

Level Excitation Cross Sections of Atomic Fragments in Low-Energy Electron Impact Dissociation of Group IV Hydrides

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The decay curves of atomic emissions observed in the low-energy electron impact excitation of GeH_4 , SiH_4 , and CH_4 molecules were measured to evaluate the contributions of cascade transitions to the line emissions. By separating the cascade contributions from the fragment emission cross sections, level excitation cross sections were determined for the $\text{Ge } 1\text{ } 5s\text{ } ^1\text{P}^\circ$, $\text{Si } 1\text{ } 4s\text{ } ^1\text{P}^\circ$, and $\text{C } 1\text{ } 3s\text{ } ^1\text{P}^\circ$ levels. The measurements were carried out at the electron energies of 100 eV and around 30 eV. In every case, it was found that about half of these emissive fragments were produced by the radiative cascade from higher levels.

KEYWORDS: dissociative excitation, methane, silane, germane, electron impact cross section

§1. Introduction

The group IV hydride molecules (methane, silane and germane) are extensively used in the plasma chemical vapour deposition of semiconductor thin films. The fundamental properties of these molecules have thus become increasingly important in understanding the mechanisms of plasma processing.

In recent years, several authors¹⁻⁷⁾ have reported the emission cross sections of the fragments produced by the electron impact dissociation of these molecules. The emission cross section of a fragment generally involves two contributions: (i) direct formation of the emitting excited state by the dissociation of the parent molecule, and (ii) formation of the excited state by radiative cascade from higher-lying states which are formed by molecular dissociation. Because of the latter contribution, the response of the optical emission to the time-dependent excitation may differ from that expected from the radiative lifetime of the excited state under observation. To interpret the time-resolved optical emission spectroscopy data of the processing plasmas, knowledge of the cascading contribution to the fragment emission induced by the low-energy electron impact excitation of the molecules is required.

Recently, Sato *et al.*⁸⁾ measured the emission decay curves of the Si I excited fragments observed in the 100-eV pulsed electron beam excitation of SiH_4 molecule, and separated long-life cascade component contributions from the decay curves to determine the level excitation cross sections (LECSs or the cross sections of the direct formation of the levels). They found that a large (typically 50%) cascade contribution exists for all the observed Si I emissions.

In this work, we have extended the work of Sato *et al.*⁸⁾ to the measurements for germane and methane molecules and also to the lower excitation energies. The measurements were carried out for the $\text{Ge } 1\text{ } 5s\text{ } ^1\text{P}^\circ$, $\text{Si } 1\text{ } 4s\text{ } ^1\text{P}^\circ$, and $\text{C } 1\text{ } 3s\text{ } ^1\text{P}^\circ$ levels produced by the dissociation of the parent XH_4 molecules (with $\text{X}=\text{Ge, Si, C}$) at 100 eV and

at the lower energies near the onset energies of their excitation functions.

§2. Experimental Method and Data Analysis

The experimental details and the data analysis procedure are similar to those described in ref. 8 and only the salient features of the experimental method will be briefly described in this paper. The instrument consisted of an electron gun, a collision chamber and a Faraday cup. The optical emission was detected from a direction perpendicular to the electron beam axis using a monochromator and a photomultiplier. The gas pressure in the chamber was kept below 0.1 Pa.

The gas was excited by electron beam impulses of about 2.5- μs duration, which is sufficiently long to establish a steady-state population distribution over the excited levels. The emission decay curves after the beam cutoff were recorded in the time-correlated single-photon counting mode, using a combination of a time to amplitude converter, an AD converter and a personal computer which served as a multi-channel analyser (MCA). The electron pulse excitation was repeated until the decay curve had a sufficient statistical accuracy; typically about 2×10^4 counts were accumulated for the channels near the beam cutoff $t=0$.

