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A MASS SPECTROMETRY STUDY OF CHROMIUM-SULFUR CLUSTER IONS AND AN INVESTIGATION OF THEIR RELATIVE STABILITIES

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The study of transition metal clusters and binary metal-element clusters (M_xO_y, M_xS_y, M_xC_y etc.) is a very active research area motivated, in part, by the search for novel catalytic, photographic and magnetic materials. The two research groups involved in this present study have previously reported extensive studies on M-S binary clusters by laser ablation time-of-flight and Fourier transform ion cyclotron resonance mass spectrometry. We have studied many of the first row transition metal sulfides, some second and third row transition metal and main group sulfides: Sc_xS_y, Ti_xS_y, V_xS_y, Mn_xS_y, Fe_xS_y, Co_xS_y, Ni_xS_y, Cu_xS_y, Zn_xS_y, Ta_xS_y, Ag_xS_y, and Al_xS_y. The TOF-MS experiments have often involved tandem photodissociation studies of the metal sulfide cluster cations. In the FT/ICR-MS studies we have also used laser ablation to generate positive-ion metal atoms of calcium and up to twenty nine transition metal atoms in the same oxidation state as well as metal clusters of lanthanum which have subsequently been reacted with S_8 vapor. In this present paper we report on the TOF-MS and FT/ICR-MS of the *chromium-sulfur* ion clusters. Three different methods were used to prepare at least 100 of the ionic clusters; laser ablation of chromium-sulfur mixtures or the compound chromium sulfide (Cr_2S_3) and laser ablation of chromium to form chromium (I) cations followed by reaction of the bare cation with vapor phase sulfur, S_8. Dissociation of the cluster ions has been carried out using laser photodissociation (TOF-MS) and rf-collision induced dissociation (FT/ICR-MS).

The general formation, photodissociation and gas phase ion chemistry of a selection of these metal sulfur clusters will be discussed. By combining our different mass spectrometric and sample ablation techniques we have been able to shed more light on the formation, stability and structure of such naked cluster ions. The mass spectrometers used in this study consisted of a 3 m home-made TOF-MS and a Spectrospin CMS-47 FT/ICR-MS, equipped with a 4.7T superconducting magnet. Density functional theory calculations (DMol 400 and Gaussian 94) have been used to calculate the structures of a variety of Cr_xS_y neutral and ionic clusters. The calculations have involved the use of a double numerical basis set and the BLYP functional.

Our experiments and calculations reveal that there are preferred Cr_xS_y neutral and ionic clusters and that the experimental probe-time and laser power (gas pressure) play crucial roles in determining the form of the resulting laser ablation TOF- and FT/ICR-mass spectra.

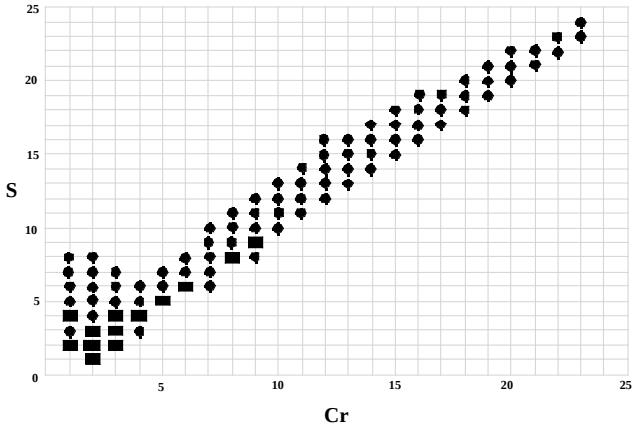

FIG. 1. A composite ion map of $[Cr_xS_y]^+$ cations formed by laser ablation TOF-MS of a pressed mixture of chromium metal and sulfur powders. ■ >10% and ● < 10% peak intensity relative to that of $Cr_4S_4^+$.

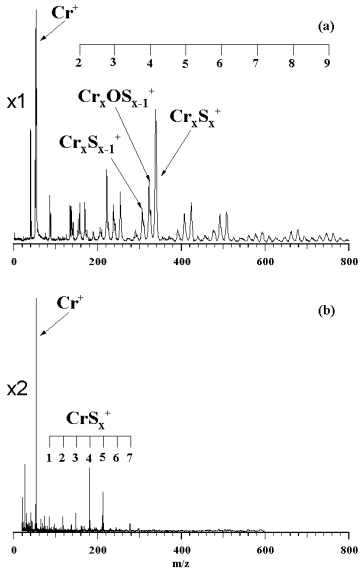

FIG. 2. Laser ablation positive-ion (a) TOF and (b) FT/ICR mass spectra of Cr_2S_3.