

Relaxation processes of resonances in SiH₄ in the vicinity of the silicon 2*p* threshold

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Photoelectron spectroscopy with monochromatic synchrotron radiation (100–115 eV) is used to study the silicon 2*p* excitation and ionization in the silane molecule. Valence main bands and satellites are observed when SiH₄ is excited below the Si 2*p* edge and off resonance. Auger lines are seen for excitation energies above the edge. The excitation of a core electron into the lowest antibonding molecular orbital results in dramatic changes in the spectrum. In addition to autoionization and resonant Auger processes, which lead to SiH₄ with one-hole and two-hole–one-particle (or multiple-hole) excited configurations, respectively, an unexpected relaxation pathway due to the purely repulsive character of the core-excited state is proposed to explain the existence of very low binding energy resonating lines. It consists of a very fast dissociation into SiH₃* + H followed by autoionization of the core-excited SiH₃* fragments.

I. INTRODUCTION

Resonances observed in the photoabsorption spectra of gas-phase molecules in the vicinity of atomic core-excitation edges have been the subject of recent investigations in photoelectron and photoion studies. The possible observation of site-selective fragmentation processes^{1–3} is of great photochemistry interest. The use of synchrotron radiation plays a significant role in this kind of study, for its tunability allows the selection of specific resonances (valence excited states, Rydberg states, or shape resonances). In the particular case of the 2*p* core photoabsorption spectra^{4,5} of the second-row hydride molecules, among which is the silane molecule SiH₄, two kinds of resonances are generally seen: (i) narrow lines assigned to Rydberg series converging to the core ionization threshold and (ii) at lower energy, much broader and intense features which have a strong valence character.^{5,6} The latter result from the excitation of a core electron into an antibonding orbital and consequently are specific for the molecule under consideration and do not exist in the spectrum of the isoelectronic atom, i.e., argon.

The nature of the final state of the core-excited electron, i.e., valence, Rydberg, or continuum, strongly influences all subsequent electronic-relaxation processes. The ejection of a 2*p* electron into the continuum is usually followed by an Auger process (*LVV*) which leaves the molecule with two holes in the valence shells and an electron of a well-defined energy. This molecular Auger process has often been studied in many systems using x-ray tubes,⁷ electron impact,^{7,8} and more recently synchrotron radiation^{9–11} as excitation sources. A core-excited state may also decay through a similar Auger process but the presence of the excited electron (spectator or not) results in a residual excited ion. It can either be described with a one-hole, two-hole–one-particle, or multiple-hole configuration. As opposed to normal Auger, such resonant

Auger process has been established for atoms¹² and in very few cases for molecules^{9–11,13,14} because the low cross section requires monochromators with high transmission, when synchrotron radiation is used,^{9–11,13,15,16} or more sophisticated detection methods such as electron-electron coincidence spectroscopy¹³ when electron impact is used. This scheme can, of course, be extended to the cases in which the relaxation processes involve the ejection of two, three, or more electrons. If the initial step is the ejection of the 2*p* electron, we call these processes double, triple, etc., Auger, and the final state will be an ion with three, four, or multiple charges; if, on the other hand, the first step is the excitation of the inner-shell electron, we will likewise speak of double, triple, etc., resonant Auger processes, and the final states will consist of doubly, triply, etc., charged ions.

In this paper, we report on the photoelectron and Auger spectra of the silane molecule SiH₄, measured in the 100–115-eV photon-energy range, which encompasses the silicon 2*p* edge (2*p*_{3/2}, 107.2 eV; 2*p*_{1/2}, 107.8 eV) (Refs. 17 and 18) and associated (valence and Rydberg) resonances previously identified in photoabsorption spectra.^{4,5}

Special attention is given to the analysis of final ionic states formed through normal and resonant Auger processes. In addition, we propose a two-step decay process for a valence resonance, namely, a fast dissociation followed by the autoionization of the excited fragment, in close analogy to a recent observation in HBr, near the bromine 3*d* edge.¹⁹

