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VIBRATIONAL SPECTRA AND ROTATIONAL ISOMERISM OF BIS (TRIFLUOROMETHYL) OXALATE

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As part of a study on the vibrational properties of perfluorinated methyl esters of carboxylic acids [1], detailed results concerning bis(trifluoromethyl) oxalate (BTFMO) [2] are now reported.

Present results include IR spectra of the substance as gas, solid, matrix isolated and in CCl_4 solution. Raman spectra of the solid and liquid substance are reported as well. The IR (gaseous) and Raman (liquid) spectra of 13C partially substituted BTFMO are also presented. Assignments are proposed for the spectral features.

Interestingly, new Raman bands appear when going from the solid to the liquid phase. The intensities of some of these new bands show a temperature dependence.

In the spectrum of the gaseous phase, new bands are also seen in comparison with the spectrum of the solid but no clear temperature dependence could be noted in this case. These facts could be taken as evidences for the existence of at least two conformers in the fluid phases, the most stable having apparently trans-planar structure. Upon melting it isomerizes supposedly by the rotation of both CF_3O groups in the same amount but in opposite senses out of the skeletal plane.

The comparison of the IR and Raman spectra of the solid shows that the mutual exclusion rule is operative, suggesting a centrosymmetric structure for the molecule in the solid phase (point group symmetry C_{2h}), in accordance with the mentioned trans-planar structure.

1 E.L.Varetti and P.J.Aymonino, J.Mol.Struct.1,39(1967-68); E.L.Varetti and P.J.Aymonino, J.Mol.Struct.7,155(1971).
2 E.L.Varetti and P.J.Aymonino, Anales Asoc.Quím.Argentina 55,153(1967).