INVESTIGATION OF GASEOUS CHLORINE COMPOUNDS BY X-RAY ABSORPTION SPECTROSCOPY

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INVESTIGATION OF GASEOUS CHLORINE COMPOUNDS
BY X-RAY ABSORPTION SPECTROSCOPY

by

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INVESTIGATION OF GASEOUS CHLORINE COMPOUNDS BY X-RAY ABSORPTION SPECTROSCOPY

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We measured the x-ray absorption spectra of gaseous (Cl₂, CC₁₄) and H₄C₂Cl₂. The samples were mixed with N₂ at approximately 1000 ppm concentration and flowed through the detector/sample cell(2). This consisted of a cavity in a 1.3 cm Lucite block covered front and back with 6 mil aluminized Mylar windows. At the center was a thin electron-collecting grid of Ni mesh. The windows were connected to -45 V while the positive battery terminal was connected to the ground of the electrometer. The e-yield signal was collected at 10⁸ gain from the center mesh. Absorption and fluorescent mode data were also collected but were much inferior in quality. The Si(111) double crystal monochromator was detuned 80% to reduce harmonics. A 1 mm entrance slit gave an energy resolution ΔE/E=0.5 eV(2). Early data for Cl₂ gas was published by Stephenson et al.(3). Their data was obtained in the absorption mode, cranking the spectrometer and recording the data by hand. Although their first peak was attenuated by the thickness effect, the spectra are comparable with ours to 10 eV. In the region from 10-24 eV we found an interesting double series resonance which is blown up in scale in the inset to Fig. 1. By analogy to N₂ data(4) these features are due to transitions to unfilled orbitals of the molecule in its various charged states.

The data of Fig. 1 were placed absolutely in energy by noting the impurity Ar ls resonance at 3203.3 eV(5) at the end of each scan. The zero of energy of Fig. 1. is 2833.4 eV. The π resonance peaks were located at -2.6, 0.0 and 0.2 ± 0.2 eV for Cl₂, CC₁₄, and H₄C₂Cl₂, respectively. The σ resonance energy as defined by Sette et al.(6) moves with bond distance as noted for smaller molecules(6). The Ar K-edge spectrum is shown for comparison, E₀=3203.3 Note that no feature similar to the Ar double electron ionization (ls3p) at 23 eV (the vertical arrow) occurs in the Cl spectra. The EXAFS of Fig. 2 was terminated by the ubiquitous Ar impurity in the x-ray path. Considerably more EXAFS could be measured if this could be corrected. The Cl-Cl phase-corrected

Fig. 1 Near edge spectra of gas phase Cl₂, CC₁₄, H₄C₂Cl₂ and Ar all normalized to unit edge jump. The π and σ maxima are indicated. The Ar ls3p edge is marked by the vertical arrow. A region of the Cl₂ spectrum is blown up in the inset to illustrate a double series resonance.

Fig. 2 Normalized EXAFS of gas phase Cl₂, CC₁₄ and H₄C₂Cl₂.
Fig. 3  \( K^1 \), Cl-Cl phase corrected Fourier transforms of gas phase \( \text{Cl}_2, \text{CCl}_4 \) and \( \text{H}_4\text{C}_2\text{Cl}_2 \) all plotted to the same scale.

Fourier transforms are given in Fig. 3. The Cl peaks were found at the expected distances of 1.99, 2.90 and 2.97 Å, top to bottom. The shorter Cl-C bonds are clearly resolved and could easily be analyzed. Any sample with appreciable vapor pressure may be introduced into an ion chamber with a diluent gas. With a long beam path a sensitivity of 1 ppm is possible. This remarkable sensitivity occurs because of the nominal 4\( \pi \) collecting efficiency.

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