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Absorption by Some Molecular Gases in the Extreme Ultraviolet*

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The absorption spectra of several polyatomic molecules (hydrides and fluorides) have been measured in the range of photon energies 100–200 eV. High resolution was obtained by the use of synchrotron radiation and a grazing-incidence spectrometer. Rydberg series were observed with sharp structure converging upon the $L_{\mathrm{III,II}}$ edges of SiH_4, PH_3, H_2S, and HCl. These molecules all have argon as a united atom and the observed series correspond to excitation of a $2p$ core electron to s- and d-like final states. In silane the d-like final states show a splitting due to the molecular field. The assignments are confirmed by a molecular-orbital calculation which will be reported elsewhere. The $L_{\mathrm{III,II}}$ spin-orbit splittings and threshold energies are compared with other experimental and theoretical data.

I. INTRODUCTION

During the last few years much new information has been obtained about the response of matter to electromagnetic radiation in the vacuum and extreme ultraviolet. Source difficulties have been overcome with the use of synchrotron continuum radiation, and high-resolution absorption spectra have now been obtained from the lithium fluoride cutoff at 1050 Å out to the carbon K edge at 44 Å. Although much information on inner electron shells[1] has been obtained by means of electron spectroscopy for chemical analysis (ESCA) or electron emission spectroscopy,[2,3] it is still possible, using finely ruled gratings, to achieve higher resolution with absorption spectroscopy. For example, the 99.6-eV $L_{\mathrm{III,II}}$ edge of a thin etched crystal of silicon has recently been measured with 0.04-eV resolution and is observed to rise with nearly this steepness.[4] It would appear that lifetime broadening for L excitation of the lighter elements is less than previously thought. Many sharp threshold features have been obtained for ionic crystals (see, for example, the papers by Sagawa *et al.*,[5] Brown *et al.*,[6] and Cardona *et al.*[7]). In addition, Madden and co-workers[8] have obtained highly resolved spectra of the rare gases, especially of multiple excitation sequences in the vacuum ultraviolet.

In the present work we show absorption spectra for a number of molecular gases taken in the 100–200-eV range using synchrotron radiation. Many spectral details were found which can be understood in terms of molecular-orbital theory. Earlier studies of molecular absorption in the higher-energy region, using crystal spectrometers and x-ray tubes, were carried out by Glaser,[9] who investigated the absorption of GeH_4, $GeCl_4$, and $GeBr_4$ in the vicinity of the K edge of germanium (11 103 eV). Mott[10] measured the absorption of $SiCl_4$ in the vicinity of the K edge of silicon (1839 eV) and the absorption of $GeCl_4$ in the vicinity of the L edges of germanium (1217 eV). Absorption studies of SF_6 and H_2S were carried out in the region of the K edge of sulfur (2470 eV) by DaVilla and Deslattes[11] and theoretical considerations given by Best.[12] The L edges of sulfur (170 eV) in SF_6 have been studied by Zimkina and Fomichev[13] and an interpretation of certain features given by Nevedov.[14] In general, these spectra show structure arising from the excitation of core electrons to excited molecular states.

We have previously reported an analysis of the absorption spectrum of BF_3 gas in the region of the boron K edge (~200 eV)[15] and the Russian workers[16] have also discussed this case. Here we will describe the results of a study of the L absorption of SiH_4, SiF_4, PH_3, H_2S, and HCl and of the M absorption of GeH_4. The L spectra show Rydberg series with sharp structure converging on ionization edges. We have already given a preliminary account of our work[17] on SiH_4; however, a more detailed account is given below in Sec. III A. Moreover, a comparison is made between the L spectrum of SiH_4 gas and the spectrum for solid silicon reported by Gähwiller and Brown.[4]

Our discussion of the molecular spectra frequently centers around a united-atom approach. In using the united-atom concept, we allow the distance between the nuclei to become zero so that the Hamiltonian for the molecule reduces to that of an atom whose nuclear charge is the sum of the nuclear charges of the atoms composing the molecule.[18–20] Each molecular orbital may be labeled by the united-atom orbital into which it degenerates when the nuclei are brought together. The united atom for SiH_4 is argon, and the L spectrum of argon has been observed in the 240-eV region by Nakamura *et al.*[21] and by Watson and Morgan.[22] Two groups of Rydberg series are found in argon arising from excitation of a single $2p$ electron to $4s$ and higher s levels and to $3d$ and higher d levels. We observe the corresponding series in SiH_4, but in this case the united-atom d orbitals are split into two components by the molecular field which we assume to have point symmetry T_d (see, however, Sec. III A). Our measured splitting of the united-atom $3d$ orbital is 0.7 eV and of the $4d$ orbital is 0.3 eV. Argon is also the united atom for PH_3, H_2S, and HCl, but in these cases the molecular-field splitting of the united-atom d levels is not resolved and the spectra are atomic in appearance.

Both photoelectron and absorption spectroscopy have been carried out on some of the molecules mentioned above at energies up to about 14 eV. Transitions in this lower-energy region quite often give rise to broad bands because bonding electrons are involved; excitation of a bonding electron to a nonbonding or an antibonding orbital can result in an appreciable change of equilibrium nuclear configuration and vibrational motion. In the present investigation we are exciting core electrons which are effectively nonbonding and the contribution of vibrational motion to linewidths is reduced.

Theoretical work carried out in the past on the electronic structure of hydrides of second-row atoms has been largely concerned with ground-state energies, bond lengths, and bond angles.[23–25] Calculations on the high-energy excited, as well as ground, states of SiH_4 have been carried out by Kunz using the one-center expansion method (OCE).[26] These results are in good agreement with the spectroscopic observations reported here and in Ref. 17.

