LOW FREQUENCY CATION VIBRATIONS IN HIGH TEMPERATURE SALT MOLECULES: AN EVALUATION OF NEW EXPERIMENTAL DATA

J. S. Ogden and P. D. Gregory

Department of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK

High temperature salt molecules have been known for many years, and are known to play a significant role in several high temperature transport and corrosion processes. Accurate thermodynamic modelling of such systems requires knowledge of molecular vibration frequencies, and the initial aim of this paper is to consider the errors in selected thermodynamic parameters arising from uncertainties in low frequency vibrations. This is followed by a presentation of results from recent experiments designed to locate metal-oxygen modes in a variety of high temperature oxo-anion salt molecules. In particular, matrix isolation far IR studies on alkali metal nitrates show characteristic M-O stretches at ca. 225 and 189 cm\(^{-1}\) (M=K), 179 and 144 cm\(^{-1}\) (M=Rb), 164 and 130 cm\(^{-1}\) (M=Cs). Force constant parameters are evaluated, and the possibility of transferability to other salt molecules is discussed.

INTRODUCTION

High temperature chemistry presents a challenging area of research to the experimentalist, and although techniques such as molecular beam mass spectrometry may be used routinely to identify high temperature molecules, and to establish parameters such as heats of formation, other in situ techniques, such as electron diffraction, have often encountered problems of interpretation - particularly where the species of interest contain low frequency cation vibrations. Here, the "shrinkage" associated with large vibrational amplitudes has sometimes led to erroneous structure determinations, and although this effect can often be corrected by a knowledge of the molecular vibration frequencies, this latter data is often incomplete. Furthermore, the vibration frequencies which are often unavailable are the very same low frequencies upon which primarily depend not only the refinement of electron diffraction data, but the accurate prediction of thermodynamic parameters such as molecular entropy.

The aims of this paper are firstly to assess the effect on selected thermodynamic parameters of uncertainties in the positions of low frequency modes, and secondly to discuss recent experiments designed to locate the metal-oxygen (M-O) modes in molecular alkali metal nitrates, molybdates, and tellurites. These have involved matrix isolation IR spectroscopy (1), which has become a well-established technique for studying high temperature molecules.
EXPERIMENTAL AND COMPUTATIONAL METHODS

The matrix isolation experiments described here have all involved the high vacuum vaporisation of the parent salt from silica sample holders heated resistively to temperatures within the range 900 - 1500 K. The resulting vapor was co-condensed at 10-12 K with a large excess of argon or nitrogen to form the low temperature matrix, and IR spectra were subsequently obtained using Biorad FTS65A or Bruker 113v spectrometers equipped with appropriate far IR optics. Parallel molecular beam mass spectrometric studies have served to verify the nature of the vaporising species. Subsequent vibrational analysis and modelling have been carried out using standard procedures described previously (2). Calculations of molecular entropies, and the estimation of associated errors, are based on standard equations involving the vibrational partition function, and assume a harmonic force field.

RESULTS - MODELLING OF UNCERTAINTIES

Figure 1 shows the characteristic dependence of vibrational entropy on wavenumber at a temperature of 1000 K, which may be considered typical for many high temperature salt vapors. From this plot it is evident not only that low frequency vibrations in a molecule make a major contribution to the total entropy, but that uncertainties in the position of a particular vibrational mode will have their greatest effect for low frequencies. Figure 2 shows the error in entropy at 1000 K associated with an uncertainty of 10 cm<sup>-1</sup> for a range of typical low frequency vibrations.

It is evident that such errors become very serious below ca 40 cm<sup>-1</sup>, but even at 100 cm<sup>-1</sup> the error associated with this very modest uncertainty in vibrational frequency is not negligible. At 1000 K it would translate into an error in free energy of 1 kJ/mole, and this can be expected to have a significant effect on equilibrium concentration calculations. There would clearly seem to be a need for reasonable precision in the location of low frequency modes, and ideally, this should come from experiment rather than theory.

RESULTS - FAR IR MATRIX ISOLATION STUDIES

Figure 3 summarises four well-established modes of coordination found for high temperature alkali metal salt molecules. However, in the majority of such species, the vibration frequencies corresponding to cation motion have not been determined experimentally, and for many salt molecules, even the positions the cations have not been precisely established. In this event, the mode of coordination, in MNO<sub>3</sub> or MReO<sub>4</sub> molecules for example (2,3), may be inferred from isotopic studies on anion modes which lie in the more tractable mid IR region.
Figure 4 shows a typical far ir spectrum obtained (4) for molecular CsNO$_3$ isolated in an argon matrix at 12 K. The two bands at 163.6 and 129.9 cm$^{-1}$ are assigned to the $A_1$ and $B_2$ Cs-O stretching modes, and may be compared with corresponding M-O bands at 225/189.3 and 179.3/144 cm$^{-1}$ obtained for KNO$_3$ and RbNO$_3$, respectively. Principal and interaction M-O stretching constants (mdyn/Å) for these molecules are calculated ($F_r$, $F_{rr}$) as K: 0.42, 0.08; Rb: 0.34, 0.1; Cs: 0.31, 0.1.

These molecular nitrates are some of the simplest bidentate molecular species, and might be expected to provide prototype frequencies (and force constants) for other bidentate systems - such as molecular phosphates, sulphates, chromates, molybdates, tungstates or per-rhenates. The extent to which this is realised is illustrated by recent studies on molecular Cs$_2$MoO$_4$. This species is known to have a bis-bidentate structure (Figure 3d), from which it can be shown that there are two ir active Cs-O modes, with symmetries $B_2$ and $E$, with an expected relative intensity of ca. 4.5 : 1. Experimentally, the far ir matrix spectrum of Cs$_2$MoO$_4$ shows (5) two bands with a relative intensity of ca 4 : 1 at 163 and 143 cm$^{-1}$. This data alone is not sufficient to extract the relevant force constants for direct comparison with CsNO$_3$, but these frequencies are sufficiently close to those found in CsNO$_3$ to contemplate transferability. In contrast, the frequencies found (5) in Cs$_2$TeO$_3$ are considerably lower, at 113 and 95 cm$^{-1}$, suggesting a quite different type of coordination - an expectation which receives some support from recent theoretical calculations on this molecule (6).

These results on M-O stretching modes therefore support the existing structural models proposed for high temperature salt molecules, and go some way to improving the precision of computed thermodynamic parameters. The ultimate challenge is now to obtain reliable data for the (remaining) cation bending modes in these species.

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Figure 1
Vibrational entropy at 1000 K

Figure 2
Effect on entropy of 10 cm$^{-1}$ uncertainty

Figure 3
Types of cation coordination

Monodentate
e.g. MB$\text{O}_2$

Bidentate
e.g. MNO$_3$

Tridentate
e.g. MC$\text{O}_3$

Bis-bidentate
e.g. M$_2$MoO$_4$

Figure 4
Cs-O absorptions in molecular CsNO$_3$