The observed intensity of a spectral line is directly proportional to the population of the emitting excited level of the fragment. The free decay of the atomic population after the electron beam cutoff ($t \geq 0$) can be described with the sum of exponential functions; i.e., the population of level i can be expressed as

$$N_i(t) = C_i \exp(-\alpha_i t) + \sum_k C_k \exp(-\alpha_k t), \quad (1)$$

where α_i is the radiative decay rate of the level under observation, α_k 's are those of the cascading levels which are connected with the level i directly or indirectly, and C 's are constants which depend on the initial populations of the levels, the α 's, and the transition probabilities of the related lines. If N_{i0} is the steady-state

population before the beam cutoff ($t \leq 0$), then the quantity R , which gives the ratio of the intensity contributed by the cascade transitions to the total emission intensity, can be shown to be⁸⁾

$$R = \sum_k (1 - \alpha_k / \alpha_i) C_k / N_{i0}. \quad (2)$$

Then, from the definitions of the emission cross section σ_{ij} of the $i \rightarrow j$ transition and the LECS σ_i of level i , the latter can be derived as

$$\sigma_i = \sigma_{ij}(1 - R) / B_{ij}, \quad (3)$$

where B_{ij} is the branching ratio of the $i \rightarrow j$ transition.

The cascade contribution R in eq. (2) can be determined from the experimental decay curves by decomposing them into multiexponential functions using a nonlinear least-squares fitting routine. The fitting function actually used was essentially the time average of eq. (1) over a finite channel width (time resolution) Δt :

$$I_B + (I_0 - I_B) \sum_j C_j \frac{1 - \exp(-\alpha_j \Delta t)}{\alpha_j \Delta t} \exp(-\alpha_j t), \quad (4)$$

where I_B is the background constant and I_0 is the constant signal intensity before the electron beam is cut off.

The emission decay of each transition was recorded using two different channel widths, one being 1.35 ns and the other 17.9 ns, corresponding to the time windows of 345 ns and 4.45 μ s, respectively, for the 256-channel record length. The two curves were fitted simultaneously using common values of C_j 's and α_j 's, and the value of I_0 was fixed at the observed photon counts; in this procedure, it was possible to extract more than three exponential components from the decay curves.

§3. Results

The electron energy dependence of the optical excita-

tion function of a fragment usually shows several structures or onsets at which new dissociation processes occur. As for the $ns \ ^1P^o$ excited levels of Ge($n=5$), Si($n=4$), C($n=3$) atomic fragments produced by the electron impact dissociation of the corresponding XH_4 molecules, all the excitation functions show similar structures.^{3,5-7)} We have studied the emission decays of these levels at the excitation energy of 100 eV and at possible lower energies near the onsets of the excitation functions.

The decay curves measured in this work were decomposed into four exponential terms plus a background constant. Though the decomposition into five exponential terms was possible, we did not adopt this procedure since it sometimes showed numerical instability, particularly for the low excitation energy curves for which the signal-to-noise ratio was relatively low. In any case, however, the values of the cascade contributions were nearly the same for both analytical procedures.

3.1 Ge $15s \ ^1P^o$ level from GeH_4 dissociation

In this experiment, we used a gas mixture of GeH_4 10.3% in helium and measured the decay curves of the Ge $15s \ ^1P^o-4p^2 \ ^1D$ transition (303.9 nm). The excitation function of this transition has appearance potentials (APs) at 12.5, 14, 19 and 31.5 eV.⁷⁾ We carried out the measurements at the electron energies of 100, 30, and 20 eV; measurements at lower electron energies were not possible because low electron beam current resulted in low photon yield, and deposition of germanium on the cathode surface of the electron gun prevented the long experimental runs required to improve the signal statistics. Figure 1 shows a set of typical decay curves measured with two different channel widths. These curves were plotted after the background constants were subtracted.

Table I shows the LECS σ_i , the cascade contribution R , and the results of fitting analysis obtained for the

