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Bond lengths and thermal vibrations in orthorhombic sulfur. By S. C. ABRAHAMS, *Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey, U.S.A.*

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In the preceding paper by Caron & Donohue (1965), hereafter CD, an attempt is made to correct the bond lengths in orthorhombic sulfur for the apparent motions of the atoms due to thermal vibration. This note discusses some of the assumptions made by CD and concludes that the corrections should be regarded with caution.

It may first be noted that the 'uncorrected' position coordinates obtained by CD differ from those of Abrahams (1961) and Cooper, Bond & Abrahams (1961) by no more than 0.0002, or 0.003 Å. The S-S bond lengths in the two refinements differ by a maximum of 0.005 Å, with a difference in mean bond length of only 0.001 Å. There are, however, several significant differences among the β_{ij} , e.g. the value obtained by CD for β_{33} of S(1) differs by 7.8σ , for β_{33} of S(4) by 4.0σ and for β_{13} of S(1) by 3.5σ from the earlier refinement. It is likely that these significant differences are caused by *systematic error* in the observed structure factors. The data selection by CD would then have an effect similar to that caused by changing the weights. The large effects of one such change on the apparent thermal vibrations have previously been demonstrated (Abrahams, 1961).

The systematic errors in the 1955 orthorhombic sulfur data can be fairly accurately estimated for the cases of absorption and anomalous dispersion. Lack of correction for these two effects makes the high angle measured structure factors systematically too large, by a maximum of 14% in $|F|$. Additional sources of error include the average variation of 7% in $|F|$ previously noted (Abrahams, 1955), the multi-wavelength contributions to each reflection, the approximations made in relating the density of a photographic spot to an integrated intensity and also the approximate extinction correction made by CD. In view of these errors in the structure factors, it is to be expected that the resulting 'thermal vibration' parameters, adjusted by the least-squares analysis to give the best fit, will reflect these errors. The standard deviations computed in the analysis are hence indicators of *precision* rather than *accuracy*.

The β_{ij} and their standard deviations are assumed by CD to be unaffected by these systematic errors. They further assume the S_8 molecule to be rigid. They then derive values for the translational and librational amplitudes of vibration corresponding to these β_{ij} . The numerical values obtained are 0.189, 0.213, 0.105 Å, and 5.6, 5.2, 2.5° respectively along a set of principal axes.

A very recent normal coordinate treatment of S_8 has been made by Scott, McCullough & Kruse (1964) using new far-infrared spectral data. The vibrational assignment was consistent with all the well established features of the observed spectra. As part of this analysis (Scott, 1964), the vibrational mean square amplitude matrix was evaluated. From this, the following amplitudes are obtained:

0.049 Å for the mean displacement of the S-S bond distance from its equilibrium value,

3.26° for the mean displacement of the S-S-S bond angle from its equilibrium value, and

4.93° for the mean displacement of the S-S-S-S dihedral angle from its equilibrium value. These data unequivocally establish the *non-rigid* nature of the S_8 molecule. It is interesting to note that CD's 'librational' parameters are of magnitude comparable to the internal molecular vibrations. If this is not coincidental, it could be the result of forcing somewhat unreliable data to fit an improper model. In either case, bond length 'corrections' based on the erroneous rigid-body model are of dubious physical significance.

A correct analysis of the thermal vibrations in orthorhombic sulfur must clearly await a remeasurement of all the structure factors in which the systematic errors are deliberately minimized. In addition, analysis of the resulting β_{ij} must allow for the internal molecular vibrations measured by Scott, McCullough & Kruse (1964).

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