

Anomalous Natural Linewidth in the $2p$ Photoelectron Spectrum of SiF_4

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The silicon $2p$ photoelectron spectra for SiH_4 , SiF_4 , and SiCl_4 have been analyzed to give the natural linewidths of the Si $2p$ hole states, which reflect the Auger decay rates of the states. For SiH_4 the measured width of 38 meV is in approximate agreement with the prediction of the one-center model (32 meV), but that for SiF_4 of 79 meV is more than 5 times the value of 14 meV predicted by this model. Approximate theoretical calculations indicate that valence electrons from the fluorine atoms of SiF_4 play an important role in the Auger decay via interatomic processes.

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Ionization of an inner-shell electron produces a highly excited ion. For $1s$ ionization in first-row elements and $2p$ ionization in second-row elements the ions deexcite primarily by CVV Auger decay in which one valence electron (V) fills the core hole (C) and one valence electron (V) is ejected. The lifetime, τ , for this process is reflected in the natural, or Lorentzian, linewidth, Γ , of the lines in an x-ray photoelectron spectrum or an Auger spectrum through the relationship $\tau\Gamma = \hbar = 658 \text{ fs meV}$. Linewidths of interest range from about 30 meV (Si $2p$) [1] to 270 meV (Ne $1s$) [2].

Because the core hole is strongly localized on one atom, it is expected that only valence electron density in the vicinity of the core hole influences the Auger process. For molecules this expectation leads to the one-center approximation that electron density on the atoms other than the core-ionized atom can be ignored in calculating either the Auger rate or the Auger spectrum. A consequence of the one-center approximation is that the Auger rate will be affected by the nature of the ligands attached to the core-ionized atom. Electronegative ligands withdraw valence electrons from the vicinity of the core hole, making them less available to participate in Auger decay. Such ligands are, therefore, expected to lower the Auger rate and to decrease the linewidth.

A variety of calculations based on the one-center model have supported this expectation, but experimental results, mostly on the linewidths of the carbon $1s$ core hole, show only small variations with chemical composition. See Ref. [3] for the results of recent measurements and a summary of calculated linewidths. Even so, predicted and experimental lifetimes for carbon $1s$ holes do not differ from one another by more than a factor of about 1.5, and it has appeared that the one-center approximation is at least approximately valid.

Measurements of the silicon $2p$ photoelectron spectrum for SiF_4 , which we report here, show, however, that the natural linewidth in this molecule is more than 5 times the value predicted by the one-center model. At the same time the widths for $2p$ holes in SiH_4 and SiCl_4 are approximately as predicted. We believe that these results indicate that the valence electrons from the fluorine atoms play an important role in the Auger decay process, contrary to the assumptions of the one-center model. We present the results of an approximate theoretical calculation indicating that processes in which one of the participating electrons comes from the fluorine atoms are approximately as probable as those in which both electrons come from the silicon atom.

The phenomenon we have observed is closely related to intermolecular Coulombic decay (ICD) discussed by Santra *et al.* [4] and to electron-transfer mediated decay (ETMD) investigated by Zobeley *et al.* [5] In these processes the deexcitation of a core hole on one atom involves the participation of one or two electrons on an adjacent atom. These recent works indicate that under appropriate circumstances such processes can play an important role in the deexcitation of the excited state.

The valence and silicon $2p$ photoelectron spectra of SiH_4 , SiF_4 , and SiCl_4 as well as the valence spectrum of N_2 were measured on beam line I411 of the MAX II third-generation synchrotron using a Scienta SES-200 electron-energy analyzer. The photon energy was 61 eV for the valence spectra and 150 eV for the core spectra. The monochromator and electron-energy analyzer slits and the pass energy of the analyzer were chosen to give an overall experimental broadening of about 30 meV. Measurements of valence photoelectron spectra and of photon absorption spectra at the carbon $1s$ π resonance verified that the electron-energy analyzer and monochromator were working as expected.

The measured spectra are shown in Fig. 1 where the points represent the experimental data and the lines represent least-squares fits to the data, as discussed below. Each spectrum is characterized by a spin-orbit doublet and a vibrational progression corresponding to the symmetric SiX stretching mode (X = H, F, Cl). In the SiH₄ spectrum there is no indication for an asymmetric bending mode, as was suggested by Sutherland *et al.* [6] on the basis of lower resolution data. On the basis of the data alone, we cannot exclude the possibility of other vibrational modes contributing to the SiF₄ and SiCl₄ spectra, but in the absence of such symmetry breaking effects as Jahn-Teller distortion, no other modes are to be expected. We can exclude the possibility of Jahn-Teller distortion, since this would affect only the 2p_{3/2} manifold; there are, however, no apparent differences between the line profiles of the two different manifolds.

