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Electron-impact-ionization cross sections of GaCl, GeCl, and SnCl

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Electron-impact-ionization cross sections are measured for GaCl, GeCl, and SnCl. In all three cases, the metal fragment ion has the largest cross section, and the parent-ion cross sections are somewhat smaller. A significant fraction of the metal fragment ion results from ion-pair formation. The parent-ion ionization energies are 10.1 ± 0.3 eV for GaCl, 7.2 ± 0.5 eV for GeCl, and 6.8 ± 0.3 eV for SnCl.

I. INTRODUCTION

During recent measurements of atomic ionization cross sections,[1] beams of atomic ions were formed from CCl_4 discharges in the presence of the element of interest or of one of its compounds. In addition to forming a strong beam of the atomic ions, this source also produced strong beams of the monochlorides and in some cases the dichlorides and trichlorides. Among the strongest beams were the monochlorides of Ga, Ge, and Sn. This work reports measurements of the electron-impact-ionization cross sections of the two free radicals, GeCl and SnCl, and the diatomic molecule GaCl. Because recent cross-section measurements were made with the same apparatus for 27 atoms[1] and a number of other molecules[2] and free radicals,[3-5] there is reason to believe these measurements are of comparable accuracy, ±10%.

Data on GaCl are important because it is produced when GaAs is etched by chlorine, as shown by mass spectrometry.[6-8] It is also interesting to study GaCl because

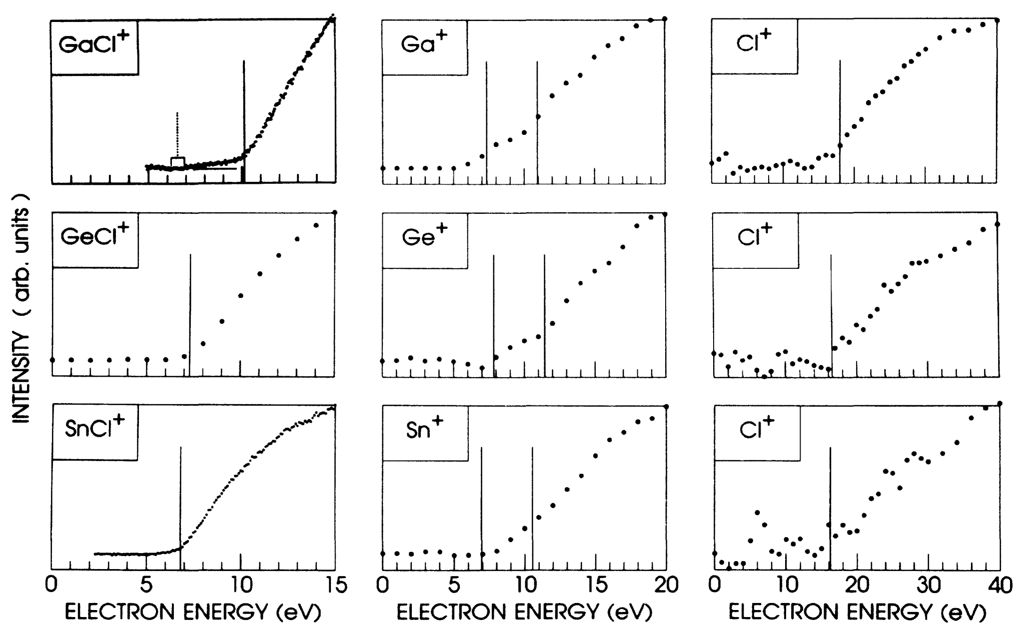

FIG. 1. Ionization thresholds. Parent ions are shown in the left column, metal fragment ions in the center, and Cl^+ fragment ions in the right column. For the parent ions, vertical lines represent the ionization energy as measured in this work. For $GaCl^+$, the dotted line points at a range of energies that encompasses the threshold for ionization of the first excited state. For the fragment ions, vertical lines represent the dissociative ionization and ion-pair threshold energies calculated from literature values of the dissociation energies.