II. EXPERIMENTAL PROCEDURE

The apparatus has been described in detail elsewhere.²⁰ Briefly, the uv synchrotron radiation emitted from the ACO (Anneau de Collision d'Orsay) storage ring at Orsay is focused on the entrance slit of a toroidal grating monochromator, providing a high photon flux (e.g., of 6×10^{11}

photons/[Å s (100 mA)] in the 100–120-eV range. The monochromator bandpass is set at 1.2 eV in order to get a reasonable counting rate. The monochromatized light is refocused at the center of the interaction chamber where it crosses an effusive jet of gas at right angles. After ionization, the ejected electrons are filtered by a 127° cylindrical electrostatic analyzer and detected by a single-channel electron multiplier. The analyzer is operated at constant pass energy of 10 eV which corresponds to a resolution of 0.7 eV, and the photoelectron spectra (PES) are obtained by scanning the potential of the ionization chamber. In order to obtain partial cross sections quickly and continuously, we simultaneously scanned the ionization-chamber voltage and photon energy. This constant ionic state method (CIS) has been described elsewhere.²⁰ All spectra were taken at the pseudo-magic-angle which eliminates angular effects. In addition, in order to reduce drastically the background noise, the electron signal is collected only when it is correlated in time with the photon pulses. A 10-ns time window, which repeats itself every 73 ns (the ACO repetition rate) makes the signal-to-noise ratio increase by a factor of ~ 7 . Spectra are then corrected for the incident light intensity (monitored by a gold-mesh photoemission) and the electron transmission of the analyzer.

The sample of silane was purchased from Air Liquide Company with a nominal purity of 99.999%. The evacuation system was equipped especially for this spontaneously flammable gas with a permanent flux of nitrogen and the exhausted silane gas was bubbled into a soda solution.

III. RESULTS AND DISCUSSION

The 1A_1 ground-state configuration of SiH₄ can be described as follows:

Core orbitals			Valence orbitals		
$1a_1^2$	$2a_1^2$	$1t_2^6$	$3a_1^2$	$2t_2^6$	
Si 1s	Si 2s	Si 2p	Si 3s	Si 3p,	H 1s (Si–H bonding)

We now present and analyze separately our results (a) on the valence photoelectron bands, (b) on the normal and resonant Auger spectra, and (c) on the dissociation spectra.

A. Valence photoelectron spectrum and partial photoionization cross sections

We present in Fig. 1 two photoelectron spectra of silane obtained at 103.2 and 100 eV photon energy in the 10–60-eV binding-energy region. Figure 1(a) corresponds to a PES recorded on-resonance and Fig. 1(b) to a PES measured off-resonance.

We observe in Fig. 1(b) two intense features at 12.8 and 18.2 eV which correspond, respectively, to the two valence bands $2t_2$ and $3a_1$. The observation and assignment of the $2t_2$ band has been made long ago, by He I photoelectron spectroscopy^{21–23} and also by x-ray photoelectron spectroscopy (XPS).²⁴ The broadening of this band was analyzed in terms of the Jahn-Teller effect.

The observation of the band at 18.2-eV binding energy has been barely possible with He I photons^{21,22} but was more clearly established by XPS experiments.²⁴ Additional observations, by threshold photoelectron spectroscopy²⁵ of Rydberg series converging to the $3a_1^{-1}$ band confirmed its existence.

The present spectrum [Fig. 1(b)] shows that the branching ratio of the $3a_1^{-1}$ main band compared to the $2t_2^{-1}$ one is equal to 35%. This ratio amounts to only 0.6% at 21.21 eV (Ref. 21) but reaches more than 200% in the x-ray range.²⁴ This clearly indicates that the $2t_2$ orbital is more diffuse; as the partial cross section is related to the Fourier transform of the radial extension of the wave function $\psi(r)$, the intensity of the corresponding photoelectron band is expected to be lower at higher energies.²⁶