The spectra have been fit by least squares [7] using fitting functions that take into account the natural linewidth, Gaussian resolution, and the interaction between

the photoelectron and the Auger electron emitted in the deexcitation of the core-hole state. This interaction is described using Eq. (12) from van der Straten *et al.* [8], which should be valid at these energies. The fitting parameters are the natural linewidth, the positions and heights of the peaks in the 2p_{3/2} manifold, the spin-orbit splitting, the ratio of 2p_{1/2} to 2p_{3/2} intensity, and a constant background. The peaks in the 2p_{1/2} manifold are linked to those in the 2p_{3/2} manifold by the spin-orbit splitting and the assumption that the relative vibrational intensities in the 2p_{1/2} manifold are the same as those in the 2p_{3/2} manifold. For the results reported here, we have assumed an experimental resolution of 30 meV, but we have also done fits with resolutions higher and lower than this. The derived results are fairly insensitive to this choice; the uncertainties quoted are based on the possibility that the resolution is uncertain by 10 meV.

Our fits do not include the effects of either hot bands or rotational broadening. In SiCl₄, about 13% of the neutral molecules will have one quantum of excitation in the symmetric stretching mode, and this could be taken into account in the fitting, but we do not expect this to have an important effect on the results presented here. The effect of hot bands for the other two molecules is negligible. The question of rotational broadening has been considered at an approximate level by Carroll *et al.* [3], and following their approach we conclude that this might produce an additional contribution (in quadrature) of about 5 meV to the resolution.

The natural, or Lorentzian, linewidths derived from the data are 38 ± 3 meV (SiH₄), 79 ± 5 meV (SiF₄), and 54 ± 6 meV (SiCl₄). These are to be compared with those calculated by Larkins [1] using the one-center model of 32, 14, and 32 meV, respectively. The agreement between experiment and prediction is reasonable for SiH₄. For SiCl₄ the experimental value is 1.6 times the predicted value; this discrepancy is within the range that has been observed for carbon 1s linewidths [3,9]. The result for SiF₄ is, however, more than 5 times the predicted value. This is the unexpected result that emerges from these measurements.

The linewidth we have found for SiH₄ is in reasonable agreement with the experimental values of 45 and 49 meV reported by Bozek *et al.* [10,11], but our width for SiF₄ is not consistent with their observation that the linewidth for SiF₄ is less than that for SiH₄ [11]. However, it is important to note that Bozek *et al.* measured their spectra with an overall resolution of about 95 meV and fit the SiF₄ spectrum with 11 peaks in each member of the spin-orbit doublet, whereas we can find evidence for only 9. As a check, we have fit our SiF₄ spectrum with peaks for which the Lorentzian width is constrained to 40 meV (about the same as for SiH₄) and the Gaussian width to 30 meV. Part of this fit is shown as the inset in Fig. 1; it is apparent that the experimental peaks are significantly broader than these parameters would suggest.

