Absorption of SiH_4 in the Extreme Ultraviolet*

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The absorption spectrum of SiH_4 gas has been measured in the silicon L region. Three spin-orbit–split Rydberg series with sharp structure have been observed converging on the $L_{\text{III},\text{II}}$ edges of SiH_4 at 107.2 and 107.8 eV. The three series correspond in a united-atom picture (the united atom for SiH_4 is argon) to transitions from a $2p$ core state to $4s$ and higher s states and to $3d$ and higher d states (d states are split into two components by the molecular field). A molecular-orbital calculation of some peak positions gives reasonable agreement with experiment.

In this Letter we report the absorption spectrum of silane gas (SiH_4) in the vicinity of the silicon $L_{\text{II},\text{III}}$ threshold near 100 eV. Very high resolution (0.03 eV) was achieved by using a grazing-incidence spectrometer (1200-line mm grating) with photon counting[1] and the synchrotron-radiation continuum from the University of Wisconsin 240-MeV electron storage ring.[2] The SiH_4 spectrum shows sharp structure. Our interpretation of the spectrum is consistent with the results of a molecular-orbital calculation. Our results are of interest in comparison with the absorption of solid silicon in the $L_{\text{II},\text{III}}$ region.[3] They also provide some guidelines for the interpretation of the K and L absorption spectra of other polyatomic molecules obtained as part of the present investigation[4] and in earlier work.[5-8]

The gases studied were contained in a cell 6.6 cm long having polypropylene windows roughly 0.8 μm thick. Pressures of about 1 Torr were employed and were measured with a sensitive Bourdon gauge.

Figure 1 shows that the absorption of SiH_4 consists of three Rydberg series labeled (a), (f), and (e) converging on a continuum. The ground configuration of Si is $1s^2 2s^2 2p^6 3s^2 3p^2$ and the spectrum arises from transfer of a single $2p$ electron of Si to excited molecular orbital states of SiH_4. The point symmetry of SiH_4 in its ground state is T_d, and in this symmetry atomic s states transform like Γ_1 and p states like Γ_5; d states split into a triplet (Γ_5) and a doublet (Γ_3). The ground configuration of SiH_4 is $1\Gamma_1{}^2 2\Gamma_1{}^2 1\Gamma_5{}^6 3\Gamma_1{}^2 2\Gamma_5{}^6({}^1\Gamma_1)$. Allowed electric dipole transitions occur to the underlined Γ_5 states in the excited configurations listed below:

$$\begin{aligned} &1\Gamma_5{}^5 n\Gamma_1(\underline{{}^{1,3}\Gamma_5}), \quad n \geqslant 4 \ \text{(a)}, \\ &1\Gamma_5{}^5 n\Gamma_5(\underline{{}^{1,3}\Gamma_5}, {}^{1,3}\Gamma_4, {}^{1,3}\Gamma_3 {}^{1,3}\Gamma_1), \quad n \geqslant 3 \ \text{(f)}, \qquad (1) \\ &1\Gamma_5{}^5 n\Gamma_3(\underline{{}^{1,3}\Gamma_5}, {}^{1,3}\Gamma_4), \quad n \geqslant 1 \ \text{(e)}, \end{aligned}$$

The united atom for SiH_4 is argon and the excitations in argon corresponding to (1) have been observed in the 245-eV region.[9,10] The lowest transition in argon corresponding to series (a) arises from excitation of a $2p$ electron to the $4s$ level. The $2p \rightarrow 3d$ excitation in argon corresponds to the lowest excitations in the (f) and (e) series and the separation of these transitions in SiH_4 is a measure of the splitting of the $3d$ level produced by going from the united atom to the molecule.