II. EXPERIMENTAL METHODS

The measurements were made using synchrotron radiation from the 240-MeV storage ring at the University of Wisconsin physical science laboratory. A description of the light characteristics of the storage ring and details of the spectrometer operation have already been given by Gähwiller, Brown, and Fujita.[27] The spectrometer was a modified 2-m grazing-incidence instrument designed by Gabriel[28] and made by Hilger and Watts. A 1200-line/mm grating was employed, with both the entrance and exit slits 10 μ in width so that the spectral bandwidth was about 0.05 Å. The spectrometer was continuously evacuated by an ion pump in such a way that it could be opened up to the ultrahigh vacuum (10^{-9} Torr) of the storage ring.

The gases investigated were obtained from the Matheson Co. and were supplied under pressure in stainless-steel cylinders. The impurity specifications are given in the company catalogs, and these levels were not of consequence in our experiments. Each gas was transferred before use into an evacuated stainless-steel sample cylinder to a gas pressure of about 1 atm. A small amount of gas was then admitted just before measurement into the absorption cell placed before the entrance slit of the spectrometer at the storage ring. Both the absorption cell (6.6 cm long) and the associated gas-handling manifold were made from stainless steel. The pressure in the gas cell was measured with a sensitive Bourdon gauge and was generally about 1 Torr. The absorption-cell windows were made from stretched polypropylene sheet and were about 0.8 μ thick.[27] Figure 1 shows the measured optical density of a 0.86-μ polypropylene window throughout the range of interest for the present measurements and up to the carbon K edge at 43 Å.

Photon counting was employed using an extended-cone channeltron and high-speed (nanosecond) circuitry. The detector counting rate, encoded wavelength information, and a digitized beam-current signal were recorded on punched paper tape during wavelength scans of intensity transmitted by the gas cell with, or without, sample gas. Because the relativistic electron beam was bunched, light from the storage ring had a time structure consisting of 3-nsec pulses every 30 nsec. The average counting rates, 10^3–10^4 sec^{-1}, were such that it was extremely improbable for more than one count to occur during a 3-nsec pulse; therefore the recorded rates were closely proportional to intensity. The data on punched tape were edited and transferred to the disk file of an XDS sigma 5 computer at a later time. Various runs could then be combined and analyzed in the computer to yield plots of optical density vs photon energy. The computer analysis provided for the spectrometer cal-

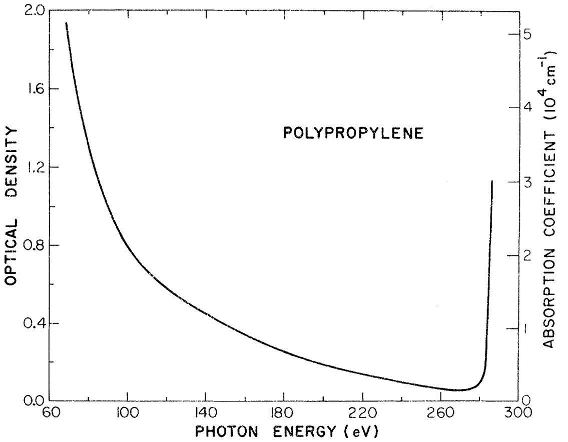

FIG. 1. Measured optical density of a 0.86-μm-thick sheet of polypropylene. The absorption coefficient in cm^{-1} is given on the right-hand side (uncertainty 20%). Two such windows were used in the gas absorption cell.

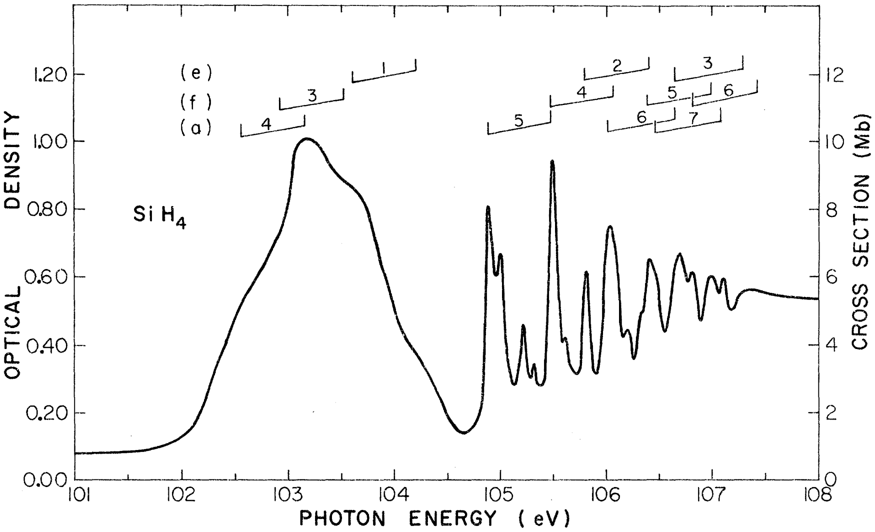

FIG. 2. Absorption spectrum of SiH_4 gas. The optical density refers to 6.6-cm thickness, room temperature, and a pressure of 1.1 Torr. The cross section in Mb per molecule is shown on the right-hand side with an uncertainty of ±20%. A spectral bandwidth of 0.04 eV was employed. Three different excitation series (*e*), (*f*), and (*a*) are classified according to Eq. (1) in the text. The $L_{\mathrm{III,II}}$ spin-orbit-split components for each member in each series are jointed by a sloping line.

ibration, stray light corrections (especially important at the higher photon energies), smoothing routines, and also for combining repeated scans when desired.