TABLE I. Threshold energies (eV).

		Measured	Calculated
GaCl →	$GaCl^+$	10.1±0.3	
	$Ga^+ + Cl^-$	6.0±1.0	7.36[a]
	$Ga^+ + Cl$	9.6±1.0	10.96[a]
	$Ga + Cl^+$	17±1	17.97[a]
GeCl →	$GeCl^+$	7.2±0.5	
	$Ge^+ + Cl^-$	7.5±1.0	7.85[b]
	$Ge^+ + Cl$	11.9±1.0	11.45[b]
	$Ge + Cl^+$	16±1	16.56[b]
SnCl →	$SnCl^+$	6.8±0.3	
	$Sn^+ + Cl^-$	8.4±1.0	6.94[c]
	$Sn^+ + Cl$	12.0±1.0	10.54[c]
	$Sn + Cl^+$	16±1	16.21[c]

[a]Using bond dissociation energy of 4.96 eV, calculated from the enthalpies of formation given by Ref. 14. (Reference 12 gives 4.95 eV, Ref. 13 gives 4.99 eV, and Ref. 11 gives 4.92 eV.)
[b]Using bond dissociation energy of 3.55 eV, calculated from the enthalpies of formation given by Ref. 14. (Reference 13 gives 3.5 eV.)
[c]Using bond dissociation energy of 3.2 eV from Ref. 13.

it has the same number of valence electrons (isosteric) as CO, CS, and N_2, so comparisons of their energy levels and spectroscopy are helpful. Similarly, GeCl and SnCl are isosteric with SiF, GeF, and NO.

II. EXPERIMENT

The apparatus is described in detail in previous papers.[1,5,9] In this work, ion beams of the diatomic chlorides were formed from dc discharges in CCl_4 with small amounts of solid Ge, Sn, or GaAs placed in the bottom of the Colutron[10] ion source. Neutral beams were then formed by near-resonant charge transfer with triethylamine (TEA). As described previously,[1] cross sections are based on calibration of the apparatus with respect to the ionization cross sections of Ar and Kr. We estimate the present measurements to be accurate (1σ) to ±10%. As in previous work,[5] the size of the ion beam at the detector is measured by scanning it with the hemispherical energy analyzer across a slit in front of the channel electron multiplier (CEM). This shows that 100% of the parent ions and metal ions are collected, but only 95, 83, and 63% of the Cl^+ ions are collected from GaCl, GeCl, and SnCl, respectively. Corrections for these losses have been made in the results reported below.

TABLE II. Measured absolute ionization cross sections (Å^2) at 70 eV.

Run No.	$GaCl^+$	$GeCl^+$	$SnCl^+$
1	1.94	4.27	3.58
2	2.11	4.06	3.52
3	2.07	4.11	3.29
4	1.93	4.13	
5	1.94		
Average	2.00	4.14	3.46
Standard dev.	0.08	0.09	0.15
Standard dev.(%)	3.8	2.2	4.3

III. RESULTS AND DISCUSSION

A. Thresholds

The ionization thresholds are shown in Fig. 1 for both parent and fragment ions. In the leastmost column, vertical lines mark the present measurements of the ionization energy (IE) of the ground states: 10.1±0.3 eV for GaCl, 7.2±0.5 eV for GeCl, and 6.8±0.3 eV for SnCl. The GeCl and SnCl radicals have much lower IE's than the stable GaCl molecule, just as the IE's of SiF, GeF, and NO (7.4, 7.5, and 9.7 eV, respectively) are much lower than those of CO, CS, and N_2 (14.0, 11.3, and 15.6 eV, respectively). No previous measurements of the