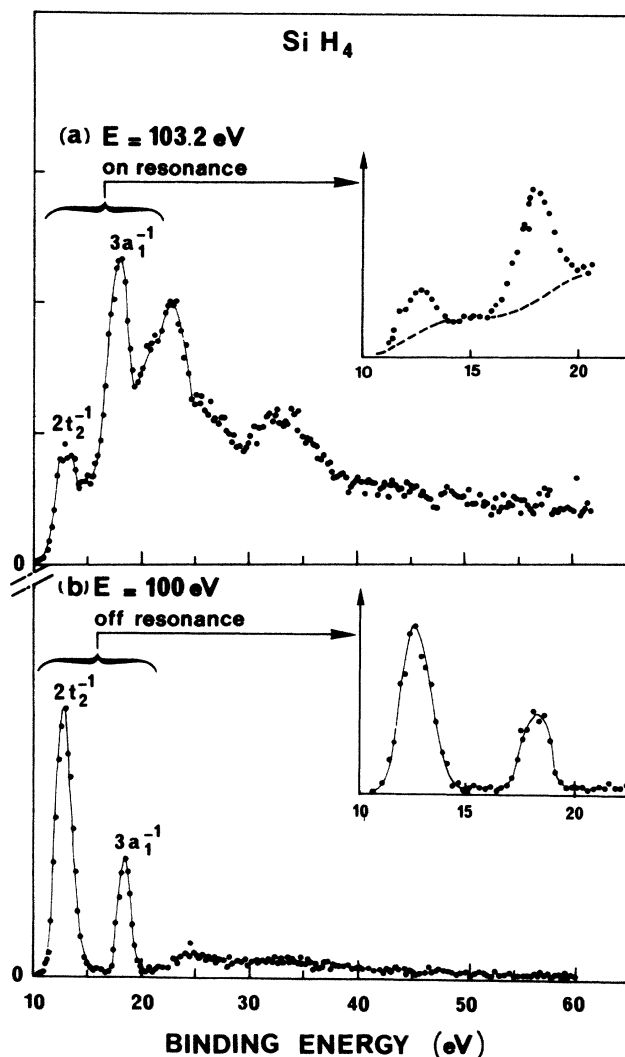


FIG. 1. Photoelectron spectrum of silane measured on the Si $2p$ resonance at 103.2 eV and (b) off-resonance at 100 eV. The inset shows an enlargement of the 10–23-eV binding-energy region in both spectra. In (a) the dashed-line contour shows the contribution of SiH_3^+ states formed through SiH_4^* dissociation (see text).

The spectrum of Fig. 1(b) shows in addition to the two main bands, weaker features above 20-eV binding energy. These structures could be clearly observed due to our very good signal-to-noise ratio (see Sec. II). We have also recorded other PES at 35 and 45 eV (not shown here) and observed them with roughly the same relative intensity. They are likely due to shakeup satellites and to double-ionization continua expected above 33.4-eV binding energy (see our Auger spectrum, Sec. III B). Notice that Perry and Jolly²⁴ observed weak bands around 24 eV by XPS but did not analyze them. At present there is no calculation available on SiH₄ to interpret this part of the spectrum.

The photoexcitation of the silane molecule on a resonant state such as the σ^* at 103.2 eV changes the photoelectron spectrum drastically [Fig. 1(a)]. This resonance can be seen in the photoabsorption spectrum of Hayes and Brown⁴ which is reproduced in the top of Fig. 2. It results from the excitation of a 2*p* electron into an antibonding orbital. New measurements of Friedrich *et al.*⁵ and calculations of Schwarz⁶ show that σ^* is composed of a_1^* and t_2^* excited states, each of them associated with the two spin-orbit components of the 2*p* hole (0.6-eV separation).¹⁸ The spectrum of Fig. 1(a) shows an enormous increase of satellite bands, i.e., above 20 eV, and of the $3a_1$ band as compared to the $2t_2$ band. In addition there is a large increase in intensity in the spectral range from 10 to 20 eV which can be more easily seen in the inset of Fig. 1(a). In order to analyze the detailed photon-energy dependence of each region of the spectrum, we have measured, using the CIS method, the relative partial cross sections for the two main bands, i.e., $3t_2$ and $3a_1$ [see Figs. 2(a) and 2(c)], for the "background" measured at 15-eV binding energy [Fig. 2(b)] and for the satellite band at 24-eV binding energy [Fig. 2(d)]. It is very striking that all features resonate in the region of the σ^* resonance. The absence of resonances in the Rydberg region is probably due to our poor resolution. We have drawn in Figs. 2(a)–2(c) a shaded region which we roughly estimate to be the contribution due to the background identified in Fig. 1(a). This clarifies the following points, observed in the latter figure.

(i) Electrons of 20-eV and higher binding energies are produced efficiently only on the resonance [see also Fig. 2(d)]; their origin will be discussed later.