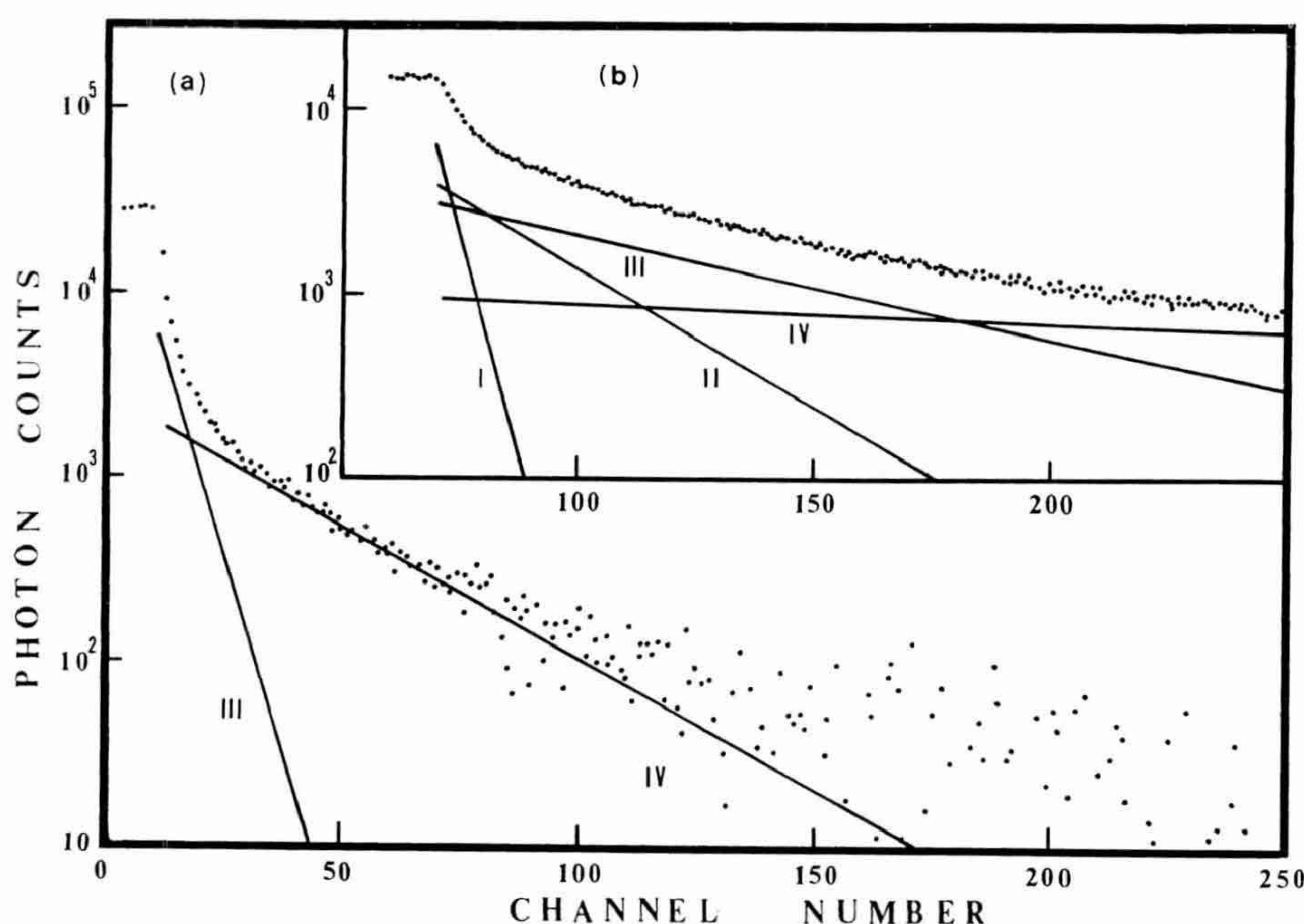


Fig. 1. A set of decay curves measured for the Ge $15s \ ^1P^o-4p^2 \ ^1D$ transition (303.9 nm) observed in the 100 eV electron impact dissociation of GeH_4 . The time resolutions are (a) 17.9 ns per channel and (b) 1.35 ns per channel. The exponential components resolved by the simultaneous fitting are drawn by the straight lines.

different excitation energies. For the evaluation of the LECSs, the emission cross section and branching ratio data were taken from our previous work.⁷⁾ The errors in the fitting parameters are quoted for the two standard deviations limit.

The observed lifetime of component I is in agreement with the reported lifetimes of the Ge I 5s ¹P° level.⁹⁻¹¹⁾ For components II and III, somewhat larger differences exist between the lifetimes obtained at different excitation energies. Their error bars, however, overlap substantially because of their relatively large uncertainties. We thus consider that each of these components still corresponds to a particular cascade level (or a group of particular cascade levels). The large uncertainties in the lifetimes probably come from the situation that these components

represent an average effect of more than two cascade levels and accordingly that the decomposition is sensitive to small errors in the experimental decay curves. From the analogy of the cases of Si and C discussed below, the major cascade levels responsible for the components II and III are expected to be the 5p ¹S, ¹P, and ¹D levels, although no lifetime data are reported for comparison with the present results. The small component IV may be interpreted as the overall effect of higher cascade levels. The value of cascade contribution *R* is as large as nearly 50% and shows no significant change for the different excitation energies.

