Vibrationally Resolved Core-Level Photoelectron Spectroscopy: Si $2p$ Levels of SiH_4 and SiF_4 Molecules

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High-resolution photoelectron spectra (total instrumental width ≤ 0.1 eV) of the Si $2p$ core levels of SiH_4 and SiF_4 were obtained using the Aladdin undulator source. The vibrationally resolved Si $2p$ photoelectron spectrum of SiH_4 yields a Si-H stretching energy of 0.295 ± 0.002 eV for the core-hole ion and a lifetime width of ~ 45 meV. Numerous vibrational lines are observed in the SiF_4 Si $2p$ photoelectron spectrum. The $Z+1$ core-equivalent model is assessed and changes in the molecular geometries and bonding properties of the molecules upon ionization are discussed.

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While vibrationally resolved photoelectron spectra have been routinely measured for the valence bands of simple molecular systems, only the C $1s$ spectrum of CH_4, vibrationally resolved using monochromatized Al $K\alpha$ radiation,[1] and the Si $2p$ photoelectron spectrum of SiH_4, exhibiting fine structure corresponding to the Si-H stretching vibration,[2] have been reported previously at resolutions of ~ 0.3 and ~ 0.2 eV, respectively. Very narrow excitation-source bandwidths and good electron energy resolutions are required to resolve the vibrational fine structure of core-level photoelectron bands. Recent advances both in high-intensity light sources, such as undulators,[3] and in monochromator design[4] have made it possible to study the vibrationally resolved core-level absorption spectra of numerous gas-phase and adsorbed molecules at photon resolutions of ≤ 0.1 eV.[5]

Photoelectron spectra of core levels with binding energies of > 30 eV have not previously been obtained with total instrumental resolutions of ≤ 0.1 eV. High-resolution core-level photoelectron spectra are simpler than absorption spectra, and provide fundamentally important information for the future development of all core-level spectroscopies (i.e., absorption, photoelectron, Auger, and fluorescence) of free molecules, adsorbates on surfaces, and solids. For example, inherent core-level linewidths need to be measured to help fully interpret the photoelectron spectra of surfaces which are complicated by surface core-level shifts and disorder broadening associated with various adsorbate-covered surfaces.[1,6] In addition, these widths are required to study the chemical dependence of core-level lifetimes and linewidths in free molecules and surfaces.[1,7] Equally important, such high-resolution measurements are urgently required for several reasons: to aid in the complete interpretation of the complex pre-edge absorption spectra of free molecules, adsorbates, and surfaces;[5] to stringently test the core-equivalent model which has been widely used to interpret core-level binding energies[8] and vibrational broadenings of core-level photoelectron,[9-13] photoabsorp-

tion,[14] and x-ray emission spectra;[15] and to study vibrational band intensities as a function of excitation energy where shape resonances are expected to affect the intensity distribution of bands within the vibrational manifold.[16]

The spectra presented here were obtained using a high-resolution photoelectron spectrometer based on a McPherson ESCA 36 electron energy analyzer which has been described recently.[2] The resolving power of the analyzer ($\Delta E/E$) is approximately $1/760$. Photons from the undulator on the Aladdin storage ring were monochromatized using a 2400-groove/mm grating in a 6-m torodial grating monochromator[3] (TGM) with an excitation bandwidth (aberration limited) of ~ 0.090 eV at 135-eV photon energy. Samples of SiH_4 and SiF_4, obtained commercially in high purity, were introduced directly into the gas cell of the spectrometer. The experimental Si $2p$ photoelectron spectra were deconvoluted with a Lorentzian-Gaussian line shape using a nonlinear least-squares procedure[17] constrained to use only one peak shape split by the Si $2p$ spin-orbit and vibrational splitting.