(ii) The $2t_2$ band does not resonate at the σ^* excited state. Indeed, the rise in intensity observed in Fig. 1(a) is due to the overlap with the strongly resonating structure centered at about 15-eV binding energy.

(iii) The $3a_1^{-1}$ band is believed to resonate at the σ^* excited state, although its intensity will also be partly influenced by the resonating band at 15-eV binding energy. Also notice that this band overlaps with a resonant Auger line, as shown in Fig. 3(b). The energy separation observed between these two bands, and the full width at half maximum (FWHM) (~ 4 eV) of the corresponding normal Auger band [Fig. 3(a)] shows that the latter will only contribute in a minor way to the intensity of the $3a_1$ band in the resonating spectrum. We can also safely say that the contribution from this band to the resonating structure observed at about 15 eV will be negligible.

The resonant character of the $3a_1$ band shows that one of the decay channels of the σ^* resonance is autoionization where the excited electron is not a spectator and participates in the relaxation of the 2*p* hole producing a one-hole SiH₄⁺ final state. This has already been observed in our tetramethylsilane study¹⁶ where the Si 3*s*-like band is greatly enhanced through a resonance right below the Si 2*p* edge.

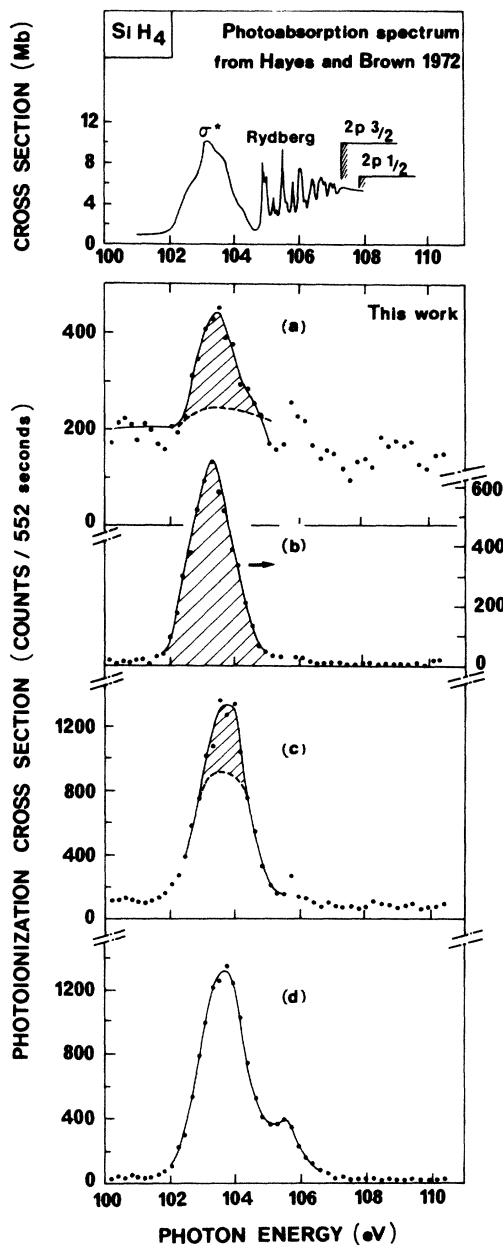


FIG. 2. Top, photoabsorption spectrum of SiH₄ measured by Hayes and Brown (Ref. 4). Bottom, partial ionization cross sections: (a) $2t_2^{-1}$ valence state, (b) continuum at 15-eV binding energy, (c) $3a_1^{-1}$ valence state, (d) satellite at 24-eV binding energy. Shaded areas represent the contribution of SiH₃⁺ formed through dissociation of SiH₄^{*} (see text).