3.2 Si I 4s ¹P° level from SiH₄ dissociation

To measure the decay curves of the Si I 4s ¹P°-3p² ¹D

Table I. Level excitation cross sections (LECS) and the results of decay curve decomposition for the Ge I 5s ¹P° level produced by the electron impact excitation of GeH₄.

Electron energy (eV)	100		30		20	
LECS (cm ²)	11×10^{-19}		11×10^{-19}		6.1×10^{-19}	
<i>R</i> (%)	49±10		48±6		47±17	
Component no.	Amplitude* %	Observed lifetime (ns)	Amplitude %	Observed lifetime (ns)	Amplitude %	Observed lifetime (ns)
I	46	4.6±1.4	48	5.4±1.4	46	5.8±2.6
II	26±7	32±16	35±5	43±11	32±6	32±26
III	21±7	88±36	10±4	138±100	17±3	92±82
IV	7±1	$(0.60 \pm 0.09) \times 10^3$	7±1	$(0.61 \pm 0.13) \times 10^3$	5±0.5	$(0.66 \pm 0.27) \times 10^3$

*1 = value of *C_j* in eq. (4), which corresponds to *C_k*/*N_{io}* in eq. (2); the quoted value of component I is determined so that the sum of all amplitudes is equal to 1, since the value directly obtained from the fitting is sensitive to small errors in the assumed *t*=0 position on the decay curves.

Table II. Level excitation cross sections (LECS) and the results of decay curve decomposition for the Si I 4s ¹P° level in the electron impact on SiH₄ molecule. The 100 eV results and the last column are taken from ref. 8.

Electron energy (eV)	100		30		
LECS (cm ²)	11.2×10^{-19}		13×10^{-19}		
<i>R</i> (%)	52.7±3.6		50±8		
Component no.	Amplitude %	Observed lifetime (ns)	Amplitude %	Observed lifetime (ns)	Dominant contributing levels with reported lifetimes (ns)
I	43.7±1.6	4.5±0.4	47	4.7±0.8	4s ¹ P° (3.9)
II	16.6±2.8	35.9±2	32±6	54±14	4p ¹ S (34), 4p ¹ D (42)
III	34.7±3.3	100±6	16±6	149±73	4p ¹ P (110)
IV	3.4±0.6	$(0.34 \pm 0.11) \times 10^3$	5±1	$(0.66 \pm 0.16) \times 10^3$	
V	1.6±0.2	$(1.49 \pm 0.34) \times 10^3$			

Table III. Level excitation cross sections (LECS) and the results of decay curve decomposition for the C I 3s ¹P° level in the electron impact on CH₄ molecule.

Electron energy (eV)	100		42		
LECS (cm ²)	1.3×10^{-19}		0.70×10^{-19}		
<i>R</i> (%)	48±4		43±5		
Component no.	Amplitude %	Observed lifetime (ns)	Amplitude %	Observed lifetime (ns)	Dominant contributing levels with reported lifetimes (ns)
I	50	3.2±0.6	54	4.1±0.8	3s ¹ P° (2.8 ^a , 3.0±0.3 ^b , 2.9±0.3 ^c)
II	24±3	40±12	25±4	44±13	3p ¹ S (28.5 ^a), 3p ¹ D (33.7 ^a)
III	19±3	150±53	17±3	145±60	3p ¹ P (114 ^a)
IV	7±2	$(0.51 \pm 0.12) \times 10^3$	4±1	$(0.52 \pm 0.09) \times 10^3$	

a) Ref. 12

b) Ref. 13

c) Ref. 14

transition (288.2 nm), a gas mixture of 47% SiH₄ in helium was used. The applied electron energy was 30 eV, which was below the fourth AP (33 eV) of the excitation function.⁵⁾ The fitting results for 30 eV curves are shown in Table II together with the data for 100 eV and the assignments of the responsible levels taken from the work of Sato *et al.*⁸⁾ Since we adopted the four-exponential decomposition procedure, the effect of long-life components IV and V of the 100-eV data is included in component IV of the 30-eV data. The LECSs given in the table were evaluated using the emission cross section and branching ratio data of refs. 6 and 8. As in the case of Ge, the cascade contribution *R* is about 50% and does not change apparently as the electron energy changes from 100 eV to 30 eV.