III. RESULTS AND DISCUSSION

A. Absorption of SiH_4 Gas and Comparison with Solid Silicon

The ground state of silicon is $1s^2 2s^2 2p^6 3s^2 3p^2$ and the $L_{\mathrm{III,II}}$ spectrum of silicon arises from transfer of a single $2p$ electron to empty conduction-band states. The $L_{\mathrm{III,II}}$ spectrum of SiH_4 arises from transfer of a single silicon $2p$ electron to empty molecular-orbital states. The point symmetry of SiH_4 in its ground electronic state is T_d, and in this symmetry s orbitals transform like A_1 and p orbitals like F_2; d orbitals split into a triply degenerate (F_2) and a doubly degenerate (E). The ground configuration of SiH_4 is $1a_1^2 2a_1^2 1f_2^6 3a_1^2 2f_2^6$ ($^1A_1$) and allowed electric dipole transitions occur to the underlined F_2 states in the excited configurations listed below:

$$
\begin{aligned}
&1f_2^5 na_1(^{1,3}\underline{F}_2)\, n \geq 4 \quad (a), \\
&1f_2^5 nf_2(^{1,3}\underline{F}_2, {}^{1,3}E, {}^{1,3}A_1)\, n \geq 3 \quad (f), \qquad (1)\\
&1f_2^5 ne(^{1,3}\underline{F}_2, {}^{1,3}F_1)\, n \geq 1 \quad (e).
\end{aligned}
$$

In this standard notation[29] the index n labels the molecular orbital in order of occurrence as a function of energy. For example, n is one or greater in the excitation series (e) because the doublet type e occurs for the first time in the excited configuration. The united atom for SiH_4 is argon (ground configuration $1s^2 2s^2 2p^6 3s^2 3p^6$) and the excitations in argon corresponding to (1) have been observed in the 245-eV region.[21,22] The lowest transition in argon corresponding to series (a) arises from excitation of a $2p$ electron to the $4s$ state. The $2p$-$3d$ transition in argon corresponds to the lowest excitations in the (f) and (e) series [note restrictions on n in Eq. (2) below], 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. The $2p \rightarrow ns$ ($n \geq 4$) and the $2p \rightarrow nd$ ($n \geq 3$) transitions in argon form Rydberg series converging on the $L_{\mathrm{III,II}}$ ionization edges. The $L_{\mathrm{III,II}}$ transitions of SiH_4 also form Rydberg series (Fig. 2) indicating a hydrogen-like potential for these highly excited molecular states. Argon is also the united atom for PH_3, H_2S, and HCl, and these molecules also show Rydberg series converging on the $L_{\mathrm{III,II}}$ edges.

The spin-orbit energy in the $2p^5$ core of silicon has been calculated by Herman and Skillman[30] to be 0.70 eV. This interaction splits each underlined F_2 state in (1) into resolved $^1F_2$ and $^3F_2$ states and allows electric dipole transitions to the triplet state. Detailed calculation by Kunz[31] shows that the exchange interaction between the electron and the hole is much less than our observed linewidths. A similar situation occurs in argon.[21,22] The $^1F_2$ and $^3F_2$ states for each of the series (a), (f), and (e) converge on ionization edges for SiH_4 associated with the $2p_{1/2}(L_{\mathrm{II}})$ and $2p_{3/2}(L_{\mathrm{III}})$ core states of silicon.

The measured positions of the lines for each series in Eq. (1) are given in Table I. We have fit the lines to the simple Rydberg formula

$$E_n = A - R/(n-\delta)^2, \qquad (2)$$

where A is the ionization limit, R is a Rydberg (13.6 eV), δ is the quantum defect, $n = 4$ for the first member of the (a) series, and $n = 3$ for the first member of both the (e) and (f) series [see Eq. (1)]. The average values of the L_{III} and L_{II}

TABLE I. Peak positions (eV) and n values of lines in the (a), (f), and (e) Rydberg series in SiH_4. Corresponding lines in spin-orbit branches are bracketed together. The unclassified lines in the (a) series are discussed in the text.

(a)	n	(f)	n	(e)	n
102.59	4	102.95	3	103.65	1
103.18		103.55		104.25	
104.92	5	105.52	4	105.84	2
105.52		106.10		106.45	
105.03		106.45	5	106.69	3
105.23		107.02		107.30	
105.34					
105.65					
106.06	6	106.78	6		
106.68		107.38			
106.21					
106.78					
106.50	7				
107.09					

edges obtained from the three series are

$$L_{III} = (107.2 \pm 0.4)\ \text{eV},$$
$$L_{II} = (107.8 \pm 0.4)\ \text{eV}. \qquad (3)$$

The quantum defect δ was found to be 2.2 for the (a) series and 1.2 for both the (e) and (f) series. It is possible to determine the $L_{III,II}$ separation more precisely than the absolute position of each edge, and we find this separation to be (0.65 ± 0.05) eV. This separation does not change noticeably along the series in any of the systems we have studied. This result is in good agreement with the calculated value of 0.70 eV for the spin-orbit energy of the $2p^5$ core of silicon.[30]

Preliminary results of a computer calculation by Kunz[31] for some SiH_4 energy levels of interest to us have been previously reported.[17] This calculation used a OCE method with a minimal angular basis.[26] The calculation gave a ground-state total energy for SiH_4 of − 289.6 Ry which may be compared with the values of − 290.1 Ry obtained by Moccia[23(a)] and − 291.2 Ry obtained by Rothenberg *et al.*[25] The transitions of interest to us in the extreme ultraviolet occur at energies of about 8 Ry, and for these the errors arising from use of a minimal angular basis are small.

