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INVESTIGATION OF GASEOUS CHLORINE COMPOUNDS BY X-RAY ABSORPTION SPECTROSCOPY

by

Farrel W. Lytle, Robert B. Greegor,
Edward C. Marques and Donald R. Sandstrom

Boeing Aerospace Company
Seattle, Washington 98124

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INVESTIGATION OF GASEOUS CHLORINE COMPOUNDS BY X-RAY ABSORPTION SPECTROSCOPY

F. W. Lytle, R. B. Greegor, E. C. Marques and D. R. Sandstrom
The Boeing Co., Seattle, WA 98124
G. P. Huffman, F. E. Huggins, University of Kentucky, Lexington, KY 40506

We measured the x-ray absorption spectra of gaseous Cl_2, CCl_4 and $H_4C_2Cl_2$. The samples were mixed with He at approximately 1000 ppm concentration and flowed through the detector/sample cell(1). This consisted of a cavity in a 1.3 cm Lucite block covered front and back with 6 μm 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 10^8 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 $\Delta E/E=0.5$ eV(2). Early data for Cl_2 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 N_2 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 1s 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 Cl_2, CCl_4, and $H_4C_2Cl_2$, 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, E_0=3203.3 Note that no feature similar to the Ar double electron ionization (1s3p) 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 measure if this could be corrected. The Cl-Cl phase-corrected

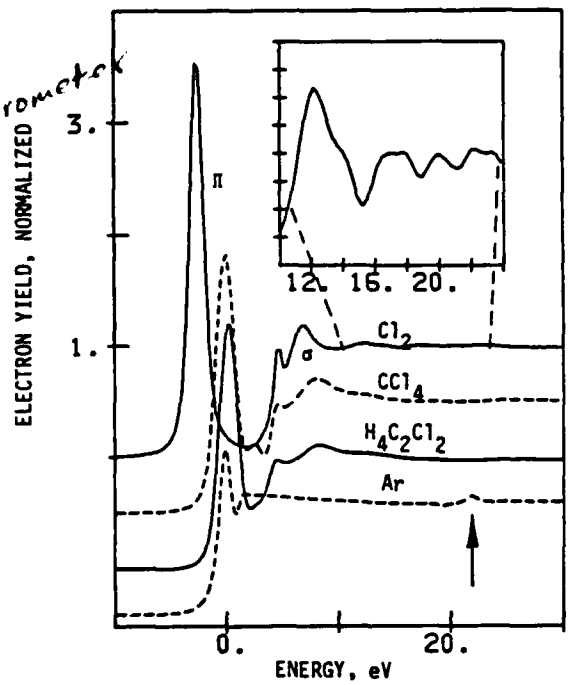

Fig. 1 Near edge spectra of gas phase Cl_2, CCl_4, $H_4C_2Cl_2$ and Ar all normalized to unit edge jump. The π and σ maxima are indicated. The Ar 1s3p edge is marked by the vertical arrow. A region of the Cl_2 spectrum is blown up in the inset to illustrate a double series resonance.

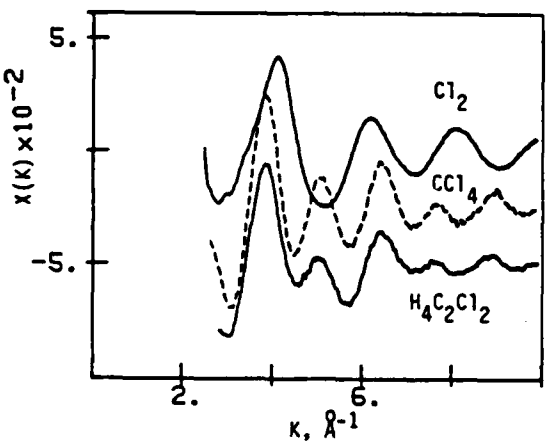

Fig. 2. Normalized EXAFS of gas phase Cl_2, CCl_4 and $H_4C_2Cl_2$.

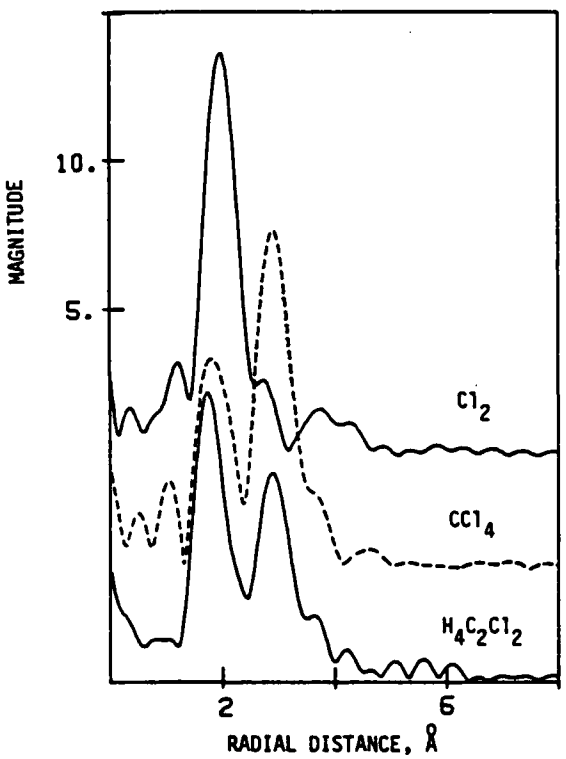

Fig. 3 K^1, Cl-Cl phase corrected Fourier transforms of gas phase Cl_2, CCl_4 and $H_4C_2Cl_2$ all plotted to the same scale.

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 4π collecting efficiency.

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References

1. F. W. Lytle et al., "GAS PHASE X-RAY ABSORPTION SPECTROSCOPY WITH AN ELECTRON YIELD DETECTOR", presented at IVth Int. EXAFS Conf., Fontevraud, France, July 1986.
2. F. W. Lytle et al., Nucl. Inst. Methods 226, 542 (1984).
3. S. T. Stephenson et al., Phys. Rev. 84,806 (1951).
4. M. Nakamura et al., Phys. Rev. 178, 80 (1969). A. Bianconi et. al., Chem. Phys. Lett. 58, 263 (1978). A. P. Hitchcock et al., J. Elec. Spec. 18, 1 (1980).
5. R. D. Deslattes et al., Phys. Rev. A27, 923 (1983)
6. F. Sette et al., Chem. Phys. Lett. 110, 517 (1984)

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