

Characterization of Rydberg transitions in the $L_{2,3}$ absorption spectra of SF_6 and PF_5

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High-resolution photoabsorption spectra of SF_6 and PF_5 at the $L_{2,3}$ edge in the gas and solid phase have been measured with synchrotron radiation. A reduction in the intensity for some of the higher-energy transitions in the condensed phase indicates significant Rydberg character associated with the terminating orbitals. This observation is consistent with the assignments suggested by multiple-scattering $X\alpha$ calculations and suggests that Rydberg orbitals can penetrate into the potential barrier created by the electronegative atoms.

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The pre-edge features in the inner-shell absorption spectra of molecules are potentially useful for providing important information on the local electronic and geometrical structures. Unfortunately, an accurate assignment of the electronic excitations in this region is a nontrivial task, and it is often difficult to reach a consensus on the interpretation of the spectra. A recent example is the dispute on the character of the weak transitions near the vicinity of the ionization threshold in the gas-phase K and $L_{2,3}$ photoabsorption spectra of $SiCl_4$ [1–4]. Two different assignments have been proposed [1,3]. It is a general conception that electronegative atoms surrounding a molecule will create an effective potential barrier dividing the molecule into an inner-well and an outer-well region [5]. The diffuse Rydberg orbitals are expected to reside in the outer-well region and will not contribute significantly to near-edge excitations [1]. This conjecture, however, contradicts the rich pre-edge structures observed in $SiCl_4$ [1,2]. To circumvent this problem, these transitions are attributed to excitations into antibonding orbitals where the degeneracy is lifted through Jahn-Teller distortion of the tetrahedral molecule in the ionic state [1]. A subsequent theoretical local-density-functional multiple-scattering (MS- $X\alpha$) calculation of the absorption spectrum gave a different interpretation [3]. It was shown that low-angular-momentum Rydberg wave function can penetrate into the inner-well region and acquire some valence character, which enhances the oscillator strengths of the transitions. The unusual nature of the transition has prompted a more extensive *ab initio* study [4], which also supports the existence of Rydberg-valence mixed orbitals, although details of the assignment are still debatable [4].

In an attempt to identify the Rydberg character of the transitions in these highly halogenated molecules, this investigation reports and compares the high-resolution $L_{2,3}$ absorption spectra of gaseous and solid SF_6 and PF_5 . It is well known that the signature of a Rydberg transition is a drastic broadening and reduction in the intensity from the gas to the condensed phase [6] due to the extended

nature of the diffuse orbital. In contrast, the intensity of the valence-valence transition will show little change. SF_6 and PF_5 were chosen for this study because fluorine is the most electronegative halogen atom and, therefore, the repulsive potential barrier effect will be most prominent in these compounds. A similar study on $SiCl_4$ has been reported recently [7].

The photoabsorption spectra for SF_6 and PF_5 were measured at the Canadian Synchrotron Radiation Facility at the Synchrotron Radiation Center, University of Wisconsin, Madison, using a Mark II Grasshopper monochromator [8]. The resolution of the grating at the energy region 150–200 eV was better than 0.4 eV. The absolute energy scale was calibrated against the absorption spectra of gaseous and solid argon. The gas-phase spectra were measured in the transmission mode using a gas cell described previously [9]. Solid SF_6 and PF_5 were obtained by slow condensation of the gases onto a copper plate attached to a liquid-helium cryostat at 10 K. It is important to note that at low coverage if the rate of condensation is very slow the amorphous structure is favored and the absorption peaks become very broad [10]. The crystalline solid is obtained by careful adjustment of the condensation rate and the coverage [10]. The absorption spectra of the solids were recorded with the total-electron-yield method [11]. The $L_{2,3}$ photoabsorption spectra for gaseous and solid SF_6 and PF_5 are shown in Figs. 1 and 2, respectively.

The $L_{2,3}$ absorption spectrum for gaseous SF_6 has been reported many times [9,12,13] and requires no detailed description. The pre-edge absorption spectrum is rather simple with one strong spin-orbit split peak (1,1') below the $S 2p$ edge (lower curve in Fig. 1). Two or more [14] sharp transitions of much weaker intensities (2,3) are located just below the ionization threshold. There is no disagreement on the assignment of the strong pre-edge peak (1,1') to the inner-shell $S 2p (t_{1u})$ to antibonding (a_{1g}^*) transition. The assignment for the weaker structures 2 and 3 is less definitive. In view of the narrow line shape and the very low intensity, it is reasonable to assign

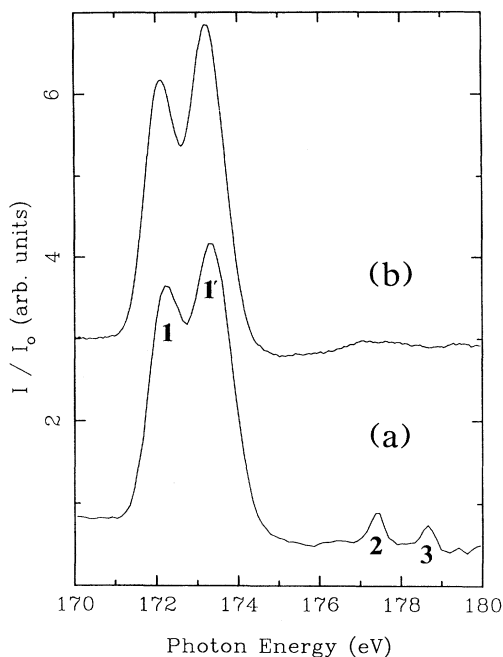


FIG. 1. Gas-phase (a) and solid-phase (b) pre- $S L_{2,3}$ edge absorption spectrum for SF_6 .

