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RESONANCES IN THE PHOTOABSORPTION SPECTRUM OF THE SILICON TETRACHLORIDE MOLECULE NEAR THE SiK AND ClK EDGES


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Abstract

Photoabsorption spectra of gas phase SiCl, molecule has been measured using the total ionization yield method, near the chlorine K edge (2800-3100 eV region). We interpret the near edge resonances by comparing the spectra with those obtained near the SiK edge, and on the basis of two independent calculations: ab-initio CI calculations and Multiple Scattering model calculations (MSMX,), both applied to the core equivalent species.

INTRODUCTION

Resonances observed in photoabsorption spectra of molecules near core ionization edges are intimately related to the chemical surroundings of the absorbing atom and thus are carrying both electronic and structural information. Among the most intense structures, discrete resonances originate often from core to bound (valence or Rydberg) excited states. Continuum resonances are rather described using the concept of shape resonances (1) i.e. the scattering of a single electron by a positive ion. However, configuration interaction mixing (2) and vibronic couplings such as the Jahn-Teller effect (3) may well complicate the spectrum and obscure the one electron simple features. Consequently, it is of fundamental interest to analyse detailed electronic effects for a system with a well defined geometrical structure, in order to extend suitable theoretical models to more complex materials.

We show in the present paper, new photoabsorption experimental results on the isolated tetrahedral molecule SiCl, near the chlorine K edge. We also present new theoretical calculations from two independent approaches: ab-initio configuration interaction and multiple scattering (MSM X,) calculations, both performed on the
core equivalent molecule. We briefly discuss
i) the interest of comparing spectra obtained near the edge of the central
atom and of the ligand,
ii) the relative intensity of Rydberg states compared to valence excited
states,
iii) the assignment of continuum resonances.

EXPERIMENTAL

Photoionization spectra are obtained using synchrotron radiation from the ACO
storage ring at LURE, Orsay. A double crystal monochromator equipped with two InSb
(111) crystals (2d = 7.4806 Å) provides a photon beam with an intensity of the
order of 10^5 photon per second in a 0.6 eV bandpass at 2800 eV. The monochromatic
beam enters a cell which contained the gaseous sample with a pressure of a few
torr. An electrode positioned in the cell along the beam direction is used to
measure to total ionization yield. The photon energy scale has been carefully
calibrated around the SiK edge using Si-C:H solid sample (3) and around the CIK
edge, using CHCl_3 as a reference system (4).

THEORETICAL

All the multiple scattering calculations (MSMX) are made using the muffin-tin
approximation (5,6) for the potential and the muffin-tin radii are chosen
following the Norman (7) prescription with 10% of overlapping. The Coulomb part
of the potentials came from charge density constructed by using the Clementi and
Roetti (8) wavefunctions while the exchange and correlation part is calculated in
the X-α approximation scheme where the α values are tabulated by Schwartz (9).
Moreover, the potential of the excited state is calculated in the Z+1
approximation but the removed 1s electron is promoted in the last occupied atomic
orbital of the absorbing species to simulate some screening of the hole. I
elastic processes are not taken into account.

Ab-initio CI calculations of term values and relative oscillator strengths are
also performed using the Z+1 approximation. The configuration interaction of all
monoexcited configurations with respect to the main ones is made in the space
spanned by the SCF molecular orbitals of the PCl_4 ion. This allows a better zero
order description of Rydberg states of PCl_4 , unlike in the MSMX approach. Moreover,
reorganization effects of orbitals between the ion and the excited
states as well as shake-up states are taken into account by this procedure.

RESULTS AND DISCUSSION

We present in Figure 1 new photoionization spectra of gas phase SiCl_4 obtained
near the CIK edge, as well as near the SiK edge. The latter resembles closely the
photoabsorption spectrum reported earlier (3). However, the energy scale is
slightly different from those of ref (3) because of our improvement of the
wavelength scanning system. Consequently, the # 3 resonance is now found close to
the ionization edge rather than in the discrete spectrum. Furthermore, we now
observe more clearly a shoulder on the low energy side (structure # 1) of the main
resonance (# 2). Although we have not mentioned this point in ref. (3), we consider
that this observation is of importance for the understanding of the spectra.

We also show in Figure 1, MSMX calculations for the SiK edge only. This
spectrum is reported on an absolute scale using the energy of the most intense
resonance (# 2) extracted from experiment, as a reference. The ab initio CI
calculated term values of all discrete resonances with their relative intensities
are also reported in Figure 1. The calculated intensity of the lowest state is
given with arbitrary units.

The first point is that the main feature of the discrete spectrum, near the SiK
edge, is well reproduced by the two independent calculations. The main feature (#
2) is indeed due to a transition into the t^*_2 unoccupied antibonding Si-Cl valence
Figure 1: Top: Experimental silicon K photoionization spectrum of SiCl₄.

Middle: Theoretical results for SiCl₄ near the SiK edge. The solid line curve is obtained by MSMXₜ calculations and vertical bars indicate the results obtained by C.I. calculations.

Bottom: Experimental chlorine K photoionization spectrum of SiCl₄.

The two edges are aligned on a vertical line and the photon energy axis have been drawn with the same relative scale.
orbital. According to CI calculations, the transitions into the \( a_1^* \) orbital (also Si-C1 antibonding) lies at lower energy compared to \( t_2^* \). In the electric dipole approximation, the \( a_1^* \) transition is forbidden from the SiK edge. The observed remaining intensity is then likely due to a vibronic coupling effect (3) which is not taken into account in the present calculations. This is because the core equivalent species PCl\(_4\) is known to have an equilibrium geometry distorted from a tetrahedron.

At the ClK edge, the situation is different. If we assume that the core hole is localized on one chlorine atom, then the relevant symmetry group is \( C_3v \) and transitions into the first unoccupied valence orbitals are all allowed. The former \( a_1^* \) stays as \( a_1^* \) and \( t_2^* \) is split into \( e^* \) and \( a_1^* \). In the ClK spectrum of Figure 1, the two first intense structures (# 1 and # 2) are interpreted as the lowest \( a_1^* \) and \( e^* \) respectively. This is based on preliminary MSMX\(_{\alpha}\) calculations. Further improvements of the latter calculations as well as CI ones are underway to confirm this analysis. Notice that the term values (SiK or ClK edges) for the same final orbitals differ by about 1 eV and thus are not transferable. This is easily rationalized using the core equivalent model. The Si\(_{\,(K)}\)Cl\(_4\) and SiCl\(_3\)Cl\(_{\,(K)}\) core excited molecules are respectively equivalent to PCl\(_4\) and SiCl\(_3\)Ar. The CI calculations of Figure 1 show also that Rydberg states can be populated but with very small probability relative to valence transitions. This shows that the # 3 feature is due to another type of transition, possibly a shake-up state.

In the SiK continuum, the MSMX\(_{\alpha}\) calculations show two intense features which are associated to the \( t_2 \) continuum which may account for the peaks # 4 and # 6. The smaller feature # 5 is likely to be a shake-up state. A detailed analysis of the continuum resonances seen in the ClK spectrum will be offered in the near future together with the corresponding theoretical results.

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