The calculated value for the center of gravity of the spin-orbit split states of the $n=4$ excitation in the (a) series is 100.6 eV, whereas the observed value is 102.8 eV. The corresponding calculated values for the $n=3$ excitation in the (f) and the $n=1$ excitation in the (e) series are 100.9 and 102.4 eV, respectively; our observed values are at 103.1 and 103.8 eV. The calculated values for the center of gravity of the spin-orbit-split states of the $n=4$ excitation in the (f) and the $n=2$ excitation in the (e) series are 103.5 and 104.0 eV, and the observed values are 105.7 and 106.0 eV (see Table I).

From the numbers given above it is apparent that the observed molecular-field splittings of the united-atom $3d$ and $4d$ states are 0.7 and 0.3 eV and that these are about one-half of the calculated values. The calculation indicates that the (e) series is higher in energy than the corresponding (from a united-atom viewpoint) (f) series. It appears that the hydrogens in SiH_4 provide a net attractive potential for the f_2 excited electron which is distributed closer to the SiH bond directions (but is largely outside of the hydrogens) than the excited e electron. This is perhaps not unreasonable if the silicon valence-electron density remains fairly close to the silicon core. An excited core electron might therefore be placed upon or beyond the hydrogens with less energy in f_2 than in e. The hydrogens interact very little with each other, and it will be recalled that the extra electron in the H^- ion is bound.[32] The calculation of Kunz is self-consistent in that the molecule expands slightly upon excitation to the F_2 state. Actually, a careful decomposition of components in Fig. 2 seems to bear out the calculated order although this is not entirely certain. It should thus be stated that the ordering of (e)-(f) labels in the figure is based primarily upon results of the calculation. The situation in SiH_4 can be compared with the splitting of the $3d$ level of a transition-metal ion tetrahedrally coordinated to negatively charged ions in solids, where the e-f_2 splitting is somewhat larger than that found here and has the opposite sign (see McClure[33] for a review).

With each of the second-row hydrides discussed below in Secs. IIIC–IIIE, the linewidth of the first member of each Rydberg series is considerably greater than that of succeeding members (see Figs. 2, 5, 6, and 7). The SiH_4 line at 105.84 eV (Fig. 2 and Table I) is the narrowest observed and is 0.06 eV wide at half-height. This width is very close to our spectral bandwidth (0.04 eV). In the Rydberg series of argon a pronounced narrowing with increasing principal quantum number has been observed by Madden, Ederer, and Codling.[8] This is ascribed to lifetime effects caused, for example, by autoionization. The large linewidth of the lowest transitions in the hydrides 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, the possibility of some vibrational contribution to the linewidth also arises. We have only measured the total absorption spectra and do not separate out ionization and dissociation contributions.

Three peaks not classified in Fig. 2 occur between 105.0 and 105.5 eV, and these may be vibronic transitions associated with the $n = 5$ line in the (*a*) series at 104.92 eV (see Table I). 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 energies may be compared with the vibrational energies $\nu_1(A_1) \simeq \nu_3(F_2) = 0.274$ eV, $\nu_2(E) = 0.121$ eV, and $\nu_4(F_2) = 0.113$ for the ground electronic state of SiH_4.[34] Consideration of product representations shows that single vibronic excitations involving these normal modes are allowed for transitions originating on $\nu = 0$ vibrational levels. The weak lines at 105.65 and 106.21 eV in the (*a*) series (see Table I) may be vibronic lines associated with the classified electronic lines at 105.52 and 106.06 eV. A measurement of the spectrum of SiD_4 would be helpful in assigning the unclassified lines, but this gas was not available to us.

A study of SiH_4 and GeH_4 using photoelectron techniques has been made by Pullen *et al.*[35] (This paper contains references to earlier work on radiolysis of SiH_4 and GeH_4.) They find a band about 1.5 eV wide at 12.5 eV which shows partial resolution into two components separated by about 0.5 eV and they suggest that this structure is due to a Jahn-Teller effect (see Coulson and Strauss[36]). The band also shows partly resolved vibrational structure with components separated by 0.10 eV. Pullen *et al.*[35] point out that the interaction between ultraviolet light and SiH_4 gives rise to decomposition products of the molecule. In our case, consideration of the radiation intensity (Gähwiller *et al.*[27]) and our gas volume (which includes the relatively large volume of the Bourdon gauge) shows that the concentration of decomposition products is not of consequence in our experiments. We find that the spectrum of SiH_4 obtained immediately after exposure to the synchrotron radiation is identical with that obtained after some hours exposure.

It appears in the present case that lines in the (*e*) and (*f*) series are not as strongly coupled to vibrations as lines in the (*a*) series, and this is not inconsistent with the extremely diffuse nature of the calculated wave functions for the excited states in the (*e*) and (*f*) series.[31] It should be emphasized that since we are exciting a core electron, which is effectively nonbonding, we do not expect equilibrium internuclear distances in the excited states to be appreciably different from those in the ground state (a slight effect occurs in the calculations as noted above), and we do not expect vibrational motion of the molecule to be strongly excited.