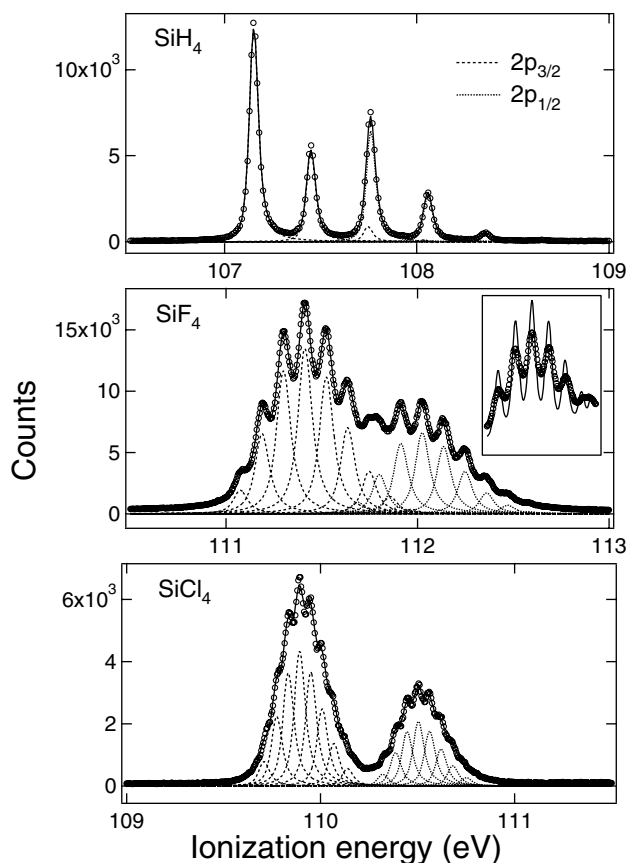


FIG. 1. Silicon 2p photoelectron spectra of SiH₄, SiF₄, and SiCl₄. The circles show the data and the solid lines show least-squares fits to the data. The dashed and dotted lines show the individual components of the 2p_{3/2} and 2p_{1/2} manifolds. The overall experimental broadening is 30 meV. The inset shows a portion of a fit to the SiF₄ data with the Lorentzian width constrained to 40 meV.

The one-center model takes its theoretical justification from the work of Matthew and Komninos [12] who derived approximate expressions for the Auger rate for processes involving valence electrons from atoms other than the one with the core hole. In one (inter-intra Auger decay) one of the participating electrons originates from the atom with the core hole and the other from an adjacent atom. In inter-inter Auger decay both participating electrons originate from an adjacent atom. (These processes are also referred to as ICD [4] and ETMD [5] as noted above.) For an AB molecule with the core hole on A, the inter-intra decay rate ($1/\tau$) as given by Matthew and Komninos is

$$\tau_{\text{inter-intra}}^{-1} = c^4 \sigma_{k\nu}^B \tau_{\text{radA}}^{-1} / \omega^4 R^6. \quad (1)$$

On atom A an electron goes from orbital λ to orbital μ , and τ_{radA}^{-1} is the rate for the x-ray transition between these states, with energy ω . On B, an electron goes from ν to k (the continuum) and $\sigma_{k\nu}^B$ is the cross section for photoionization of this electron by a (virtual) photon of energy ω . (The conjugate term is ignored.) R is the interatomic distance. For the inter-inter transitions, the expression is essentially the same, except that the radiative rate is replaced by the radiative rate for the crossover x ray from orbital ξ on B to orbital μ on A. Using Eq. (1) Matthew and Komninos showed that the interatomic Auger rates are expected to be negligible for a carbon $1s$ hole in CH_4 and CF_4 .

More recently, Santra *et al.* [4] and Zobeley *et al.* [5] have indicated that there are conditions where interatomic Auger processes may be significant. These typically involve a deep valence hole on an atom in a van der Waals dimer or cluster. Favoring the interatomic processes are the low energy of the transition and, for clusters, the large number of final states arising from the large numbers of nearest neighbors. While SiF_4 does not exactly meet these criteria, the transition energy is not large and there are four nearest-neighbor fluorine atoms. Moreover, the bond length in SiF_4 is considerably less than is found in van der Waals molecules. Since the interatomic rates scale as the 6th power of this distance, it is possible that these effects could be important in SiF_4 . We investigate this possibility using the expression given by Matthew and Komninos.

Since this expression has been subject to some criticism [13], we first test it on a problem that has been studied by Zobeley *et al.* [5], the interatomic rate in a neon-argon dimer with an initial hole in the neon $2s$ shell. This decays to a state with one hole in the neon $2p$ shell and one in the argon $3p$ shell. Zobeley *et al.* have calculated this rate for interatomic distances between 2.5 and 3.5 Å. For this comparison, we take 26.9 eV as the energy for the $2s^{-1} \rightarrow 2p^{-1}$ transition in neon ion [14]. The cross section for ionizing a $3p$ electron from argon with a photon of this energy is 8.1 Mb [15]. The radiative transition rate

(4.1×10^{-7} atomic units) has been calculated from Hartree-Fock wave functions for atomic neon [16] using Eq. (8) given by Walters and Bhalla [17]. At interatomic distances of 2.5, 2.9, and 3.5 Å, Eq. (1) gives lifetimes of 6, 15, and 45 fs, respectively. These are to be compared with the corresponding results from Zobeley *et al.* of 3, 10, and 30 fs. While the agreement is not perfect, the comparison indicates that Eq. (1) gives results that are qualitatively correct and not orders of magnitude different from those obtained by other methods.

Applying Eq. (1) to the SiX_4 series we obtain the results given in Table I. For these calculations the x-ray energy is taken to be the $L_{\text{II,III}}$ x-ray energy of silicon, 91.5 eV [18]. For the inter-intra process, the radiative rate is 1.65×10^{-7} a.u. [19]. The cross sections are 13.2 (F), 4.6 (Cl), and 0.12 (H) Mb. For the halogens these are equal to the sum of the atomic $2s$ and $2p$ (or $3s$ and $3p$) cross sections [15] at 90 eV multiplied by 4 (because there are four ligand atoms). For hydrogen it is 4 times the atomic cross section. The bond lengths for the core-ionized molecules are taken to be 1.50 Å (SiF_4), 1.42 Å (SiH_4), and 1.96 Å (SiCl_4). These are each 0.06 Å shorter than the equilibrium bond length of the neutral molecule, reflecting the bond contraction that accompanies core ionization.