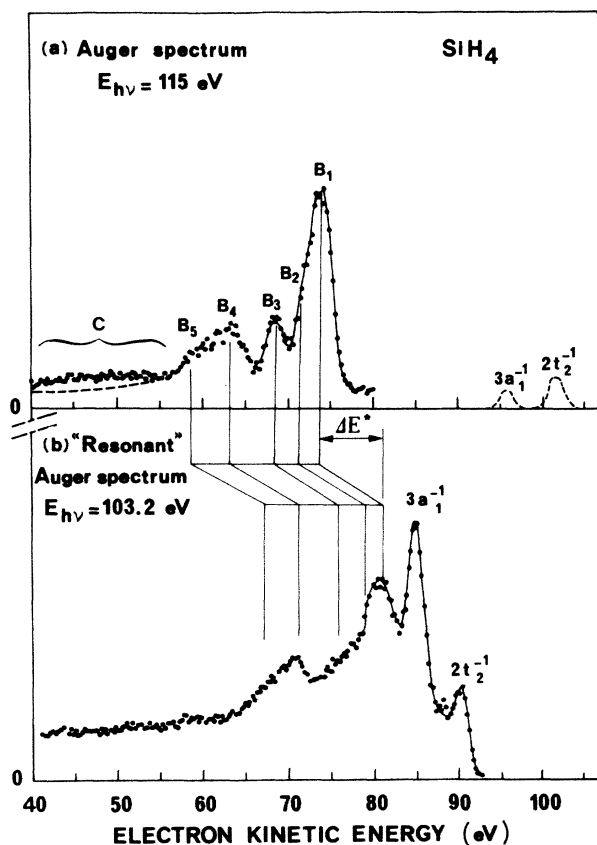


FIG. 3. (a) Auger spectrum of silane measured off-resonance at 115 eV and (b) resonant Auger spectrum on the $\text{Si } 2p \rightarrow \sigma^*$ resonance at 103.2 eV. The observed shift in the lines is indicated by ΔE^* .

In order to analyze the detailed structures above 20 eV, we start by studying the normal Auger spectrum. Then we will consider the continuumlike resonant feature below 20 eV, in Sec. III C.

B. Normal and resonant Auger spectra

We have measured the normal Auger spectrum in the $\text{Si } 2p$ continuum, i.e., at 109 and 115 eV. The observed lines were found at constant kinetic energy. The 115-eV Auger spectrum is reported in Fig. 3(a). We observe various structures labeled B_1 – B_5 and C following usual nomenclature.²⁷

These observations are in very good agreement with the early result of Moddeman²⁸ but vary somewhat with the more recent result of Maracci, Platania, and Salomone,²⁹ and Rye and Houston,³⁰ who found a 2-eV shift of the main bands towards lower energies as compared to this work. In addition they find a splitting of the B_3 band which is not observed here nor in Ref. 27. Lastly, Maracci, Platania and Salomone,²⁹ and Rye and Houston³⁰ find more intense bands in the 63–66.5-eV region. They also show no evidence of the wide C band which is undoubtedly present in our spectrum. Besides the sometimes-difficult background subtraction in the electron impact work,

there seems to be no simple explanation for the discrepancies between the present work and Refs. 29 and 30.

In order to test for a possible post-collisional effect in our spectra, we also measured the Auger spectrum at 107 eV. Besides a slight asymmetric behavior at the B_1 band, no energy shift could be observed within our energy resolution. We have reported in Table I our observations and those of Refs. 28–30 together with the theoretical results of Tarantelli *et al.*³¹ based on the algebraic diagrammatic construction (ADC) method. Most of the intense bands can be then assigned to two-hole states either $2t_2^{-2}$, $3a_1^{-1}$, $2t_2^{-1}$, or $3a_1^{-2}$. Knowing the $\text{Si } 2p$ ionization energy, we have calculated the vertical double-ionization potentials of SiH_4 , as reported in Table I.

The weak and continuous structures observed below 55 eV (peak C) are probably associated to double Auger ($\text{SiH}_4^{3+} + 2e_A$) or satellite double Auger ($\text{SiH}_4^{2+*} + e_A$) which usually lie on the low kinetic energy side, compared to the main bands.^{27,31}

Let us analyze the spectrum measured below the $\text{Si } 2p$ threshold, at 103.2 eV, and which is shown in Fig. 3(b). Besides the bands associated with the main states, $2t_2^{-1}$ and $3a_1^{-1}$, and whose intensities have changed drastically, as already mentioned, intense bands can also be observed, roughly below 83-eV kinetic energy. This coincides in energy with the satellite lines which were observed above 20-eV binding energy in Fig. 1(a). We consider these bands to be due either to a resonant Auger process or to autoionization processes (or both) involving the SiH_3 radical, formed by dissociation of the core-excited SiH_4^* molecule, as discussed below. As to the first possibility, the σ^* excited electron interacts with the $2p$ hole through a Coulomb interaction, and as a result the Auger bands will also be seen in the 103.2-eV spectrum, but shifted with respect to the energy positions observed in the normal Auger spectrum [Fig. 3(a)]. An average 7-eV shift has been observed; notice that this value is larger than the term value associated with the σ^* resonance. Taking from the assignment of Friedrich *et al.*⁵ σ^* as being a_1^+, t_2^* we find that the highest term value ($2p \rightarrow a_1^+$) amounts to 4.4 eV. Similar observations have been made for several molecules.^{9,10,13,15} It is evident that detailed assignments of the observed lines require configuration-interaction calculations on SiH_4^+ which are not yet available.

