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PES OF HIGHER TEMPERATURE VAPORS

by

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PES OF HIGHER TEMPERATURE VAPORS

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The study of high temperature species by photoelectron spectroscopy is about 7 years old. We began this work in the early 1970's, using a newly-designed cylindrical mirror analyzer. Significant information was obtained on a number of inorganic systems, particularly metal halides and metal atoms. One significant difference that appeared was the characterization of bonding orbitals in the conventional (covalent) sense and bonding orbitals when ionic bonding is dominant. [Many high temperature species tend to be ionically bonded, whereas normally volatile materials tend to be covalently bonded.]

Our work (and those of other groups) seemed to reach a temperature barrier of ∿1000°, for several reasons. In order to surmount this barrier, we designed a new apparatus. It consists of a hemispherical electron energy analyzer with a retarding-foccussing entrance lens, and a radiatively heated oven, basically of the Nuclide Analysis Associates design. The oven has been modified from the Knudsen cell style by surmounting a large, thin tube. The base oven and the tube are independently heated by non-inductively wound heaters. The uncancelled magnetic fields of the two heaters are opposed, reducing the residual field further. Double-oven capability is thereby achieved, and temperatures in excess of 2000°C should be possible.

The electron energy analyzer is largely isolated from the oven and heating system. It can rotate (in θ and ϕ), enabling angular distribution studies to be performed. Scanning is achieved with the retarding lens, keeping the electron pass energy through the analyzer fixed.

We describe below one recently completed study, and make reference to others completed or underway.

The Alkali Halide Vapors

Early mass spectrometric work had revealed the presence of dimers, trimers, even tetramers in alkali halide vapors. This work showed that the complexity of the vapor increased from Cs → Rb → K → Na → Li halides. For cesium halides, dimers were ca. 1% of vapor, higher polymers insignificant. For lithium halides, dimers were ∿50% of vapor, trimer around 10%. PES has heretofore been confined to Cs, Rb, K and Na halides, presumably for two reasons.

a) Temperatures required are somewhat higher for lithium halides.

b) Large dimer component would confuse the photoelectron spectrum.

The basic observations of this earlier work are:

a) In the VUV range, ionization occurs from the halogen end of an M^+-X^- diatomic molecule.

b) This p– like orbital splits in cylindrical symmetry into π and σ. The π splits further by spin-orbit interaction into $\pi_{3/2}$ and $\pi_{1/2}$.

c) One can therefore anticipate 3 peaks, but in most cases 2 of the peaks are not separated and one sees a doublet.

d) A dimer peak can be seen at somewhat higher energy, increasing in intensity as the percent of dimer increases.

The present work was performed on lithium halides, which have the largest dimer concentrations. Two types of spectra were obtained, one with essentially the saturated vapor, the other with superheated vapor. Some peaks were dramatically lower in the superheated vapor, and could immediately be assigned to dimer. Normalization and subtraction of the two spectra enabled us to obtain "pure" monomer and dimer spectra. The monomer spectra were about as expected from extrapolation and prediction of the other alkali halides. The dimer spectra were completely new. Six peaks are anticipated for these rhombic structures. In the case of Li_2I_2, we see 5 of these.

Conclusions

a) The first I.P. of dimer is higher than that of monomer in each lithium halide.

b) This can be obtained by ionic model calculations, and also by molecular orbital calculations. We have done such calculations using the Xα– DVM method. The calculations were performed by Dr. G. L. Goodman.

c) These calculations predict that trimer has lower IP than dimer, and tetramer has higher IP than trimer.

d) Electron impact measurements on LiF agree with this oscillatory trend, through trimer.

e) A crude ionic model calculation can also rationalize this behavior (assuming hexagonal trimer and distorted cube for tetramer).

A complete description of this work will appear shortly in the Journal of Chemical Physics. The partial cross sections of atomic iodine have also been studied, and will appear in the same journal.

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