It is possible that there are additional contributions to the decay rate from inter-inter decay processes, as suggested for the NeAr dimer by Zobeley *et al.* [5], with both electrons originating from the same atom (fluorine). The multipole expansion used by Matthew and Komninos in deriving Eq. (1) is, however, valid only if the two electrons are on separate atoms, and, hence, this expression is not useful for predicting this rate.

What credence can be attached to the results obtained using Eq. (1)? This expression is strictly valid only in the limit of large interatomic distance. Agreement with the results obtained by Zobeley *et al.* [5], mentioned above, improves as the interatomic distance increases, but at the smallest distance for which a comparison could be made the prediction of Eq. (1) is a factor of 2 lower than the value given by Zobeley *et al.* Thus, the predictions of this model could be too low by a factor of 2 or more. On the other hand, the values of τ_{radA}^{-1} have been calculated for neutral silicon atom. These should be reduced in the molecule to take into account the withdrawal of valence electrons from silicon by the electronegative halogens. Using Mulliken populations for SiF_4 , we estimate that this effect of ionic bonding might lower the calculated

TABLE I. Calculations of intra-atomic and interatomic Auger transition rates in SiF_4 , SiH_4 , and SiCl_4 . The results are given as the Lorentzian linewidth in meV.

	SiF_4	SiH_4	SiCl_4	
intra-atomic	14	32	32	Ref. [1]
inter-intra	11	0.14	0.79	

rate by a factor of about 2. Thus, we might conclude that these quantities can be described only as estimates of the possible importance of interatomic transitions.

Keeping this reservation in mind, we see from Table I that the theory of Matthew and Komninos predicts interatomic Auger rates for SiF_4 that are comparable to the rates for intra-atomic transitions. On the other hand, interatomic transitions appear to play little role in SiH_4 and SiCl_4 , in agreement with the observation that the measured linewidths for these molecules are of the same order as those predicted by the one-center model.

Why are the effects of interatomic transitions so much less for SiCl_4 and SiH_4 than for SiF_4 ? For SiCl_4 , the major factor is the SiX bond length, which enters to the 6th power. For core-ionized SiCl_4 , this is 1.96 Å, whereas for SiF_4 it is 1.5 Å. In addition, the cross section for ionization of Cl in SiCl_4 , which appears in Eq. (1), is less than half that for SiF_4 . For SiH_4 , the bond length (1.42 Å) favors interatomic transitions, but the cross section for ionization of hydrogen is only 1% of the cross section for ionization of fluorine.

These calculations give an estimate of the effect of interatomic transitions in SiF_4 . It is useful to look at this also from the point of view of the charge distribution of the valence electrons. This can be estimated either from Mulliken populations or from the electrostatic potential at the van der Waals radius. For these molecules, the two methods are in approximate agreement, and indicate that the silicon atom in core-ionized SiF_4 has about 1.5 fewer valence electrons than SiH_4 and SiCl_4 . This difference is reflected in the much smaller linewidth predicted for SiF_4 by the one-center model. That this lower rate is not found experimentally points strongly to the participation of electrons that are localized on the fluorine atoms, and hence to a breakdown of the one-center approximation for this molecule.

The SiF_4 LVV Auger spectrum is consistent with the view that interatomic transitions play an important role in the decay process. A calculation by Larkins *et al.* [20] using the one-center model predicts only four groups of peaks in this spectrum, whereas six are observed. The extra peaks, which according to their calculations involve hole states localized on the fluorine atoms, can be understood if there are significant interatomic processes. However, this spectrum does not, by itself, provide definitive evidence for such transitions, since later calculations by Gottfried *et al.* [21], using a higher level of theory, indicate that the silicon Auger spectrum of SiF_4 can in fact be accounted for within the framework of the one-center model.

In conclusion, our results for SiF_4 indicate that interatomic effects can, under the right circumstances, play an important role in the Auger process. It is likely that other examples of this phenomenon will be found where there

are multiple ligands with high ionization cross sections located close to the atom with a core hole (as, for instance, in the systems suggested by Santra *et al.* [4] and by Zobeley *et al.* [5]).

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