C. Dissociation of the core-excited molecule

The observation of a large spectral change on resonance and below 20-eV binding energy [Fig. 1(a)] cannot be interpreted as due to the formation of excited SiH_4^+ states because the lowest satellite lines lie above 20-eV binding energy [Fig. 1(b)].

Consequently, we propose another relaxation process, based on a mechanism which has been recently established for the HBr molecule excited near the bromine $3d$ edge.¹⁹ In HBr excitation to an empty σ^* orbital is followed by a fast dissociation process and by autoionization of the core-excited fragment.

In the present case, there are two σ^* antibonding orbitals, a_1^* and t_2^* , associated with the four Si-H bonds.

TABLE I. Auger lines and vertical double-ionization potentials for silane.

Band	Experimental kinetic energy (eV) of Auger electrons				Relative vertical double-ionization potentials (eV): SiH ₄ ²⁺ states		
	Maracci, Platania, and Salomone (Ref. 29)	Rye and Houston (estimated from Ref. 30)	Moddeman Ref. 28	This work	Assignment: Tarantelli <i>et al.</i> (Ref. 31)	Theory (Ref. 31)	Experimental (this work)
B ₁	75.8	74.7	73.7	73.8	¹ E ₁ , 2t ₂ ⁻²	0.00 ^a	0.0 ^b
B ₂ (Shoulder)	73.4		71.0	71.3	¹ T ₂ , 2t ₂ ⁻²	2.02	2.5
B ₃	70.9	70.0	68.0	68.4	¹ A ₁ , 2t ₂ ⁻²	4.97	5.4
	69.7				³ T ₂ , 3a ₁ ⁻¹ 2t ₂ ⁻¹	5.71	
B ₄	65.5	65.2	63.3	63.4	¹ T ₂ , 3a ₁ ⁻¹ 2t ₂ ⁻¹	10.92	10.4
B ₅			58.5	59.0	¹ A ₁ 3a ₁ ⁻²	15.09	14.8
C				40.55			

^aThis line calculated at 31.80 eV is taken as the origin.

^bThis line observed at 33.4 eV is taken as the origin.

The excitation of the Si 2*p* electron into such a σ* valence orbital leads to four resonant states because of the Si 2*p* spin-orbit splitting, as shown by Friedrich *et al.*⁵ The very large width (~1.5 eV) of the overall σ* resonant state (Fig. 2, top) compared to Rydberg states (~0.06 eV) strongly suggests that it has a repulsive character, in contrast to the Rydberg states which are bound.³²

A first question is how to identify the relevant dissociation coordinate in such a polyatomic molecule. Using the