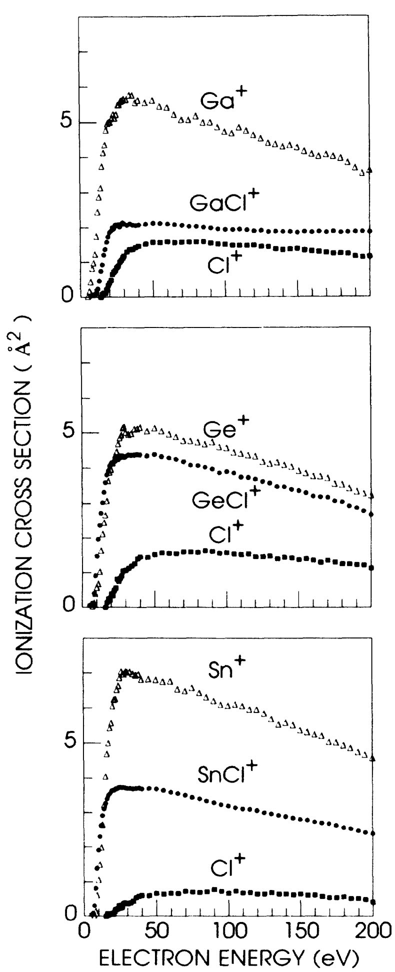

FIG. 2. Ionization cross sections (Å^2) for GaCl, GeCl, and SnCl to form parent and fragment ions.

TABLE III. Measured ratios of fragment-to-parent–ion cross sections at 70 eV.

Parent	Fragment	Ratio σ(fragment)/σ(parent)	No. of measurements
$GaCl^+$	Ga^+	2.50±0.12	3
	Cl^+	0.78±0.02	3
$GeCl^+$	Ge^+	1.15±0.01	3
	Cl^+	0.39±0.01	2
$SnCl^+$	Sn^+	1.87±0.01	3
	Cl^+	0.21±0.01	3

TABLE IV. Cross sections (Å^2) for electron impact ionization of GaCl, GeCl, and SnCl.

Electron energy (eV)	GaCl $GaCl^+$	GaCl Ga^+	GaCl Cl^+	GeCl $GeCl^+$	GeCl Ge^+	GeCl Cl^+	SnCl $SnCl^+$	SnCl Sn^+	SnCl Cl^+
5		0.00		0.00			0.00		
6		0.15		0.02			0.05		
7	0.00	0.41		0.09	0.00		0.27	0.00	
8	0.03	0.80		0.37	0.11		0.78	0.12	
9	0.01	0.96		0.87	0.37		1.35	0.59	
10	0.04	1.21		1.44	0.55		1.87	1.04	
11	0.08	1.73		1.93	0.65		2.26	1.48	
12	0.20	2.43		2.33	1.01		2.59	1.96	
13	0.42	2.85		2.69	1.62		2.87	2.63	
14	0.70	3.11	0.00	2.99	2.10		3.07	3.20	
15	0.89	3.72	0.09	3.28	2.43		3.22	4.02	0.00
16	1.17	4.11	0.12	3.56	2.64	0.00	3.36	4.67	0.08
17	1.33	4.33	0.12	3.77	3.06	0.14	3.46	4.98	0.03
18	1.54	4.76	0.22	3.89	3.62	0.25	3.50	5.41	0.08
19	1.69	4.95	0.33	4.02	3.85	0.21	3.57	5.55	0.05
20	1.82	5.00	0.41	4.10	3.93	0.39	3.60	6.03	0.05
21	1.86	4.99	0.48	4.11	4.12	0.34	3.61	6.22	0.12
22	1.96	5.10	0.65	4.14	4.22	0.48	3.64	6.24	0.19
23	1.92	5.21	0.72	4.27	4.29	0.56	3.64	6.51	0.21
24	2.04	5.10	0.76	4.29	4.44	0.81	3.68	6.62	0.31
25	2.03	5.21	0.85	4.21	4.66	0.75	3.69	6.84	0.30
26	2.05	5.47	0.89	4.26	4.83	0.83	3.68	7.02	0.24
27	1.98	5.48	1.01	4.30	4.91	0.91	3.69	6.94	0.36
28	2.06	5.58	1.06	4.30	5.12	1.05	3.67	6.95	0.39
29	2.10	5.60	1.13	4.27	5.15	1.05	3.66	7.02	0.37
30	2.06	5.64	1.18	4.29	4.99	1.07	3.66	7.01	0.35
32	2.03	5.62	1.30	4.33	4.94	1.12	3.66	7.01	0.39
34	2.06	5.75	1.36	4.32	4.96	1.19	3.65	6.95	0.44
36	2.03	5.74	1.37	4.33	5.09	1.26	3.66	6.92	0.54
38	2.02	5.54	1.43	4.34	5.09	1.41	3.66	6.94	0.58
40	2.04	5.60	1.47	4.33	5.13	1.46	3.64	6.80	0.61
45	2.06	5.53	1.52	4.30	5.02	1.44	3.66	6.91	0.60
50	2.08	5.60	1.57	4.35	5.11	1.53	3.64	6.78	0.67
55	2.08	5.43	1.57	4.29	5.03	1.58	3.60	6.73	0.65
60	2.06	5.40	1.60	4.25	4.94	1.57	3.54	6.75	0.68
65	2.04	5.20	1.57	4.21	4.86	1.55	3.51	6.53	0.67
70	2.02	5.05	1.58	4.14	4.76	1.61	3.46	6.47	0.73
75	1.99	5.05	1.58	4.04	4.75	1.60	3.39	6.56	0.71
80	1.99	5.15	1.59	4.03	4.71	1.60	3.35	6.42	0.70
85	1.97	4.97	1.59	3.99	4.66	1.64	3.29	6.29	0.72
90	1.95	4.98	1.55	3.94	4.72	1.63	3.24	6.19	0.78
95	1.92	4.84	1.53	3.83	4.58	1.57	3.19	6.08	0.73
100	1.90	4.70	1.51	3.86	4.55	1.58	3.15	6.04	0.68
105	1.90	4.65	1.48	3.82	4.43	1.54	3.10	6.09	0.73