these peaks to Rydberg transitions. No theoretical calculation is available for comparison in this region. The photoabsorption spectrum for condensed SF_6 is shown as the upper curve in Fig. 1. It is quite clear that the major features in $1,1'$ remain unchanged. On the other hand, the sharp but weaker peaks 2 and 3 are no longer visible in the solid spectrum. The disappearance of the absorption peak in the condensed phase is a good indication of the Rydberg character of the terminating orbital [6]. The breadth of a Rydberg absorption in a condensed phase is inversely proportional to the electronic relaxation time. The excessive line broadening shows that the lifetime of the excited electron is very short, which is typical for molecular crystals.

The gas-phase $L_{2,3}$ pre-edge absorption spectrum for PF_5 is surprisingly complex. The gas-phase spectrum presented here is in good agreement with the high-resolution spectrum obtained from electron-energy-loss spectroscopy (EELS) [15]. The D_{3h} molecular symmetry undoubtedly permits more symmetry-allowed transitions. The excitations into the two antibonding $P-F$ orbitals of a_1 and e symmetry are accessible from the $P 2p$ core level. Previously [15], the two lowest-energy absorption bands have been assigned to $P 2p$ to antibonding transitions and the higher-energy peaks to Rydberg transitions. Theoretical $MS-X\alpha$ calculations [16] support these assignments. As the details of the calculations will be published elsewhere [16], it is sufficient to note that the calculation suggests that the strong lower-energy peaks $1,1'$ are due to spin-orbit split transitions from the $P 2p$ core-to-valence antibonding a_1^* orbital. The transitions to the "p"-type e^* orbitals are much less intense and contribute heavily to band 2 and partially to band 3. Overlapping

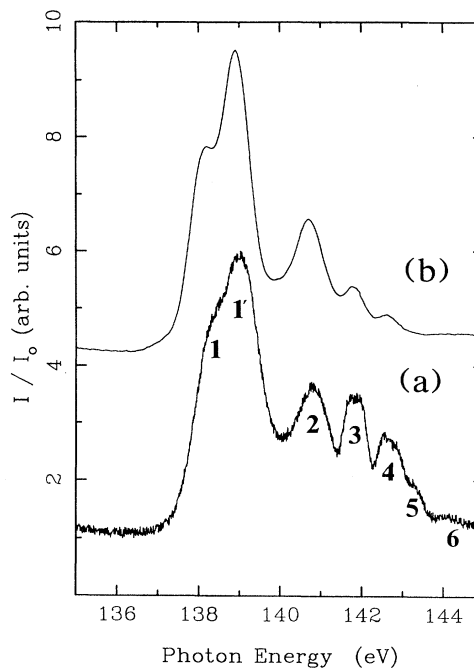


FIG. 2. Gas-phase (a) and solid-phase (b) pre- $P L_{2,3}$ edge absorption spectrum for PF_5 .

mixed Rydberg-valence transitions are responsible for the intensities of bands 3–5, with the Rydberg s -valence transitions being of lower energy than the Rydberg p -valence transitions. These transitions signal the onset of the $P 2p \rightarrow ns$ and the $2p \rightarrow np$ Rydberg series. The $2p \rightarrow np$ excitations are allowed because of the lower molecular symmetry that permits the mixing of s and d characters into the np orbitals [15,16]. The higher-energy excitations are primarily Rydberg in character. The $L_{2,3}$ absorption for condensed PF_5 is shown as the upper curve in Fig. 2. As described above, the first absorption band $1,1'$ is mostly of core-valence character, its intensity is not expected to change in the condensed phase, and it can be conveniently used as a reference for intensity comparisons. It is quite clear that, relative to $1,1'$, the higher-energy absorptions have either broadened and reduced in intensity or are missing from the solid spectrum. Despite the fact that the resolution is slightly better in the solid spectrum than in the gas phase [14], as is evident from the well-developed shoulder on the low-energy side of band $1,1'$, the intensity of bands 3 and 4 has dropped significantly and band 5 has disappeared into the background. This observation is consistent with the proposed assignment that the first two peaks $1,1'$ and 2 are predominantly core-valence in nature and that the higher-energy structure is due to mixed Rydberg-valence or Rydberg transitions.

The present experimental results substantiate an earlier suggestion [3] that Rydberg orbitals can penetrate and mix with valence orbitals even in highly fluorinated molecules of large effective potential barrier. The high-energy peaks observed in the inner-shell absorption spectrum are most probably due to transitions to these orbitals, which

gain oscillator strength from the mixing with valence antibonding orbitals. A similar observation was made in a recent study of the Si $2p$ core-level excitations in condensed SiCl_4 [7]. From the behavior of the absorption peaks in the condensed phase, it is also concluded that the high-lying pre-edge absorption is best described as one-electron core-Rydberg transitions, and there is no need to invoke multielectron processes such as transitions to localized, doubly excited states [4]. The results from a

recent discrete-variational $X\alpha$ study on SiCl_4 [17] are in full agreement with the MS- $X\alpha$ calculation [3] and support the assignment made here.

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