High-resolution photoelectron spectra of the Si $2p$ core levels of SiH_4 and SiF_4 obtained using 135-eV photons are shown in Figs. 1 and 2. The spectra were obtained with the same experimental resolution [$\Gamma_{\text{expt}} = (\Gamma_{\text{photon}}^2 + \Gamma_{\text{electron}}^2)^{1/2} \approx 95$ meV] but they differ significantly in overall appearance. Vibrational structure is easily identified and fully resolved in the photoelectron spectrum of SiH_4. This spectrum, with total experimental linewidths of 117 meV (from the fit), exhibits the narrowest core-level photoelectron linewidth observed for a molecule with resolved vibrational structure.[1,2] The Si $2p$ photoelectron spectrum of SiF_4 is much broader and less resolved than that of SiH_4.

A representation of the fitted parameters for the SiH_4 photoelectron spectrum is shown in Fig. 1 together with the experimental data. The calculated spectrum consists of a series of three vibrational bands, each split by the Si
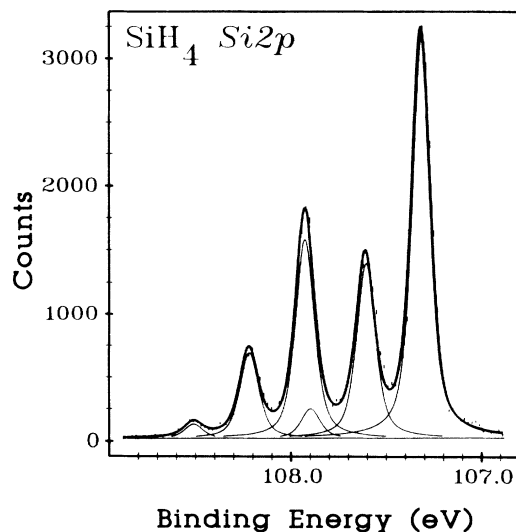
FIG. 1. Experimental (error bars) and calculated (heavy line) Si $2p$ photoelectron spectrum of SiH_4. The calculated spectrum was constructed using parameters obtained from a nonlinear least-squares fit of the experimental data. Contributions from the individual bands and the base line are represented by the lighter lines.
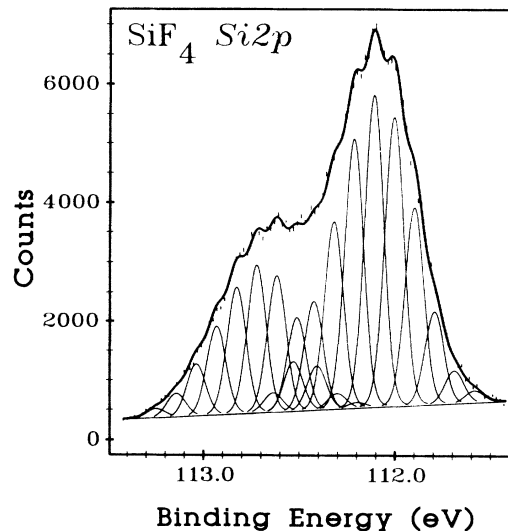

FIG. 2. Experimental (error bars) and calculated (heavy line) Si $2p$ photoelectron spectrum of SiF_4. The calculated spectrum was constructed using parameters obtained from a nonlinear least-squares fit of the experimental data constrained as described in the text. Contributions from the individual bands and the base line are represented by the lighter lines.

$2p$ spin-orbit splitting. Spectral parameters were determined from four different Si $2p$ photoelectron spectra of SiH_4 and averaged to obtain a set of precise values. The six component lines of the calculated spectrum shown in Fig. 1 have a line shape described by a linear combination of 43% Gaussian and 57% Lorentzian line shapes with half-height full widths of 0.117 eV. The adiabatic ionization energy, corresponding to the binding energy of the vibrational-ground-state ($v'=0$) Si $2p_{3/2}$ photoelectron line (the most intense peak in Fig. 1), was found to be 107.31 ± 0.05 eV as compared with previous values of 107.31 and 107.28 eV.[18] Post-collision interaction (PCI) shifts the positions of inner-shell photoelectron peaks to slightly higher binding energy and broadens the peaks with a pronounced asymmetry at high binding energy when the kinetic energy of the photoelectron peak is less than that of the subsequently ejected Auger electron.[19] The effects are not large, with an expected binding energy shift of < 0.10 eV, since the photon energy used is ~ 30 eV above the Si $2p$ threshold and the effects of PCI decrease with increased kinetic energy of the ejected photoelectron. The Si $2p$ photoelectron peaks are not noticeably asymmetric and hence corrections for PCI were not made to the line shape. The spin-orbit splitting was found to be 0.612 ± 0.001 eV with a Si $2p_{3/2}$ to Si $2p_{1/2}$ intensity ratio of 0.500 ± 0.005 eV, corresponding exactly with the statistically expected value. This accurately determined Si $2p$ spin-orbit-splitting value compares favorably with the value of 0.608 eV from the latest and highest-resolution previous study.[1] The vibrational splitting was found to be 0.295 ± 0.002 eV from