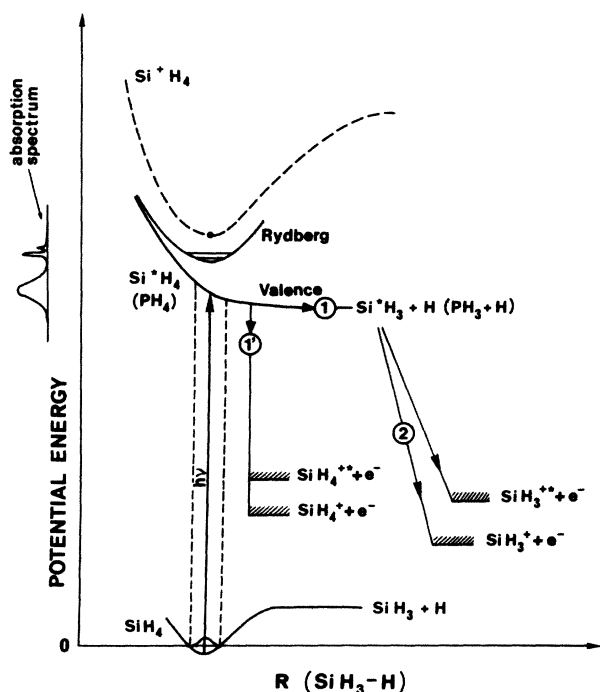


FIG. 4. Relevant potential energy curves for SiH₄ and SiH₄⁺ (with a Si 2*p* core hole) along the SiH₃—H coordinate. Only the lowest-valence core-excited state (Si 2*p*→σ*) and a pure Rydberg state (Si 2*p*→Rydberg) are indicated (see text for discussion).

Z + 1 core analogy model,⁶ the core-excited silicon atom may be replaced by a phosphorous atom. The core-excited Si*H₄ state can then be compared with the PH₄ radical. Janssen, Wisser, and Bruck³³ have established that the PH₄ radical dissociates without energy barrier into PH₃+H (see also Ref. 7) with an excess energy of 1.4 eV. We then reduce the dissociation pattern into the stretching of a single SiH₃—H bond. We present in Fig. 4 the relevant potential energy curves for SiH₄ and SiH₄⁺, using a quasidiatomic picture. We consider now a fast dissociation leading to the ejection of an H atom, followed by the relaxation of the Si*H₃ fragment. Two key questions have now to be answered in order to analyze the relevance of such a two-step process.

(i) What would be the electron energy of the corresponding autoionizing lines of the Si*H₃ fragment?

(ii) Is the Si*H₄ core-excited lifetime large enough to permit the inner-hole relaxation to occur at a larger SiH₃—H distance than in the original SiH₄ molecule?

1. Electron spectrum associated with the autoionization of Si*H₃

The determination of the kinetic energy spectrum following the relaxation of the core hole in Si*H₃ depends solely on the relative position of energy levels (or rather potential curves) of Si*H₃ and SiH₃⁺ as shown below. From the diagram of Fig. 4 we can estimate the electron kinetic energy ε₂, when SiH₃⁺ is produced in its ground state, as

$$\epsilon_2 = h\nu - D^* - D_0 - I_f^0,$$

where $h\nu$ is the resonance energy, D^* is the kinetic energy released in the Si*H₃+H dissociation process, D_0 is the dissociation energy of ground state SiH₄ into SiH₃ (ground state) + H, and I_f^0 the vertical ionization of the SiH₃ fragment. Notice that the quantity $h\nu - D^*$ represents the absolute energy of the Si*H₃+H dissociation limit and does not depend upon photon energy, just as ε₂ which is also only related to the SiH₃ potential curve manifold. The value of D^* can be estimated from the

properties of the $Z+1$ analogue, i.e., PH₄ (see above). The kinetic energy released in the PH₃+H dissociation process (1.4 eV) is taken as a good approximation to D^* . We then obtain for the a_1^* resonance state ($2p_{3/2}$) located at 102.7 eV, $h\nu - D^* = 101.3$ eV (102 eV for $2p_{1/2}$). Knowing from infrared studies³⁴ the dissociation energy D_0 of SiH₄ into SiH₃+H, i.e., 3.89 eV, and the first ionization potential of SiH₃ from Dyke *et al.*,³⁵ we obtain $\epsilon_2 = 88.7$ eV for the $2p_{3/2}, a_1^*$ resonant state and 89.4 eV for the $2p_{1/2}, a_1^*$ state. This corresponds to an "apparent" binding energy of 14.5 eV (or 13.8 eV) as seen in Fig. 1(a). The production of Si^{*}H₃ (PH₃-like) is very probably accompanied by a large vibrational excitation because the Si^{*}H₄ state (PH₄-like), from which it is derived, is known to be largely distorted from the equilibrium geometry (tetrahedron) of the SiH₄ ground state (X^1A_1) and so its formation will also be associated to a rich vibrational structure. On the other hand, Si^{*}H₃ is probably pyramidal at equilibrium geometry because of its resemblance to PH₃. Then, even if the structure of SiH₃⁺ is not known, it is very likely that in the autoionization process, this SiH₃⁺ ion will be produced with a large vibrational structure, giving rise also to electrons with kinetic energy lower than the nominal value ϵ_2 calculated above. One expects then that autoionization of Si^{*}H₃, originating from the dissociation of the a_1^* ($2p_{3/2}, 2p_{1/2}$) resonant states will produce broad bands in the electron spectrum below 89.4-eV kinetic energy or above 13.8 eV on a binding energy scale.