We have carried out a computer calculation of the positions of some of the excited states of SiH_4 of interest to us using a one-center expansion method with a minimal angular basis.[11] As a check on our calculation we obtained a ground-state energy for SiH_4 of − 289.6 Ry which compares satisfactorily with the value of − 290.1 Ry obtained by Moccia[12] using a more accurate calculation. We are interested here in transition energies of about 8 Ry (1 Ry = 13.6 eV), and the errors introduced in using a minimal angular basis

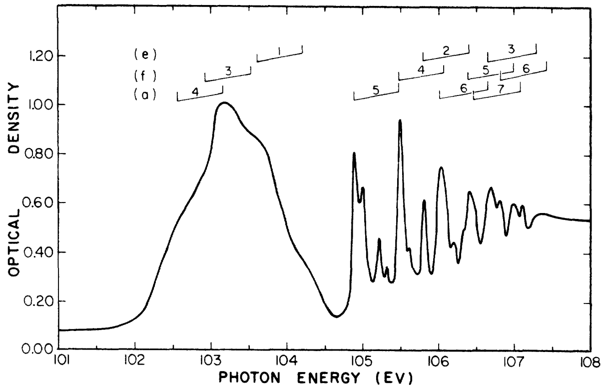

FIG 1. Absorption at room temperature and at a pressure of 1.1 Torr of a column of SiH_4 gas 6.6 cm long. A spectral bandwidth of about 0.05 eV was used. For an explanation of the series labeled (a), (e), and (f), see Eq. (1) in the text. For each n value in each series [see Eq. (1)] the spin-orbit–split components are joined by a sloping line.

are small.

We find that the calculated multiplet splitting in our spectra due to Russell-Saunders coupling arising from electron-hole exchange interaction is negligible compared to experimental linewidths. In the calculation we rely on the Herman and Skillman[13] value for the spin-orbit interaction in the silicon $2p^5$ core. This interaction splits each Γ_5 state in (1) into $^1\Gamma_5$ and $^3\Gamma_5$ branches and transitions are allowed to the triplet branch because of spin-orbit interaction. A similar situation occurs in argon.[9,10] The $^1\Gamma_5$ and $^3\Gamma_5$ branches for series (a), (f), and (e) converge on ionization edges for SiH_4 associated with the $2p_{1/2}$ (L_{II}) and $2p_{3/2}$ (L_{III}) core states of silicon.

We have made an approximate fit of each series in (1) with a simple Rydberg formula, and the average values of the L_{II} and L_{III} edges for SiH_4 obtained from the three series are $L_{\text{III}} = 107.2 \pm 0.4$ eV, $L_{\text{II}} = 107.8 \pm 0.4$ eV. We can determine the L_{II}-L_{III} separation more precisely than the absolute position of each edge and we find this separation to be 0.65 ± 0.05 eV. This result may be compared with the value of 0.70 eV calculated for the spin-orbit energy of the $2p^5$ core of silicon.[13]

Our calculated value for the center of gravity of the spin-orbit branches of the $n=4$ transition in the (a) series is 100.6 eV and our observed value is 102.8 eV. The corresponding calculated values for the $n=3$ transition in the (f) and $n=1$ transition in the (e) series are 100.9 and 102.4 eV and our observed values are at 103.1 and 103.8 eV. The calculated values for the center of gravity of the spin-orbit–split branches of the $n=4$ transition in the (f) and $n=2$ transition in the (e) series are 103.5 and 104.0 eV and the observed values are 105.7 and 106.0 eV. Our observed splittings of the united-atom $3d$ and $4d$ states, 0.7 and 0.3 eV, are about half of the calculated values. Our calculation shows that the Γ_3 states (e) are higher in energy than the corresponding (from a united-atom viewpoint) Γ_5 states (f) becuase the hydrogen nuclei provide an attractive potential for electrons. This result is in contrast with the splitting of the $3d$ level of transition-metal ions tetrahedrally coordinated to negatively charged ions in solids where the Γ_3-Γ_5 splitting is somewhat larger than that found here and is generally assumed to have the opposite sign.[14]