the average of the four fits, and Franck-Condon factors of $(66.3 \pm 0.3)\%$, $(29.1 \pm 0.3)\%$, and $(4.6 \pm 0.2)\%$ were obtained for the ground-, first-excited, and second-excited vibrational states ($v'=0$, 1, and 2) of the core-hole ion, respectively.

The distribution of Franck-Condon factors, with the vibrational ground state ($v'=0$) being the most populated upon ionization, indicates that the equilibrium atomic positions for SiH_4 change slightly upon removal of the Si $2p$ electron. The change in the Si-H vibrational energy upon ionization is further evidence for a change in bonding properties of the molecule when a Si $2p$ electron is removed. The SiH_4 ground-state vibrational energy of the totally symmetric (v_1) vibration is 2180 cm^{-1},[20] whereas the vibrational frequency observed in the photoelectron spectrum for the Si $2p$ core-hole state is 2379 ± 16 cm^{-1} $(0.295 \pm 0.002$ eV). The $\sim 10\%$ increase in the vibrational energy upon removal of a Si $2p$ electron indicates that the Si-H bond is stronger in SiH_4^+ (Si $2p^{-1}$) than in the electronic ground-state molecule. The change in equilibrium nuclear positions noted above therefore corresponds to a shortening of the Si-H bond. This results from the Si outershell electrons (valence electrons in the molecule) contracting around the nuclear core[21] when the Si $2p$ electron is ejected.

In the $Z+1$ analogous-molecule model, the properties of a molecular ion with a core hole are presumed to be reasonably approximated by those of the analogous molecule with a $Z+1$ atom in the place of the one with the core hole.[8,15] The $Z+1$ model compound for Si-$2p$-core-ionized SiH_4^+ is PH_4^+. The totally symmetric vi-

brational frequency (v_1) for PH_4^+ measured in the solid state has been reported as 2295 cm^{-1},[20] which is closer to the 2379 cm^{-1} observed for SiH_4^+ (Si $2p^{-1}$) than is the ground-state SiH_4 vibrational energy of 2180 cm^{-1}. The symmetric stretching frequency of gaseous PH_3, 2327 cm^{-1}, is a better value to compare with the Si-H stretching frequency of Si-$2p$-ionized SiH_4 since the P-H stretching frequencies in PH_4^+ may be lowered due to hydrogen bonding with counter ions in the sample.[20] In a previous study of the vibrational excitations accompanying the C $1s$ ionization of CH_4, the first vibrational level was found to be 3154 cm^{-1} above the ground vibrational state of the core-hole ion.[1] This value compares more favorably with the vibrational frequency of NH_4^+, 3040 cm^{-1},[20] than it does with the ground-state vibrational frequency of CH_4, 2916.5 cm^{-1}.[20] For both SiH_4 and CH_4 the vibrational energies of the core-hole states are more closely approximated using the $Z+1$ analogous molecules and ions than the ground-state molecules. Neither, however, gives exact results.