We must take into account that this autoionization process may also be accompanied by electronic excitations. This will then give rise to lines at higher apparent binding energies. This process could complete with the resonant Auger spectrum discussed in Sec. III B.

We have shown above that one possible explanation for the broadness observed in the Si^{*}H₃ autoionizing lines would be vibrational excitation associated primarily to the initial dissociation process. This lack of sharpness contrasts with the HBr case.¹⁹ Of course, in this case one is dealing with the autoionization of an atomic species (Br^{*}), which gives rise to well-defined sharp lines. In the case of SiH₄, the observed broadness can also be due to any of the following.

(i) The C_{3v} symmetry of the equilibrium geometry of Si^{*}H₄ (PH₄-like) should produce a splitting of the t_2^* resonance (not a_1^*) into e, a_1 components, similarly to other silicon molecules.³⁶

(ii) Autoionization of Si^{*}H₃ may lead to repulsive SiH₃⁺ (or SiH₃²⁺) states.

(iii) The existence of an additional resonant state t_2^* close to the a_1^* considered so far,⁵ implies, in a simple adiabatic picture, four different dissociation limits (considering the spin-orbit splitting). Our present photon-energy resolution is not sufficient to resolve them.

2. Time-scale analysis

The 0.06-eV observed width⁴ of the Rydberg series seen in Fig. 2 is directly associated to the inner-hole relaxation processes, i.e., to the coupling of these resonant states with the different continua of SiH₄⁺ and SiH₄²⁺ (in other words, autoionization and/or single- or double-resonant

Auger processes, represented by 1' in Fig. 4. Notice that the resonant $3a_1$ valence line, discussed in Sec. III B, indeed shows that such 1' processes do occur). From this width we can obtain a lower limit (10^{-14} s) for the inner-hole $2p^{-1}$ lifetime τ .

Let us now inquire what would be the internuclear separation d (SiH₃^{*}—H) at a time τ following the $2p \rightarrow \sigma^*$ transition. The energy released in the dissociation has been estimated, as discussed in Sec. III C 1, to be $D^* = 1.4$ eV. Assuming this energy to be entirely transferred to the H atom and considering also that this energy is immediately converted into kinetic energy for this atom we obtain $d = Re + (2D^*/m_H)^{1/2} \tau$ where the equilibrium SiH₃—H distance (Re) is known to be 1.48 Å from Boyd³⁷ and Luke *et al.*³⁸ and m_H is the hydrogen atom mass. We obtain the estimated value of $d \approx 3.15$ Å, which seems to be large enough to justify *a posteriori* the sequential two-step relaxation.

IV. CONCLUSIONS

The photoelectron spectrum of SiH₄ measured below the silicon $2p$ edge, off-resonance (100 eV), shows two well-defined valence bands and broad, but weak, satellite bands extending from 20- to 60-eV binding energy. The normal Auger spectrum measured above the silicon $2p$ edge has been discussed in terms of two-hole states and excited configurations. The photoelectron spectrum measured at the Si $2p \rightarrow \sigma^*$ resonance at 103.2 eV shows dramatic spectral changes which we attribute to (i) selective autoionization into the $3a_1^{-1}$, SiH₄⁺ state; (ii) resonant Auger processes leading to excited states, SiH₄⁺*; (iii) fast dissociation into Si^{*}H₃+H followed by autoionization of the excited fragment into various states of SiH₃⁺ or SiH₃²⁺.

In order to further clarify the described processes, measurements with higher photon-energy resolution would be highly desirable. Knowing that the kinetic energy associated with the electrons originating from the two-step process does not depend on the incident photon energy, one could distinguish between such autoionization lines and resonant Auger lines by scanning the photon energy across the resonance, as tested successfully in the HBr case.¹⁹

Theoretical calculations are underway³⁹ to obtain SiH₃⁺ main lines and satellites; they will also allow the assignment of higher-energy autoionizing lines of Si^{*}H₃ which may interfere with the resonant Auger spectrum.

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