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Note

Thermodynamic properties of allyl mercaptan

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The vapor infrared and liquid Raman spectra of allyl mercaptan (2-propen-1-thiol) have been recently reported by Hsu[1]. His vibrational assignments have been based on the structure determined from microwave studies by Sastry et al.[2], who have shown the existence of only the gauche form of allyl mercaptan.

TABLE 1

VIBRATIONAL SPECTRUM OF ALLYL MERCAPTAN[a, b]

Assignment	*Frequency*
vinyl CH_2 stretching	3098
vinyl C–H stretching	3021
asymmetric CH_2 stretching	2996
vinyl CH_2 stretching	2973
symmetric CH_2 stretching	2940
S–H stretching	2600
C=C	1646
methylene CH_2 deformation	1441
vinyl CH_2 deformation	1413
=CH– rocking	1287
methylene CH_2 wagging	1243
$=CH_2$– wagging	1208
methylene CH_2 twisting	1075
$-CH=CH_2$ twisting	995
$-CH=CH_2$ wagging	929
C–C stretching	918
CSH bending	794
methylene CH_2 rocking	728
C–S stretching	669
=CH– out-of-plane deformation	616
C–C–C skeletal deformation	410[c]
CCS bending	288[c]
thiol torsion	(190)[c]
CH_2SH torsion	(100)[c]

[a] Taken from ref. 1. [b] Frequencies in cm^{-1}. [c] Estimated from liquid Raman spectrum from ref. 1.

TABLE 2

THERMODYNAMIC PROPERTIES OF ALLYL MERCAPTAN[a]

Temp. (K)	$C_p°$	$S°$	$-(G° - H_{298}°)/T$	$H° - H_{298}°$
100.0	11.52	57.45	88.85	−3139.3
200.0	15.78	66.71	75.61	−1779.8
298.15	20.61	73.89	73.89	0.0
300.0	20.71	74.03	73.90	41.3
400.0	25.45	80.65	74.76	2353.6
500.0	29.48	86.78	76.56	5105.6
600.0	32.81	92.45	78.74	8224.0
700.0	35.59	97.73	81.08	11646.7
800.0	37.96	102.64	83.47	15326.4
900.0	40.00	107.23	85.86	19225.9
1000.0	41.76	111.54	88.22	23315.0
1100.0	43.29	115.59	90.52	27568.0
1200.0	44.61	119.42	92.77	31963.0
1300.0	45.76	123.03	94.96	36481.2
1400.0	46.75	126.46	97.09	41106.2
1500.0	47.62	129.72	99.43	45824.3
1600.0	48.38	132.09	101.17	50623.4
1700.0	49.04	135.77	103.11	55493.5
1800.0	49.62	138.59	105.01	60425.7
1900.0	50.14	141.29	106.85	65412.7
2000.0	50.59	143.87	108.63	70448.0
2100.0	51.00	146.35	110.37	75526.1

[a] The units for $C_p°$, $S°$, and $-(G° - H_{298}°)/T$ are cal deg^{-1} mol^{-1}; and the units for $H° - H_{298}°$ are cal mol^{-1}.

In the present communication, the specific heat, entropy, enthalpy, and Gibbs free energy of the gauche isomer of allyl mercaptan have been calculated at selected temperatures using fundamental frequencies of vibration and structural parameters.

An ideal gas, rigid rotor, harmonic oscillator at 1 atm pressure has been used as the model for the calculations, which have been performed using the well-known methods[3] of statistical mechanics. The atomic weights[4] C = 12.011, H = 1.0079, and S = 32.064, and the physical constants recommended by Taylor et al.[5] have been employed. The rotational constants A = 20041.68 mHz sec^{-1}, B = 2795.72 mHz sec^{-1}, and C = 2701.10 mHz sec^{-1} have been taken from the work of Sastry et al.[2], while the vibrational assignments listed in Table 1 are those given by Hsu[1].

The results are shown in Table 2. The actual quantities reported correspond to the definitions given in the JANAF tables[6].

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