3.3 C I 3s ¹P^o level from CH₄ dissociation

The decay curves of the C I 3s ¹P^o–2p² ¹D transition (193.1 nm) were measured using a gas mixture of 49% CH₄ in helium. The electron energies applied were 100 eV and 42 eV, which is below the third AP (45.1 eV) of the C I excitation function.³⁾ Use of methane gas permitted relatively stable and long experimental runs (*e.g.*, about 40 hours to obtain a set of curves) because of less deposition on the cathode surface of the electron gun, but measurements at lower energies were not possible due to the smaller emission cross section of the transition and poor spectral detection efficiency below 200 nm. The LECS and results of the decay curve decompositions are presented in Table III. The LECSs are based on the emission cross section and branching ratio data of refs. 3 and 12. Again, the cascade contribution *R* has a similar feature to those for Ge or Si; *i.e.*, it is about 50% and its variation with the excitation energy is small.

Table III also lists the assignments of the levels from which dominant contribution to the components I–III originates. The observed lifetime of the component I is in agreement with the reported lifetime of the 3s ¹P^o level.^{12–14)} For the major cascade components II and III, the dominant contribution is expected to come from the singlet levels in the 3p configuration because the following reasons can be given with the aid of the transition probability data reported in the literature.^{12,15–19)} (1) Among the *np* levels, which decay directly to the 3s ¹P^o level, the 3p levels are the lowest, and thus are expected to have larger excitation (or formation) cross sections than other cascade levels; these singlet 3p levels decay to the 3s ¹P^o level with branching ratios close to 1, while higher *np* levels decay to the 3s ¹P^o level with smaller branching ratios (less than 0.4, *e.g.*, for the 4p level). (2) Among the indirect cascade levels, the 3d and 4s levels are low-lying and may have relatively large excitation cross sections; they decay indirectly to the 3s ¹P^o level via the 3p levels, but the branching ratios for the 3p levels are at most 0.1 except for the 3d ¹D level with the corresponding branching ratio of 0.4. By comparing the observed lifetimes of components II and III with the 3p-level lifetimes available in the literature,¹²⁾ we can correlate them as shown in the table. This assignment is the same as in the case of Si shown in Table II except for the change of principal quantum number.

§4. Discussion

As stated before, the optical excitation functions of the Ge I (303.9 nm), Si I (288.2 nm), and C I (193.1 nm) lines have similar structures. The highest clear AP observed in the 0–100 eV range is above 30 eV, and this AP probably corresponds to the beginning of dissociative ionisation processes in which one of the dissociation partners of the group IV atomic fragment is the ionised species (H⁺, H₂⁺, or H₃⁺). The excitation function of the fragment has a local minimum at this AP, and hence we can expect that the dominant dissociation processes at 100 eV are those in which the group IV atomic fragment accompanies the ionised fragments, and that, at the low excitation energies below about 30 eV, the dissociation produces only neutral fragments. The values of the cascade contribution *R*, on the other hand, are measured to be about 50% at both of the excitation energies of 100 eV and near the AP around 30 eV. Thus we may infer that, for either of the above two modes of dissociation, about half of the *ns* ¹P^o fragments are produced by cascade from high-lying levels.

For the GeH₄ molecule, the measured cascade contribution at 20 eV (near the third AP) is also about 40% (see Table I); thus, in spite of the restriction of the dissociation channels of the parent molecule, we have detected no appreciable change of the cascade contribution. It is likely that each AP of the optical excitation function of the *ns* ¹P^o level corresponds to an overlapping of the successive thresholds of the dissociation processes leading to the production of a series of levels which cascade to the *ns* ¹P^o level, rather than to a single dissociation process leading directly to the *ns* ¹P^o level production. Based on this discussion, we can reasonably expect a similar amount of cascade contribution to the *ns* ¹P^o level production at still lower excitation energies (except probably just above the lowest AP). One should be careful of this cascading effect when interpreting time-resolved plasma optical emission spectroscopy data.

§5. Conclusions

We have reported the level excitation cross sections of the *n* ¹P^o levels of the Ge(*n*=5), Si(*n*=4) and C(*n*=3) atomic fragments by analysing the decay curves of their emissions induced by the dissociative excitation of XH₄ molecules by pulsed electron impact. The study shows that cascade contribution constitutes about 50% of all the emissions of atomic excited levels. The dominant cascading levels are expected to be the *np* levels just above the *ns* ¹P^o levels monitored. In the measurements at 100 eV and at the lower electron energy region where the dissociation modes of the parent molecules are limited, we found no apparent change in the cascade contribution.

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