Figure 3(a) shows the absorption of SiH_4 over an extended energy range which includes the L_{I} edge. For comparison we show in Fig. 3(b) the absorption of a thin film of silicon measured by Gähwiller and Brown[4] in the same energy range. Notice also that the absorption cross section per silicon atom is given on the right-hand side in megabarns for both cases. Except for the strong threshold resonances in the gas [the excitation series are unresolved in Fig. 3(b) because of a relatively rapid scan], the step heights are rather similar in the two cases. This indicates similar overlap of final-state wave functions with Si core wave functions and therefore similar transition matrix elements in both cases. The position of the L_{I} edge is at about 150 eV in both silane and silicon. As in silicon, the ionization continuum shows a slow rise beyond the $L_{\mathrm{III,II}}$ edges, and this would appear to be a consequence of the delayed onset due to centrifugal effects of transitions from the core $2p$

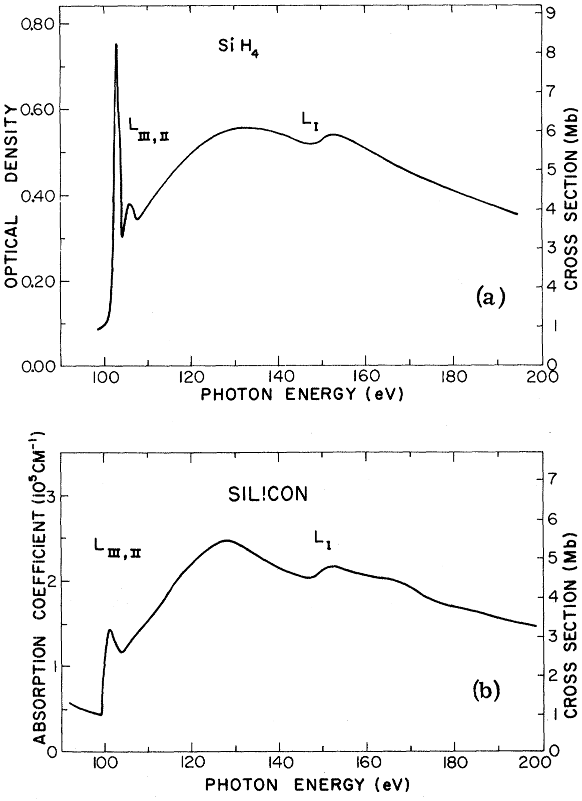

FIG. 3. (a) Showing the absorption of 1.1 Torr of SiH_4 gas in Fig. 2, but over an extended range. (b) The spectrum over an extended range for an evaporated silicon film (from Gähwiller and Brown, Ref. 4). The data taken during relatively fast scans so that the detailed structures very close to threshold are not resolved. The scales at the right-hand side give the cross sections per silicon atom in Mb (uncertainty ±20%) for both the gas and the solid.

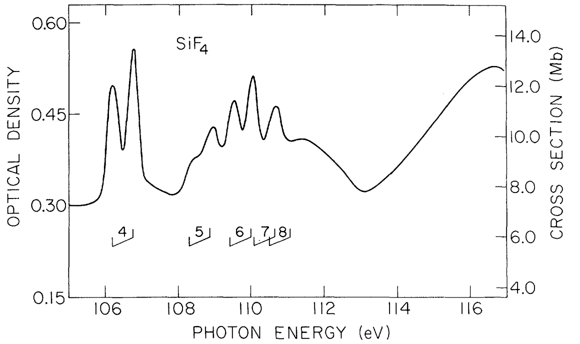

FIG. 4. Absorption of SiF$_4$ gas just above the $L_{\mathrm{III,II}}$ edge. The optical density refers to 6.6-cm thickness, room temperature, and a pressure of 0.45 Torr. The cross section in Mb is given on the right-hand side with an uncertainty of ±20%. A single spin-orbit-split Rydberg series is identified.

level to continuum d-type states (see Fano and Cooper[37]). Very recently, Toyozawa[38] has explained similar gross spectral contours for inner-shell photoabsorption of solids in the case of closed-shell ions. The situation is more complicated for a valence crystal like silicon, but apparently like features occur far above threshold. In Toyozawa's terminology, the gradual rise at about 25 eV or more above threshold is a "giant" band associated with l to $l+1$ transitions. Orthogonalization of final-state wave function with core wave function is not involved in the case of Si since there are no inner filled d bands. In the solid, weaker "subgiant" bands can occur about 10 eV above threshold, and these are associated with l to $l-1$ transitions rising sharply from threshold. Here orthogonalization with inner filled s shells is important. In the case of gases, such effects are mixed with the excitation sequences which have relatively large binding energies. In solids, core excitons can conceivably occur but, because of dielectric polarization or screening, much smaller binding energies are likely involved.

Finally, Dehmer has recently discussed[39] the absorption spectra of SF$_6$ and a number of other polyatomic molecules above the K and L thresholds. He stresses the importance of potential barriers associated with the tendency for electrons in similar quantum states to keep away from each other according to the Pauli exclusion principle.

B. Absorption of SiF$_4$ and GeH$_4$

The absorption of SiF$_4$ near the $L_{\mathrm{III,II}}$ edges is shown in Fig. 4. Our results agree with those of Zimkina and Vinogradov.[40] Only one Rydberg series is resolved (see Table II) and, because there is no observable molecular-field splitting in the lowest transitions, we will assume that it is the analog of the (a) series in Fig. 2. The apparent lack of observable intensity in the (e) and (f) series may be due in part to very different excited-state wave functions and a consequently small overlap with the compact silicon $2p$ core. There is no pronounced variation in linewidth (0.4 eV at half-height for the $n=4$ line) through the series, and this is in contrast with the hydrides. The two spin-orbit states of the (a) series converge on the ionization edges,

$$\begin{aligned} L_{\mathrm{III}} &= (110.8 \pm 0.3)\ \mathrm{eV}, \\ L_{\mathrm{II}} &= (111.4 \pm 0.3)\ \mathrm{eV}. \end{aligned} \tag{4}$$

More precisely, we estimate the L_{III} and L_{II} edge separation to be (0.55 ± 0.10) eV.