The shape of the function describing the contributions of the monochromator and electron spectrometer to the total line shapes is not precisely known for the current experimental configuration, although Kr resonance Auger spectra obtained at 90-eV photon energy indicate that it is very close to Gaussian. It is, however, possible to estimate the natural linewidth of the Si $2p$ photoelectron lines using line-shape analyses which have been described previously.[22] Assuming the experimental contribution (photon+electron) to the line shape to be Gaussian, we obtain a natural Lorentzian linewidth of $\sim$45 meV. This is in reasonable agreement with the width obtained from the high-resolution photoabsorption spectrum of SiH_4,[23] but does not compare favorably with the value of 15 meV estimated by Krause.[24] A natural lifetime width of 49 meV, in excellent agreement with the value obtained here, is obtained using the statistical treatment of Coville and Thomas[7] with the experimental Ar $2p$ linewidth.[24]

A manifold of vibrationally and spin-orbit-split bands was also fitted to the Si $2p$ photoelectron spectrum of SiF_4. Since numerous partially resolved peaks combine to give the resulting SiF_4 Si $2p$ photoelectron spectrum, it is difficult to unequivocally determine the spectral parameters using a least-squares procedure. The fitting procedure is simplified using the $Z+1$ analogous molecule PF_3, with a symmetric stretching frequency of 893 cm^{-1}.[20] Since the experimental contributions to the linewidth are similar for both spectra, the peak widths in the SiH_4 and SiF_4 spectra are also assumed to be similar. The SiF_4 Si $2p$ spectrum was fitted with nine vibrational levels with a separation of 0.105 eV (847 cm^{-1}), each split by the Si $2p$ spin-orbit coupling, and the results are shown in Fig. 2. Since the bands are not completely resolved in the spectrum no anharmonicity could be included in the fitting procedure. The low intensity of the

first vibrational band ($v'=0$) causes uncertainty about other lower-intensity bands preceding it in the vibrational manifold. If the first peak in the photoelectron spectrum corresponds to the vibrational ground-state band ($v'=0$) then the adiabatic ionization energy for the Si $2p$ level of SiF_4 is 111.57 ± 0.05 eV. This compares reasonably with values of 111.70 and 111.79 eV from previous studies,[18] in which no vibrational fine structure was resolved. The component lines in Fig. 2 are described by a linear combination of 95% Gaussian and 5% Lorentzian line shapes with half-height widths of 0.116 eV. Franck-Condon factors for the eleven vibrational levels fitted to this spectrum are 1%, 2%, 6%, 13%, 18%, 20%, 17%, 12%, 7%, 3%, and 1% for the $v'=0-10$ levels, respectively. Better instrumental resolution is still required to estimate the chemical effect on the Si $2p$ linewidths.[7]

The implication of the large number of vibrational bands in the SiF_4 Si $2p$ photoelectron spectrum is that the equilibrium geometry of SiF_4 changes to a larger extent upon ionization than does the equilibrium geometry of SiH_4. The increased vibrational frequency for the molecular ion indicates a stronger Si-F bond in the core-hole ion which implies a shorter bond length in SiF_4^+ (Si $2p^{-1}$) than in the neutral molecule.

It will be possible to measure vibrationally resolved partial cross sections or branching ratios above the Si $2p$ core level with equivalent or slightly improved experimental resolution. Variations of $\geq 5\%$ in the Franck-Condon factors should be easily detectable at the resolution used to obtain the spectra reported here. Previous measurements of vibrationally resolved branching ratios for the $3\sigma_g$ and 5σ valence molecular orbitals of N_2 (Ref. 16) and CO,[25] respectively, have shown that shape resonances have a noticeable effect on vibrational band intensities. Similar effects are expected for the vibrational manifolds of core-level ionizations when excitation energies corresponding to the shape resonances are used.[16]

Very-high-resolution Si $2p$ photoelectron spectra of SiH_4 and SiF_4 have been reported, and parameters describing the spectra determined using an iterative non-linear least-squares procedure. The spin-orbit splitting and Franck-Condon factors were also accurately determined for SiH_4. A comparison of the vibrational frequency of the Si $2p^{-1}$ core-hole state with the neutral ground-state frequency and frequencies of the $Z+1$ analogous compounds led to the conclusion that the $Z+1$ compounds accurately describe the Si $2p^{-1}$ state. Changes in equilibrium geometry upon ionization were shown to account for the observed vibrational splittings. The results reported here highlight the possibility of obtaining vibrationally resolved cross sections of core levels over wide photon energy ranges using synchrotron radiation. These results also show that much narrower core-level widths can still be obtained for the Si $2p$ and many

other levels if even narrower bandwidth photon sources are used.

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