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Tetrahydrofuran: vibrational assignment, chemical thermodynamic properties, and vapor pressure

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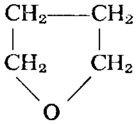
A vibrational assignment is proposed for tetrahydrofuran and used with available structural, energetic, and calorimetric data to compile a table of the chemical thermodynamic properties. Determinations of the vapor pressure also are reported.

1. Introduction

Tetrahydrofuran,



exhibits pseudo-rotation hindered by a very low barrier. The energy levels for pseudo-rotation and the rotational constants of the molecule are known from the microwave studies of Engerholm, Luntz, Gwinn, and Harris.(1) The only further requirement for calculating thermodynamic functions by methods of statistical mechanics is an assignment of the fundamental vibrational wavenumbers.

2. Vibrational assignment

The molecular spectra of tetrahydrofuran at room temperature(2–8) have broad, diffuse bands because of unresolved pseudo-rotational fine structure, a circumstance that makes difficult their interpretation for purposes of a vibrational assignment. However, the infrared spectrum of the crystalline state at low temperatures(8, 9) has sharp well-resolved bands expected for a substance with rigid molecules; apparently pseudo-rotation is prevented by crystal forces as it is in Crystals III of cyclopentane.(10, 11)

As a guide to interpreting the molecular spectra, normal coordinate calculations were made for the puckered configuration of C_2 point-group symmetry that the molecule assumes during the course of pseudo-rotation. Approximations in the force field were similar to those used earlier(10) for cyclopentane; torsional forces about single bonds were neglected as also were small interactions that apply strictly to the staggered orientation of CH_2 groups. Values of force constants were based on the work of Snyder and Zerbi(12) on aliphatic ethers. The details of this approximate calculation may be obtained from the author upon request. The calculated values of the wavenumbers are listed in table 1, along with the observed values assigned by reference to them. Observed values selected for use in the statistical thermodynamic calculations are in boldface type; braces denote assumed unresolved bands.

TABLE 1. Calculated and observed wavenumbers σ for tetrahydrofuran [a, b]

σ(calc)/cm^{-1}		σ(obs)/cm^{-1}
97	B	Pseudo-rotation
203	A	**278** R l; about 278 IR v
604	B	**596** R l; 584 IR c
652	A	**654** IR v; 651 R l; 654 IR l; 666 IR c
883 884	A B	**821** IR v; 838 IR c
917	A	**881** IR c d
938	A	**912** IR v; 913 R(p) l; 908 IR l; 915 IR c d
959	B	**964** R l; 954 IR c
1029	B	**1029** R l; 1030 IR l; 1043 IR c
1074	A	**1076** IR v; 1071 R l; 1076 IR l; 1058 IR c
1124	A	**1114** R l; 1108 IR c
1136 1144 1153	B A A	**1150** IR c
1194	B	**1177** IR v; 1174 R l; 1177 IR l; 1179 IR c
1217 1226	B A	**1238** IR v; 1234 R l; 1234 IR l; 1241 IR c
1268	B	**1289** IR l; 1315 IR c d
1313	A	**1339** IR c
1326	B	**1366** IR v; 1364 IR l; 1368 IR c
1479	A	1458 IR v; **1452** R l; 1461 IR l; 1441 IR c
1484	B	**1486** R l; 1476 IR c d
1524 1525	B A	**1517** IR c[c]
2858 2859 2859 2862	B A B A	**2847** IR v
		(C—H stretching bands in R l, IR l, and IR c not tabulated)
2944 2945 2949 2954	B A B A	**2970** IR v

[a] Symbols used: A and B, species of point group C_2; R, Raman; IR, infrared; v, vapor; l, liquid; c, crystals; (p), polarized; d, doublet from crystal field splitting, Fermi resonance, or other cause.

[b] Bands in IR c not assigned as fundamentals have plausible explanations as follows: 1421, 584 + 838 = 1422; 1506[c], 666 + 838 = 1504; 1541[c], 584 + 954 = 1538; 1558[c], 666 + 881 = 1547.

[c] Observed in this laboratory.

3. Thermodynamic functions

Thermodynamic functions were calculated by standard methods. From the work of Engerholm *et al.*,⁽¹⁾ the product of the principal moments of inertia is 2.978×10^{-114} g^3 cm^6. Engerholm *et al.*⁽¹⁾ have listed the first 15 energy levels for pseudo-rotation. Additional levels needed for statistical thermodynamic calculations were estimated to provide a smooth continuation of those listed and to approach the distribution for free pseudo-rotation with increasing energy. The formula used was:

$$E/\mathrm{cm}^{-1} = 3.25n^2+5.489+9.786/n, \qquad (n > 7),$$

where n is an index that numbers pairs of effectively doubly degenerate levels.