Comparison of Eqs. (3) and (4) shows a chemical shift of the $L_{\mathrm{III,II}}$ edges to higher energy of 3.6 eV on going from SiH$_4$ to SiF$_4$. Comparison of Figs. 3(a) and 3(b) shows that the onset of L absorption in SiH$_4$ occurs 2.5 eV higher in energy than that of silicon. This effect appears to be due primarily to delocalization of silicon valence wave functions and loss of charge (oxidation) when compounds are formed, leading to an increase in core potential and to higher transition energies (see Coulson and Zauli[41] and Siegbahn *et al.*[2,3]). Only a very small effect on the $L_{\mathrm{III,II}}$ separation is expected.

We have also investigated the M absorption of GeH$_4$, involving excitation of a $3p$ electron to excited molecular orbitals. However, the background absorption due to this molecule in the M region was intense, and we observed only two lines in the $M_{\mathrm{III,II}}$ spectrum, each about 1 eV wide, 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 for the $3p^5$ core of germanium[30]; it is considerably smaller than the value of 7.1 eV quoted for the $M_{\mathrm{III,II}}$ splitting of Ge in the review of Bearden and Burr.[1]

TABLE II. Peak positions (eV) and n values of lines in the (a) series in SiF$_4$. Corresponding lines in spin-orbit branches are bracketed together.

(a)	n
106.14 106.70	4
108.26 108.83	5
109.44 109.97	6
110.02 110.57	7
110.40 ...	8

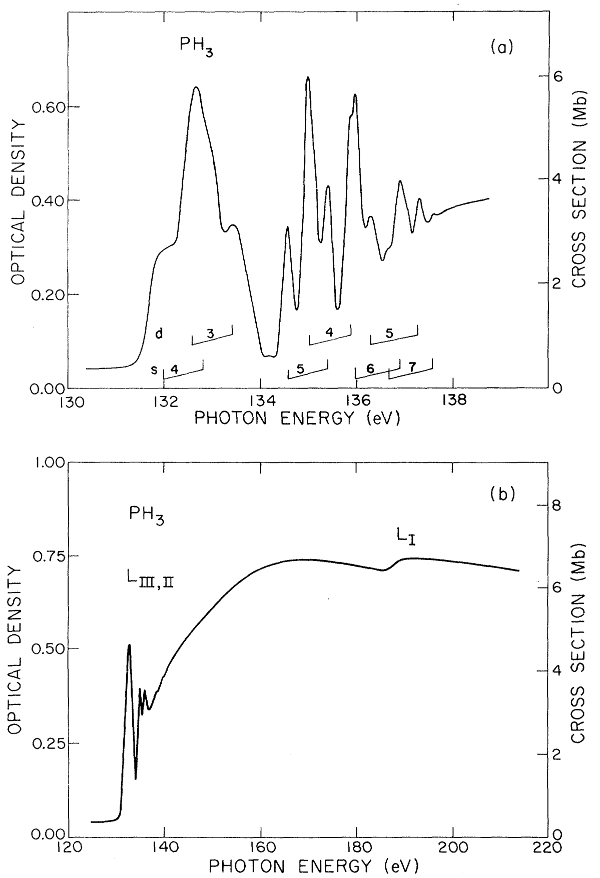

FIG. 5. (a) Absorption spectrum of PH_3 gas with spectral bandwidth 0.06 eV. The optical density refers to 6.6-cm thickness, 1.2 Torr, and room temperature, and cross sections are given at the right-hand side with an uncertainty of ±20%. Spin-orbit-split d- and s-like excitation series are identified. (b) Absorption of PH_3 gas under similar conditions as (a) except over an extended range.

C. Absorption of PH_3

It is generally accepted that the molecule PH_3 is pyramidal in structure (point group C_{3v}) in its electronic ground state. For descriptions of spectroscopic investigations of this molecule at energies below 11 eV see Humphries *et al.*[42] who observed a Rydberg series, and Branton *et al.*[43] PH_3 is isoelectronic with SiH_4 and has argon as its united atom. In C_{3v} symmetry, atomic p states split into a singlet (A_1) and a doublet (E), whereas atomic d series split into a singlet (A_1) and two doublets (E). If we ignore the effect of the molecular field on the $2p$ core state of phosphorus, we might expect the $L_{\text{III,II}}$ spectrum of PH_3 to show a Rydberg series analogous to the $2p \rightarrow ns\,(n \geq 4)$ series of argon and three Rydberg series corresponding to the $2p \rightarrow nd\,(n \geq 3)$ series of argon. In fact, only two series are observed [Fig. 5(a) and Table III] apparently because the molecular-field splitting of the united-atom d states is not resolved. Each series has two well-resolved spin-orbit states. Because the spectrum is atomic in appearance, we have, for simplicity, used a united-atom notation and labeled the series s and d with lowest principal quantum numbers 4 and 3.

Inspection of linewidths shows that the over-all molecular-field splitting of the united-atom $3d$ state is less than about 0.5 eV and of the $4d$ state is less than about 0.3 eV; these limits are somewhat smaller than the observed molecular-field splittings in SiH_4 (see Sec. III A). As in the case of SiH_4, the first members of each series are broader than higher numbers [Fig. 5(a)].