TABLE IV. (*Continued*).

Electron energy (eV)	GaCl $GaCl^+$	GaCl Ga^+	GaCl Cl^+	GeCl $GeCl^+$	GeCl Ge^+	GeCl Cl^+	SnCl $SnCl^+$	SnCl Sn^+	SnCl Cl^+
110	1.90	4.83	1.48	3.71	4.40	1.53	3.07	6.04	0.69
115	1.89	4.73	1.48	3.69	4.35	1.55	3.06	5.94	0.69
120	1.85	4.61	1.49	3.65	4.32	1.47	3.02	5.94	0.65
125	1.87	4.50	1.44	3.59	4.17	1.47	2.96	5.82	0.66
130	1.82	4.37	1.43	3.54	4.10	1.49	2.92	5.66	0.69
135	1.84	4.33	1.38	3.44	4.15	1.41	2.88	5.51	0.65
140	1.83	4.27	1.35	3.44	4.07	1.45	2.85	5.56	0.66
145	1.83	4.31	1.37	3.37	4.02	1.43	2.81	5.50	0.63
150	1.81	4.24	1.38	3.33	3.91	1.38	2.77	5.36	0.66
155	1.83	4.13	1.33	3.27	3.83	1.41	2.74	5.30	0.62
160	1.82	4.06	1.31	3.17	3.76	1.37	2.70	5.23	0.62
165	1.84	3.99	1.30	3.15	3.75	1.30	2.66	5.19	0.59
170	1.82	4.04	1.27	3.14	3.69	1.36	2.64	5.01	0.55
175	1.84	4.00	1.24	3.03	3.54	1.31	2.59	5.00	0.55
180	1.80	3.94	1.24	3.00	3.51	1.25	2.53	4.91	0.57
185	1.82	3.82	1.23	2.89	3.42	1.25	2.49	4.83	0.52
190	1.82	3.66	1.16	2.83	3.32	1.23	2.43	4.72	0.52
195	1.83	3.51	1.14	2.75	3.26	1.22	2.38	4.64	0.49
200	1.82	3.60	1.15	2.64	3.21	1.14	2.35	4.55	0.41

GaCl, GeCl, and SnCl IE's have been reported.

