Thermodynamic Properties of SF_4 and SOF_4

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The Raman and infrared spectra of SF_4 molecule have been investigated by Dodd et al. [1]. They have concluded that this molecule belongs to the point group C_{2v} having nine fundamental frequencies falling under four species. The potential constants of this molecule have been calculated by Venkateswarlu and Pillai [2] by the Wilson's group theoretical considerations.

Molecular parameters	Principal moments of inertia amu Å^2	Type	Observed frequencies
S–F = 1.58 Å	I_{xx} = 78.1901	A_1	889 cm^{-1}
$\measuredangle$ F$_1$–S–F$_4$ =	I_{yy} = 142.3021		235
$\measuredangle$ F$_1$–S–F$_2$ = 90°	I_{zz} = 125.6228		557
			715
		A_2	645
		B_1	532
			867
		B_2	463
			728

Table 1. Molecular parameters, principal moments of inertia and the observed frequencies of SF_4.

Goggin et al. [3] have studied the infrared and Raman spectra of the SOF_4 molecule. Of the three models suggested for the structure of this molecule, they have concluded that the structure is derived from a trigonal bipyramidal arrangement similar to that of SF_4 with the oxygen atom in the equatorial position and the point group C_{2v}. It has twelve fundamental frequencies falling under four species. The normal coordinate treatment has been carried out and the potential constants have been evaluated using Wilson's $F-G$ matrix method by Radhakrishnan [4].

Molecular parameters	Principal moments of inertia amu Å^2	Type	Observed frequencies
S–F$_1$ = S–F$_3$ = 1.56 Å	I_{xx} = 124.8238	A_1	1367 cm^{-1}
			797
$\measuredangle$ F$_3$–S–F$_4$ = $\measuredangle$ F$_3$–S–O = 120°	I_{yy} = 147.9430		741
$\measuredangle$ F$_1$–S–O = $\measuredangle$ F$_1$–S–F$_4$ = 90°	I_{zz} = 161.8344		589
			309
		A_2	189
		B_1	933
			643
			555
		B_2	933
			479
			272

Table 2. Molecular parameters, principal moments of inertia and the observed frequencies of SOF_4.

Temp.	$(H^0 - E_0^0)/T$	$-(F^0 - E_0^0)/T$	S^0	C_p^0
100° K	8.2139	47.6541	55.8679	9.0175
200	9.5186	53.6946	63.2130	12.9439
273.16	10.8611	56.8530	67.7141	16.0352
300	11.3732	57.9001	69.2733	17.0159
400	13.1504	61.4179	74.5683	19.7803
500	14.8010	64.6483	79.4493	21.6528
600	16.0342	67.4328	83.4670	22.7621
700	16.9356	69.8466	86.7822	23.4141
800	17.7776	72.1598	89.9374	23.9321
900	18.4862	74.2993	92.7855	24.3053
1000	19.0810	76.2786	95.3596	24.5784
1100	19.5849	78.0917	97.6766	24.7864
1200	20.0203	79.8278	99.8481	24.8987
1300	20.4146	81.4643	101.8789	25.0738
1400	20.7546	82.9994	103.7540	25.1765
1500	21.0561	84.4326	105.4887	25.2594

Table 3. Heat content, free energy, entropy and heat capacity for SF_4 molecule for the ideal gaseous state at one atmospheric pressure.

The values are in cal. deg.$^{-1}$ mole^{-1} and E_0^0 is the energy of one mole of perfect gas at absolute zero temperature.

[1] R. E. Dodd, L. A. Woodward and H. L. Roberts, Trans. Faraday Soc. **52**, 1052 [1956].

[2] K. Venkateswarlu and K. Pillai, Optics and Spectroscopy **11**, 26 [1961].

[3] P. L. Goggin, H. L. Roberts and L. A. Woodward, Trans. Faraday Soc. **57**, 1877 [1961].

[4] M. Radhakrishnan, J. Mol. Spectroscopy, in press.

Temp.	$(H^0 - E_0^0)/T$	$-(F^0 - E_0^0)/T$	S^0	C_p^0
100° K	8.6152	48.9487	57.5639	10.3549
200	10.7658	55.5456	66.3114	15.5303
273.16	12.7857	59.5270	72.3127	19.1679
300	13.1548	60.3629	73.5177	20.1112
400	15.3264	64.4525	79.7789	23.3785
500	17.1753	68.0888	85.2640	25.5849
600	18.7139	71.3690	90.0829	27.0862
700	19.9764	74.3085	94.2849	28.1263
800	21.0533	77.0694	98.1227	28.8749
900	21.9543	79.6085	101.5628	29.4204
1000	22.7066	81.9356	104.6422	29.8236
1100	23.3763	84.1243	107.5006	30.1439
1200	23.9425	86.1593	110.1018	30.3868
1300	24.4743	88.1914	112.6662	30.5918
1400	24.9271	90.0521	114.9792	30.7536
1500	25.2884	91.6956	116.9840	30.8718

Table 4. Heat content, free energy, entropy and heat capacity for SOF_4 molecule for the ideal gaseous state at one atmospheric pressure.

The values are in cal. deg.$^{-1}$ mole^{-1} and E_0^0 is the energy of one mole of perfect gas at absolute temperature.

In the present investigation the thermodynamic properties such as heat content, free energy, entropy and heat capacity, of these molecules have been calculated using the fundamental frequencies reported by the earlier authors. The calculation is for the ideal gas at one atmospheric pressure assuming a rigid-rotator harmonic oscillator model. The influence of nuclear spin and anharmonicity has been omitted. The molecular parameters, observed frequencies and calculated principal moments of inertia are given in Tables 1 and 2. The symmetry number used for this calculation for both molecules is 2. The values obtained for the thermodynamic properties of SF_4 and SOF_4 molecules are presented in Tables 3 and 4.

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