequencies, but only six for each are considered here. First the totally symmetric nondegenerate frequencies are rigorously treated and second, certain vibrations are calculated assuming that each methyl group behaves like a single atom.

The totally symmetric nondegenerate frequencies of  $C(CH_3)_4$  and  $Si(CH_3)_4$  can be conveniently treated by considering the symmetric vibrations of a single methyl group against a carbon or a silicon atom of infinite mass. This simplifying device can be used because the central atoms are not involved in the motion of those particular vibrations, except insofar as they move with the centers of gravity of the molecules. Assuming valence forces, the secular equations for the totally symmetric nondegenerate frequencies of  $C(CH_3)_4$  and  $Si(CH_3)_4$  are the same as the equation for the symmetric (Raman active) nondegenerate

TABLE I. *Tabulation of results.*

OBSERVED FREQUEN- CIES <sup>3, 4</sup>	CALCULATED FREQUENCIES	
	A	B
Tetramethylmethane		
331 cm <sup>-1</sup>		(331) cm <sup>-1</sup> (2)
415		383 (3)
732	(732) cm <sup>-1</sup>	(732) (1)
1248		1264 (3)
1452	(1452)	
2892	2894	
Tetramethylsilicon		
202		(202) (2)
239		220 (3)
598	(598)	(598) (1)
863		793 (3)
1427	1427	
2905	2893	
	$k_{C-H} = 4.76 \times 10^5$ dynes/cm	$k_{C-R} = 4.71 \times 10^5$ dynes/cm
	$k_\theta = 0.468$	$k_\theta(CR_4) = 0.321$
	$k_{C-C} = 5.14$	$k_{Si-R} = 3.14$
	$k_{Si-C} = 3.31$	$k_\theta(Si-R_4) = 0.120$

frequencies of ethane,<sup>1, 2</sup> except that the Hooke's law force constant for the carbon-carbon single bond of ethane is replaced by *one-half* the Hooke's law constant for the carbon-central atom bond of the tetramethyl molecule. The methods employed in arriving at the equation, except as noted, are the same as those described in an earlier paper.<sup>1</sup>

Assuming the methyl groups behave like single atoms of atomic weight 15, four vibrations for each of the molecules  $CR_4$  and  $SiR_4$  can be calculated. The equations used are the valence force type equations applicable to molecules of the methane type,  $XY_4$ . Of the four "methane-like" vibrations, one is totally symmetric and nondegenerate and accordingly was also considered by the first method of calculation described above.

The results of the numerical computations are given in Table I. Under column A are given frequencies calculated by the first described (rigorous) method and under column B, those computed by the second (approximate) method. The figures in parentheses following the numbers in column B are the degeneracies of the vibrations. Beneath the columns are given the values of the force constants used. The constant  $k_\theta$  refers to bending of angles in the methyl group, and the constants  $k_\theta(CR_4)$  and  $k_\theta(SiR_4)$  refer to bending of the angles in the molecules indicated for which the central atom forms a vertex. The constant  $k_{C-H}$  was taken from reference 1, while the other constants were determined by using those frequencies enclosed in parentheses.

The general agreement between calculated and observed results is good enough to justify the assignment of frequencies. Rank and Bordner,<sup>3</sup> by means of analogies, made different assignments for the higher triply degenerate frequencies here considered. However, our calculations seem to point fairly conclusively to the assignments in the table.

It will be observed that the values for  $k_{C-C}$  and  $k_{Si-C}$  are, respectively, greater than those for  $k_{C-R}$  and  $k_{Si-R}$ . This would be expected because of the failure to take into account interactions within the methyl groups in obtaining the values for the latter. This result is in accordance with recent observations in connection with ethane and related molecules.<sup>5</sup>

Department of Chemistry,  
University of Illinois,  
Urbana, Illinois,  
January 7, 1938.

F. T. WALL  
C. R. EDDY

<sup>1</sup> G. Glockler and F. T. Wall, J. Chem. Phys. **5**, 813 (1937).

<sup>2</sup> J. B. Howard, J. Chem. Phys. **5**, 442 (1937).

<sup>3</sup> Rank and Bordner, J. Chem. Phys. **3**, 248 (1935).

<sup>4</sup> Kohlrausch and Köppl, Zeits. f. physik. Chemie **B26**, 209 (1934); D. H. Rank, J. Chem. Phys. **1**, 572 (1933); Kohlrausch and Barnés, Anales Fisica y Química **30**, 733 (1932).

<sup>5</sup> F. T. Wall, J. Am. Chem. Soc. **60**, 71 (1938).

### Alterations in the Infrared Absorption Spectrum of Water in Gelatin

The absorption spectra in the region 1–2.5 $\mu$  have been recorded in the four following instances with a self-registering instrument of slit widths equivalent to 0.003 $\mu$ : (1) a 0.20 mm specimen of gelatin dried to constant weight at 120°C; (2) a portion of the same specimen after it had absorbed an amount of water equal to 35.7 percent of the total weight and swollen to a thickness of 0.28 mm; (3) a 0.09 mm cell of water at room temperature; (4) a 0.17 mm cell of water. The spectrum of (1), in spite of the complexity of the protein molecules involved, can readily be interpreted in terms of CH and NH vibrations; any absorption by OH groups or by possible residual water is not observable. Although there may be slight changes in the NH bands, the main differences in the percentage transmission curves obtained from the reduction of (1) and (2) and of (3) and (4) can fairly certainly be ascribed to alterations in the water spectrum. Since equal effective thicknesses (0.08 mm) of water were involved, these alterations must arise from differences in the structure or in the environment of the water. The following modifications are observed, and provisional causes are assigned.