Calculated values of heat capacity are compared in table 2 with observed values.⁽¹³⁾ No empirical anharmonicity corrections are included in the calculated values, as agreement within the estimated uncertainty of 0.2 per cent is obtained without such corrections. The calculated values of the thermodynamic functions for selected temperatures up to 1000 K are listed in columns 2 to 6 of table 3. The experimental value of Pell and Pilcher⁽¹⁴⁾ for ΔH_f° (298.15 K) and values of the thermodynamic functions of C(c, graphite), H_2(g), and O_2(g)⁽¹⁵⁾ were used in computing values of ΔH_f°, ΔG_f°, and $\log_{10} K_f$; they are listed in columns 7 to 9 of table 3.

TABLE 2. Calculated and observed heat capacity C_p of tetrahydrofuran
(cal = 4.184 J)

T/K	328.2	349.2	399.2	449.2	500.2
			C_p/cal K^{-1} mol^{-1}		
Translation and overall rotation	7.949	7.949	7.949	7.949	7.949
Vibration	11.378	12.876	16.415	19.792	22.992
Pseudo-rotation	1.004	1.003	1.001	0.999	0.998
Total, calculated	20.33	21.83	25.36	28.74	31.94
Observed	20.34	21.85	25.37	28.79	31.96
Observed − calculated	0.01	0.02	0.01	0.05	0.02

4. Vapor pressure

The vapor pressure was determined by comparative ebulliometry⁽¹⁶⁾ with a sample purified from commercial material in this laboratory. The difference between the boiling and condensation temperatures of this sample at 1 atm was 0.009 K. The results are tabulated in table 4 and compared with values calculated from the Cox equation:

$$\log_{10}(p/760\ \mathrm{Torr}) = \log_{10}(p/101.325\ \mathrm{kN\ m^{-2}}) = A(1-339.114\ \mathrm{K}/T),$$

in which $\log_{10} A = 0.829\,231 - 6.77774 \times 10^{-4}\,(T/\mathrm{K}) + 6.91492 \times 10^{-7}\,(T/\mathrm{K})^2$.

TABLE 3. Chemical thermodynamic properties of tetrahydrofuran in the ideal gas state [a]

T / K	$-(G^\circ - H_0^\circ)/T$ / cal K^{-1} mol^{-1}	$(H^\circ - H_0^\circ)/T$ / cal K^{-1} mol^{-1}	$H^\circ - H_0^\circ$ / kcal mol^{-1}	S° / cal K^{-1} mol^{-1}	C_p° / cal K^{-1} mol^{-1}	ΔH_f° [b] / kcal mol^{-1}	ΔG_f° [b] / kcal mol^{-1}	$\log_{10} K_f$ [b]
0	0	0	0	0	0	−37.37	−37.37	∞
200	56.29	9.997	1.999	66.29	12.46	−41.89	−27.13	29.64
273.15	59.57	11.17	3.051	70.74	16.55	−43.50	−21.47	17.18
298.15	60.57	11.69	3.193	72.26	18.22	−44.03	−19.43	14.24
300	60.64	11.73	3.519	72.37	18.35	−44.07	−19.28	14.04
400	64.35	14.27	5.708	78.62	25.42	−46.00	−10.71	5.85
500	67.84	17.16	8.583	85.00	31.93	−47.56	−1.70	0.74
600	71.23	20.10	12.06	91.33	37.44	−48.77	7.59	−2.76
700	74.54	22.91	16.04	97.45	42.03	−49.69	17.06	−5.33
800	77.78	25.55	20.44	103.3	45.89	−50.34	26.64	−7.28
900	80.93	28.00	25.20	108.9	49.16	−50.79	35.97	−8.73
1000	83.99	30.26	30.26	114.3	51.94	−51.04	45.99	−10.05

[a] To retain internal consistency, some values are given to one more decimal place than is justified by the absolute accuracy.

[b] The standard enthalpy, Gibbs energy, and common logarithm of the equilibrium constant of formation by the reaction: $4C(c, graphite) + 4H_2(g) + \frac{1}{2}O_2(g) = C_4H_8O(g)$.

TABLE 4. Vapor pressure p of tetrahydrofuran at temperature t_t and also the temperature t_w at which water has the same vapor pressure

t_w/°C [a]	t_t/°C [a]	p(obs)/Torr [b]	{p(obs) − p(calc)}/Torr
60.000	23.139	149.41	0.02
65.000	28.362	187.57	−0.01
70.000	33.620	233.72	0.00
75.000	38.917	289.13	−0.02
80.000	44.251	355.22	−0.03
85.000	49.620	433.56	0.00
90.000	55.029	525.86	0.01
95.000	60.475	633.99	0.05
100.000	65.965	760.00	−0.02
105.000	71.489	906.06	0.01
110.000	77.054	1074.6	0.0
115.000	82.659	1268.0	0.0
120.000	88.300	1489.1	0.0
125.000	93.980	1740.8	0.1
130.000	99.700	2026.0	0.1

[a] IPTS 1948.

[b] From vapor pressures for water of Osborne, Stimson, and Ginnings.(17)

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