Mean Amplitudes of Vibration for Sulphur Tetrafluoride

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The mean amplitudes of vibration for sulphur tetrafluoride are recalculated from recent spectroscopic data. Some controversies among previous results from literature are pointed out, and the spectroscopic values are compared with those from electron diffraction.

In this work a new set of mean amplitudes of vibration for sulphur tetrafluoride from spectroscopic data is communicated. Such calculations have been performed previously by Chantry and Ewing[1] and Krishna Pillai et al.[2] The results from both of these works are quoted in Cyvin's book.[3] They are found to be rather controversial, although they are based on the same vibrational frequency assignment from Dodd et al.[4] Since then the infrared spectrum of sulphur tetrafluoride has been reinvestigated by Levin and Berney,[5] who furnished another set of calculated mean amplitudes of vibration. All these sets have been compared with observed mean amplitudes of vibration from the electron diffraction work of Kimura and Bauer.[6] As a matter of fact Levin and Berney[5] partly used the observed mean amplitudes[6] as a constraint in their force-constant calculations. In particular they used the $F(eq)F(ax)$ mean amplitude as a guide for their assignment of the infrared-inactive A_2 frequency. Here $F(eq)$ and $F(ax)$ refers to an equatorial and an axial F atom, respectively.

In the present work the set of force constants from Levin and Berney[5] was used as the initial set, which was adapted to the tentatively standardized symmetry coordinates reported elsewhere.[7] The structural parameters were taken from Tolles and Gwinn,[8] according to the quotation of Levin and Berney.[5] The force-constant set was adjusted to fit exactly the observed frequencies according to the Levin-Berney[5] assignment. This final force field in terms of the symmetrized F matrix is given in Table 1. The resulting mean amplitudes of vibration at absolute zero and 298°K are shown in Table 2, together with the values from Levin and Berney[5] and the electron diffraction results from Kimura and Bauer.[6]

The present results are seen to be comparable to those of Levin and Berney[5] (see Table 2), as could be expected. By some unknown reason, however, there

Table 1. F matrix elements for sulphur tetrafluoride (mdyne/Å).

A_1	1	2	3	4	A_2
1	6.083				1.430
2	−0.006	3.472			
3	0.010	−0.002	0.156		
4	0.310	0.242	0.016	0.888	
B_1	1	2	B_2	1	2
1	3.584		1	3.727	
2	0.250	0.881	2	0.333	0.317

Table 2. Mean amplitudes of vibration for sulphur tetrafluoride (Å).

	Spectroscopic			Electr.diff.
	Ref. 5	Present		Ref. 6
SF$_4$		$T=0$	298°K	
S−F(eq)	0.043	0.042	0.043	0.041 ± 0.005
S−F(ax)	0.050	0.044	0.046	0.047 ± 0.005
F(eq)F(eq)	0.114	0.077	0.113	0.068 ± 0.001
F(ax)F(ax)	0.070	0.056	0.060	0.059 ± 0.001
F(eq)F(ax)	0.077	0.060	0.071	0.067 ± 0.005

is a significant discrepancy for the F(ax)F(ax) distance. The present result shows much better agreement with the electron diffraction value for the same distance, and is also comparable to the earlier result of Chantry and Ewing.[1] Krishna Pillai et al.[2] have simply omitted this distance in their calculations without giving any reason for it. The present results show good agreement with the electron diffraction values also for the other distances (see Table 2), except for the F(eq)F(eq) distance, for which we must confirm the statement of Levin and Berney [5] about a discrepancy between calculated and observed values.

It is believed that the present results of mean amplitudes of vibration for sulphur tetrafluoride are about as good as can be achieved with the present knowledge of spectral data. But it is also believed that revised frequency assignments may possibly be awaited, and would make a future recalculation of the mean amplitudes desirable.

In order to facilitate a possible future discussion of mean amplitudes for sulphur tetrafluoride the symmetry properties of the various types of distances were studied. Table 3 shows the developed symmetric structures, which indicate

Table 3. Symmetric structures for the various distance types in a molecule with the C_{2v} structure of sulphur tetrafluoride.

	Distance	Symmetric structure[a]
1	S—F(eq)	$\Gamma_1 = A_1 + B_2$
2	S—F(ax)	$\Gamma_2 = A_1 + B_1$
3	F(eq)F(eq)	$\Gamma_3 = A_1$
4	F(ax)F(ax)	$\Gamma_4 = A_1$
5	F(eq)F(ax)	$\Gamma_5 = A_1 + A_2 + B_1 + B_2$

[a] Consistent with the orientation of cartesian axes specified in Ref. 7.

the various species from which the normal modes contribute to a given mean amplitude of vibration.

A special reason for undertaking this work is the existence of a recent electron diffraction reinvestigation of thionyl tetrafluoride.[9] The present results seem to be a useful starting point in the scheduled studies of mean amplitudes for thionyl tetrafluoride.

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