(a) The 1.44 $\mu$  band ( $\nu_{\pi} + \nu_{\sigma}$ ). The maximum absorption is slightly shifted to a longer wave-length in the gelatin specimen, apparently owing to the partial or complete removal of the short wave portion of the band usually associated with the water vapor molecule. This indicates that most or all of the water molecules are bound molecules. Absorption at the maximum is increased but total absorptions in the two instances are comparable owing to a diminution of continuous absorption in the 1.65 $\mu$  region.

(b) The 1.96 $\mu$  band ( $\nu_{\pi} + \nu_{\delta}$ ). The location of the maximum is practically unaltered. This need not be construed as indicating that unbound molecules are present. For, since this band is a combination of the fundamental deformation frequency (6.1 $\mu$ ) and the fundamental asymmetric valence frequency (2.7 $\mu$ ), it should show the characteristics of both fundamentals; and the temperature effects and the hydration studies of Ganz,<sup>1</sup> as well as vapor-liquid band shifts, clearly show opposite behaviors in these two bands. A statement analogous to the last sentence of (a) can also be made in connection with this band.

(c) The 1.79 $\mu$  band ( $\nu_{\pi} + \nu_{\delta} + \nu_R$ ). This band, whose frequency differs from that of 1.96 $\mu$  by an amount equal to the frequency of "hindered rotation,"  $\nu_R$ ,<sup>2</sup> is stronger and sharper than in pure water. This seems to indicate, first, that at least some of the water molecules are bound in such a way as to permit hindered rotation about the axis of least inertia and, second, that the average field of potential energy is equivalent to that in pure water but that it is more homogeneous.

(d) A new 1.35 $\mu$  band ( $\nu_{\pi} + \nu_{\sigma} + \nu_R$ ). This band is analogous to the 1.79 $\mu$  band and is doubtless observable in the gelatin specimen but not in pure water because of a greater homogeneity in the field.

(e) The 2.4 $\mu$  region. The absorption in this broad region,

more intense in the gelatin instance, is probably to be interpreted in terms of  $\nu_{\pi} + \nu_R$ .

(f) The absorption bands at 4.7 $\mu$  ( $\nu_{\delta} + \nu_R$ ) and 20 $\mu$  ( $\nu_R$ ) should, if observed in gelatin, be sharper than in pure water.

It is the authors' opinion that the absorption at 3 $\mu$  found by Buswell, Krebs and Rodebush<sup>3</sup> in a gelatin specimen dried for 14 hours at 122°C is caused by protein NH groups rather than by residual water.

JOSEPH W. ELLIS  
JEAN BATH

University of California,  
Los Angeles, California,  
January 13, 1938.

<sup>1</sup> Ganz, Ann. d. Physik. **28**, 445 (1937).

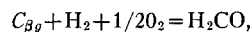
<sup>2</sup> Ellis, Phys. Rev. **38**, 693 (1931); Cartwright, Phys. Rev. **49**, 470 (1936).

<sup>3</sup> Buswell, Krebs and Rodebush, J. Am. Chem. Soc. **59**, 2603 (1937).

### Errata: Thermodynamic Functions of the Chloro- and Bromomethanes, Formaldehyde and Phosgene

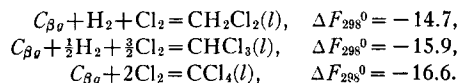
(J. Chem. Phys. **6**, 25 (1938))

Because of a systematic error the values of  $-(F^0 - E_0^0)/T$  in Tables VI and VIII are too large by 1.987 cal./°K mole. The value of  $\Delta E_0^0$  for the reaction



as calculated from the work of Newton and Dodge should be -26.0 kcal./mole instead of -27.0 kcal./mole. This leads to a final value of  $\Delta E_0^0$  for this reaction of -26.5 kcal./mole in place of -27.2 kcal./mole.

For the free energy of formation of the liquid chloro-methanes



The free energies of formation of the gases are given in Table X.

TABLE X.  $\Delta F^0$  of ideal gases.

T	H <sub>2</sub> CO	COCl <sub>2</sub>	CH <sub>3</sub> Cl	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>	CCl <sub>4</sub>
298.1	-25.2	-49.7	-13.0	-14.3	-15.1	-15.5
350	-24.8	-49.1	-11.8	-13.1	-13.7	-13.8
406	-24.4	-48.4	-10.6	-11.3	-12.3	-12.1
500	-23.5	-47.2	-8.0	-9.2	-9.5	-8.9
600	-22.5	-45.9	-5.4	-6.6	-6.7	-5.5
700	-21.5	-44.7	-2.6	-4.0	-3.8	
800	-20.5	-43.4	+0.1	-1.3	-0.7	
900	-19.4	-42.0	+3.0			
1000	-18.3		+5.8			
1100	-17.2		8.7			
1200	-16.1		11.5			
1300	-15.0					
1400	-13.9					
1500	-12.8					

D. P. STEVENSON  
J. Y. BEACH

Princeton University,  
Princeton, N. J.,  
January 14, 1938.