THE CHARACTERISATION OF MOLECUAR CESIUM BROMATE BY MATRIX ISOLATION IR SPECTROSCOPY

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It has been known for many years that inorganic oxo-anion salts can exist as stable discrete molecules in the vapor phase, and that these species often play an important role in high temperature transport and corrosion processes. Such species include alkali metal chromates and molybdates[1], and also oxo-halides such as chlorates[2] and iodates[3]. In the case of these latter species, it can be envisaged that these MXO_n species may have the capacity to act as *molecular sinks* for the removal of halogen oxides from the atmosphere. The special circumstances which would favor this process are firstly a stable salt molecule, and secondly, a source of alkali metal (as atoms or oxide molecules). As indicated above, the first of these requirements has already been demonstrated[2,3], whilst more recently, it has been established that the requisite metal species are likely to be present as result of meteor ablation[4]. The possibility therefore exists that harmful ClO_x species may be partially removed from the atmosphere by reactions such as: $MO_2 + ClO \rightarrow MClO_3$ where M is an alkali metal.

This paper describes the first characterisation of molecular cesium bromate, produced by vacuum sublimation of the parent salt. Identification is based upon IR selection rules, bromine isotope studies, and a comparison with the previously known molecular chlorates and iodates.

The significance of this molecule is that in addition to its intrinsic interest as a new chemical species, it may play a role in the removal of the equally damaging BrO_x molecules from the atmosphere by virtue of the analogous reaction : $MO_2 + BrO \rightarrow MBrO_3$.

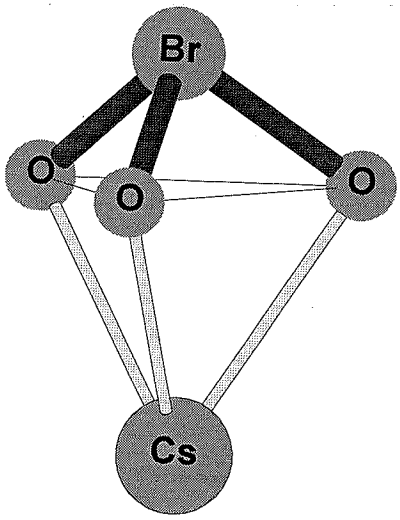
In order to assist future thermodynamic modelling of this system, this work also provides estimates of molecular geometry and all vibrational frequencies. The shape of molecular $CsBrO_3$ is indicated in the Figure below.

1 I. R. Beattie, J. S. Ogden and D. D. Price, *J. Chem. Soc. Dalton*, 505 (1982).

2 I. R. Beattie and J. E. Parkinson, *J. Chem. Soc. Dalton Trans.* 1185 (1983), L. Bencivenni, H. M. Nagarathna, K. A. Gingerich and R. Teghil, *J. Chem. Phys.*, 81, 3415, (1984)

3 K. R. Biggs, R. A. Gomme, J. T. Graham and J. S. Ogden, *J. Phys. Chem.* 96, 9738 (1992)

Figure



Table

Observed Vibration Frequencies (cm^{-1}) for Molecular $CsBrO_3$ isolated in Low Temperature Argon Matrices

Frequency	Assignment
806.0	^{79}Br-O, E stretch
804.0	^{81}Br-O, E stretch
790.5	^{79}Br-O, A_1 stretch
789.4	^{81}Br-O, A_1 stretch
432	Br-O bend, A_1
354	Br-O bend, E