Taking an average from the two Rydberg series we find that the positions of the $L_{\text{III,II}}$ edges for PH_3 are

$$L_{\text{III}} = (137.3 \pm 0.2)\ \text{eV}, \quad L_{\text{II}} = (138.2 \pm 0.2)\ \text{eV}. \tag{5}$$

More precisely, the separation of the edges is (0.95 ± 0.05) eV, and this value is in good agreement with the interpolated value of the spin-orbit energy of 0.94 eV obtained from Herman and Skillman[30] for the $2p^5$ core of phosphorus.

Figure 5(b) shows a more extended view of the L absorption of PH_3. The L_{I} edge, arising from excitation of a phosphorus $2s$ electron, is visible at (189.0 ± 0.5) eV. As in the case of SiH_4 [Fig. 3(a)], there is a delayed onset of absorption at the $L_{\text{III,II}}$ ionization edges due to centrifugal effects of continuum d-type states. It should be noted, however, that the maximum of the p-d gross contour in phosphorus is closer to threshold than in silicon. This is in agreement with the trends predicted by theory.[37,38]

D. Absorption of H_2S

Like SiH_4 and PH_3, H_2S has argon as its united atom. Earlier experiments at lower energies[44,45]

TABLE III. Peak positions (eV) and n values of lines in the s and unresolved d Rydberg series of PH_3. Corresponding lines in spin-orbit branches are bracketed together.

s	n	d	n
132.0 132.8	4	132.6 133.4	3
134.57 135.39	5	135.03 135.89	4
135.98 136.89	6	136.29 137.29	5
136.66 137.58	7	136.89 ...	6

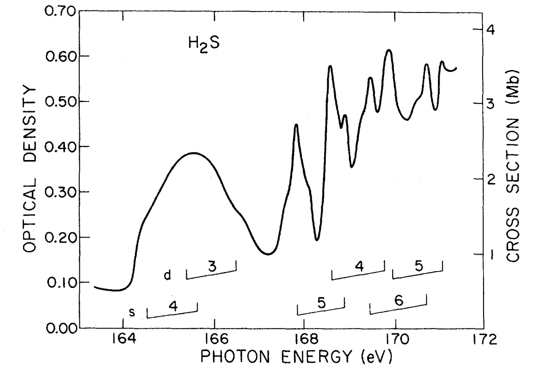

FIG. 6. Absorption of a column of H_2S gas 6.6 cm long at 1.8 Torr and room temperature. The cross section in Mb is given on the right-hand side with an uncertainty of ±20%. Spectral bandwidth about 0.1 eV. Spin-orbit *d*- and *s*-like excitation series are identified.

TABLE IV. Peak positions (eV) and *n* values of lines in the *s* and *d* Rydberg series of H_2S. Corresponding lines in spin-orbit branches are bracketed together.

s	*n*	*d*	*n*
164.5 165.6	4	165.4 166.5	3
167.86 168.94	5	168.62 169.83	4
169.52 170.75	6	170.02 171.10	5
170.50 ...	7	170.75 ...	6

showed two Rydberg series converging on an ionization limit at 10.4 eV. The point symmetry of H_2S in its ground electronic states is C_{2v}, and in this symmetry all orbital degeneracy is raised. However, as in the case of PH_3, we observe only two Rydberg series (Fig. 6 and Table IV) because the molecular-field splitting of the united-atom *d* states is not resolved, and the 2*p* core of sulphur is not appreciably affected. Again, our spectrum is in qualitative agreement with recent Russian observations.[40]

The general appearance of the H_2S spectrum is similar to that of SiH_4 and PH_3. Each series is resolved into two spin-orbit branches. Again, the lowest lines in each series are broad. Some structure is partly resolved in the $n=5$ line in the *s* series at 167.86 eV (Fig. 6). A high-energy edge is separated from the peak for about 0.23 eV and a low-energy edge by about 0.30 eV. The $n=6$ line in the *s* series at 169.52 eV also shows a partly resolved edge on the low-energy side separated from the main peak by about 0.30 eV. The normal-mode vibrational frequencies for the electronic ground state of H_2S are[34] $\nu_1(A_1)=0.32$ eV, $\nu_2(A_2)=0.16$ eV, and $\nu_3(B_1)=0.33$ eV so that the partly resolved structure may be vibronic in origin. As in the case of SiH_4 (Sec. III A), the united-atom *s* states appear to be more strongly coupled to vibrations than *d* states.

The observed series converge on the ionization edges

$$L_{III}=(171.1\pm0.3)\text{ eV},\quad L_{II}=(172.2\pm0.3)\text{ eV},\qquad(6)$$

and the $L_{III,II}$ edge separation is (1.15 ± 0.15) eV. The calculated spin-orbit energy for the $2p^5$ core of sulphur is 1.34 eV.[30] The photoabsorption series limits of Eq. (6) are 0.9 and 0.7 eV above the H_2S $p_{3/2}$ and $p_{1/2}$ binding energies given by Siegbahn *et al.*[3] from electron-emission measurements. This discrepancy, which is just outside the limits of error in the two methods, is not understood.