Figure 1 shows that the linewidth in the first member of each series is almost an order of magnitude greater than that of succeeding members. A pronounced narrowing with increasing principal quantum number in Rydberg series in argon has been observed.[15] The large linewidth of the lowest excitations in the present case may be due in part to lifetime broadening arising from autoionization into the continuum of states arising from ionization of less deeply bound electrons. However, in the present case we must also consider coupling to vibrations. Three peaks not classified in Fig. 1 occur between 105.0 and 105.5 eV and may be vibronic excitations associated with the transition to $^3\Gamma_5$ ($n=5$) in the (a) series. The first (lowest energy) line is separated from the $n=5$ electronic line by 0.109 eV, the second from the first by 0.203 eV, and the third from the second by 0.109 eV. These values may be compared with the normal-mode frequencies $\nu_1(\Gamma_1) \simeq \nu_3(\Gamma_5) = 0.274$ eV, $\nu_2(\Gamma_3) = 0.121$ eV, and $\nu_4(\Gamma_5) = 0.113$ eV for the ground electronic state of SiH_4[16]; consideration of product representations shows that vibronic transitions involving these vibrations are allowed in the present case. Weak lines at 105.65 and 106.21 eV, which are also not assigned in Fig. 1, may be vibronic lines of the (a) series. However, dynamic Jahn-Teller effects may be of consequence in the excited Γ_5 states and measurements on SiD_4 would be helpful in establishing the origins of the unclassified lines. The lowest-energy ionization spectrum of SiH_4, determined by photoelectron methods, consists of a band about 2 eV wide at 12.5 eV with a partly resolved vibrational structure with a spacing of 0.10 eV.[17]

It appears in the present case that lines in the (f) and (e) series do not appear to be as strongly coupled to vibrations as lines in the (a) series and this is not inconsistent with the very diffuse nature of our calculated wave functions for the (e) and (f) series. It should be emphasized that since we are exciting a core electron in the present case, which is largely nonbonding, we do not expect equilibrium internuclear distances in our excited states to be appreciably different from those in the ground state and we do not expect internal motions of the molecule to be strongly excited.

Figure 2 shows the absorption of SiH_4 over an extended energy range which includes the L_{I} edge. This spectrum is very similar to that of a thin silicon film measured in the same energy range.[3] The position of the L_{I} edge at 149 eV in SiH_4 is close to that found in silicon.[3] As in silicon, the ionization continuum shows a slow rise beyond the $L_{\text{II, III}}$ edge presumably associated with the delayed onset, due to centrifugal effects,[18] of transitions from the core $2p$ level to continuum

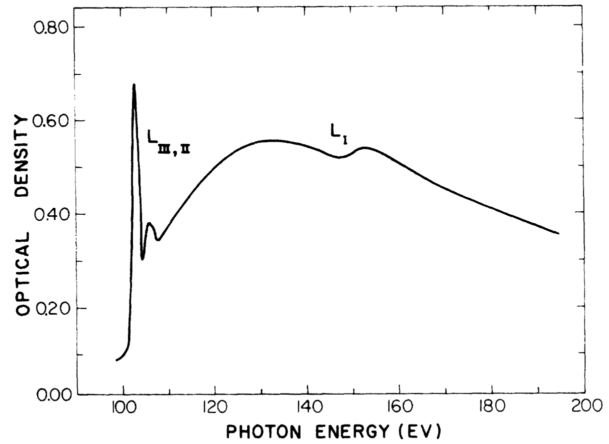

FIG. 2. Absorption of SiH_4 as in Fig. 1 but over a more extended energy range.

d-type states.

We have also measured the absorption of SiF_4 and GeH_4 in the 100–130-eV region.[4] The $L_{II,III}$ spectrum of SiF_4 is shifted to higher energy from that of SiH_4 by 3.5 eV; this chemical shift will be discussed elsewhere.[4] In the case of GeH_4 we observe only two lines in the $M_{II,III}$ spectrum at 124.7 ± 0.3 and 129.7 ± 0.3 eV; the separation of these lines (5.0 ± 0.6 eV) may be compared with the calculated spin-orbit energy of 4.35 eV for the $3p^5$ core of Ge.[13] We have also measured the $L_{II,III}$ absorption of PH_3, H_2S, and HCl which, like SiH_4, have argon as the united atom, and each shows Rydberg series before the $L_{II,III}$ edges.[4] In addition, we have measured the absorption of BF_3 in the boron *K* region.[4] More complete descriptions of our work on SiH_4 and the other molecules mentioned above will be given elsewhere.[4]

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