E. Absorption of HCl

The absorption spectrum of HCl has been investi-

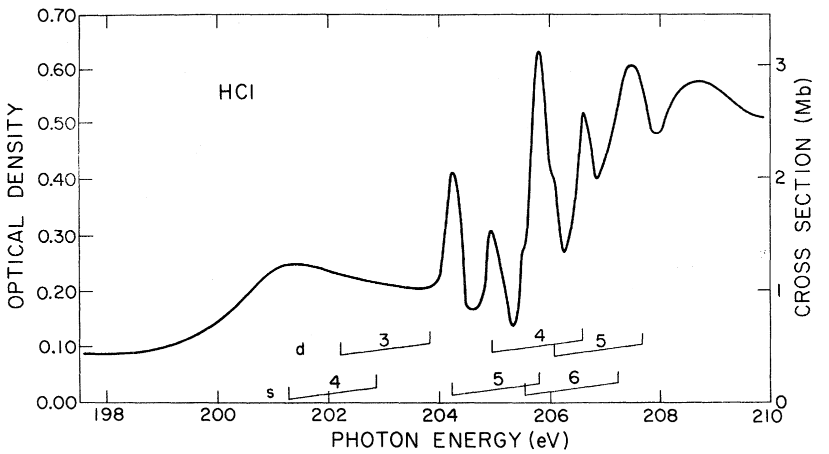

FIG. 7. Absorption of a column of HCl gas 6.6 cm long at 2.2 Torr and room temperature. The cross section in Mb is given on the right-hand side with an uncertainty of ±20%. Spectral bandwidth about 0.16 eV. Spin-orbit-split *d*- and *s*-like excitation series are identified.

TABLE V. Peak positions (eV) and *n* values of lines in the *s* and *d* Rydberg series of HCl. Corresponding lines in spin-orbit branches are bracketed together.

s	*n*	*d*	*n*
201.3	4	202.2	3
202.9		203.8	
204.25	5	204.94	4
205.81		206.62	
205.55	6	206.05	5
206.25		207.65	

gated at energies below 12 eV by Price,[46] but no well-defined Rydberg series are observed. Because the light output of the 240-MeV storage ring falls rapidly with increasing energy in the 200-eV region,[27] our signal-to-noise ratio for the $L_{III,II}$ spectrum for HCl was smaller than in the other cases. Nevertheless, the observed spectrum (Fig. 7 and Table V) was similar to the spectra of the lighter hydrides. Again, the splitting of the united-atom *d* states was not resolved, and we observed two Rydberg series, each beginning with a broad line. Each series shows a well-resolved splitting into two spin-orbit branches. The experimentally determined L_{III} and L_{II} ionization edges are

$$L_{III} = (207.1 \pm 0.5)\ \text{eV}, \qquad L_{II} = (208.7 \pm 0.5)\ \text{eV}, \tag{7}$$

and the separation of the edges is (1.65 ± 0.15) eV. This latter number may be compared with an interpolated Herman-Skillman[30] value of 1.77 eV for the spin-orbit energy of the $2p^5$ core of chlorine.

IV. CONCLUSIONS

For convenience we collect in Table VI our observed values of the energies of the $L_{III,II}$ and L_I edges of molecules containing second-row atoms. The more precise values obtained for the separation of the L_{III} and L_{II} edges are also given in Table VI and are in good agreement with values calculated by Herman and Skillman[30] for the spin-orbit energies of atomic $2p^5$ cores. These spin-orbit energies have in fact been measured for the $2s^2 2p^5 (^2P)$ ground state of the ions Si VI, P VII, S VIII, and Cl IX (Moore[47]) and are included in Table VI for comparison purposes. It is apparent that the effect of molecule formation in the core spin-orbit energy is small.

Calculations by Kunz[31] on SiH_4 (see Hayes, Brown and Kunz[17]) show that it is possible with modern computational methods to calculate the positions of excited states of second-row hydrides in the extreme ultraviolet to a few percent accuracy. Greater precision could be obtained with hydrides of first-row elements.

The present investigation was not extended to first-row hydrides because of the relatively low light output of the 240-MeV storage ring at energies higher than 200 eV. It would be feasible with some existing electron synchrotrons to study the absorption of molecules containing carbon (e.g., CH_4) in the vicinity of the carbon *K* edge (~284 eV), molecules containing nitrogen (e.g., NH_3) in the vicinity of the nitrogen *K* edge (e.g., 401 eV), and molecules containing oxygen (e.g., H_2O) in the vicinity of the oxygen *K* edge (~532 eV). Preliminary results have already been obtained on methane[48] and recent appearance-potential work on carbon[49] indicates much structure. As we have shown, high-resolution absorption measurements lend themselves to a detailed interpretation. Further experiments near the *K* thresholds of carbon, nitrogen, and oxygen might provide a powerful new method for the investigation of organic molecules, particularly those important in the early stages of the development of life. Certainly there are important questions to be answered concerning differences between the chemistry of carbon and of silicon.

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TABLE VI. The positions (eV) of the observed L_{III}, L_{II}, and L_I ionization edges of SiH_4, SiF_4, PH_3, H_2S, and HCl and the observed and calculated[a] values (eV) of L_{III}-L_{II} edge separations.

Molecule	L_{III}	L_{II}	L_I	L_{III}-L_{II} (obs) Ref. b	Ref. c	L_{III}-L_{II} (calc)
SiH_4	107.2 ± 0.4	107.8 ± 0.4	149.0 ± 0.5	0.65 ± 0.07	0.63	0.70
SiF_4	110.8 ± 0.3	111.4 ± 0.3	...	0.55 ± 0.10	0.63	0.70
PH_3	137.3 ± 0.2	138.2 ± 0.2	184.0 ± 0.5	0.95 ± 0.05	0.90	0.94
H_2S	171.1 ± 0.3	172.2 ± 0.3	...	1.15 ± 0.15	1.25	1.34
HCl	207.1 ± 0.5	208.7 ± 0.5	...	1.65 ± 0.15	1.69	1.77

[a] Herman and Skillman (Ref. 30).

[b] This paper.

[c] Moore (Ref. 45).

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