The parent-ion thresholds in Fig. 1 show that GeCl and SnCl must be in their ground electronic states; there is no evidence for ionization of the lowest excited state, which by analogy with SiF, GeF, and NO (Ref. 11) would lie 3 or 4 eV above the ground state and so produce a signal extending 3 or 4 eV below the principal threshold. For GaCl, however, there is an onset in the range of 6.2 to 6.9 eV, well below the ground-state ionization energy. This observation of metastable GaCl is consistent with observation of metastable states of CO, CS, and N_2,[2] and is the only experimental information available on the electronic energy of the lowest excited state of GaCl.

Thresholds for fragment ion formation are shown in Fig. 1 and Table I. Poor signal-to-noise ratios and data points 1 eV apart limit the accuracy with which most of them can be measured. Both dissociative ionization and ion-pair formation make major contributions to the cross sections. A similar large contribution from ion pairs was seen previously in ionization of SiF.[3] The intensities of Rydberg fragment atoms is small, so no corrections are made for them.

The expected positions of dissociative ionization and ion-pair thresholds have been calculated from dissociation energies, atomic ionization energy, and electron affinities, and are shown as vertical lines in Fig. 1. Dissociation energies to ground-state atoms are taken directly from the literature,[11–13] or are derived from enthalpies of formation.[14] The dissociation energy for GaCl appears to be well established (Table I), footnote (a). The occurrence of fragment thresholds for GaCl (Fig. 1) somewhat below the calculated values may result from dissociative ionization of metastable GaCl in the beam. For GeCl, the agreement between calculation and observation appears to be quite good. For SnCl, the observed thresholds are somewhat above the calculated ones. Possibly this is because of the uncertainty in the one value for the dissociation energy available in the literature.

B. Cross-section measurements

Measured ionization cross sections for the formation of parent ions by electron impact at 70 eV are given in Table II. The reproducibility of the measurements is better than ±5%. Following Ref. 1, the absolute accuracy is expected to be ±10%. Measured ratios of fragment-to-parent–ion cross sections at 70 eV, given in Table III, are also reproducible to better than 5%. Figure 2 and Table IV give the cross sections from threshold to 200 eV, obtained by normalizing relative cross sections to the 70-eV absolute cross sections in Table II and the ratios in Table III.

The ion with the largest cross section, in all three cases, is the metal ion fragment. This occurs, in part, because two independent processes contribute: dissociative ionization (e.g., $GaCl \rightarrow Ga^+ + Cl$) and ion-pair formation (e.g., $GaCl \rightarrow Ga^+ + Cl^-$). Ion pairs form not from ionization of the molecule but from initial excitation of the neutral molecule followed by dissociation of the excited state into a pair of oppositely charged ions. (A measurement of Cl^- formation could be used to determine the ion-pair contribution accurately, but this measurement was not made.) The chlorine ion fragment has the highest threshold and the smallest ionization cross section. An interesting feature is that the threshold for Ga^+-fragment formation lies lower than the threshold for the $GaCl^+$ parent. This results from a combination of the low ionization energy of Ga, the relatively high ionization energy of GaCl, and the occurrence of ion-pair formation.

IV. CONCLUSIONS

Ionization cross sections are reported for GaCl, GeCl, and SnCl. For all three species, the metal fragment ion is the dominant ion, with the parent-ion cross section somewhat smaller. The ionization energy of these three species are reported here to an accuracy from ±0.3 to ±0.5 eV. Thresholds for dissociative ionization and ion pair formation agree moderately well with values calculated from literature dissociation energies, atomic ionization energies, and the electron affinity of Cl.

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[1]R. S. Freund, R. C. Wetzel, R. J. Schul, and T. R. Hayes, Phys. Rev. A **41**, 3575 (1990).

[2]R. S. Freund, R. C. Wetzel, and R. J. Shul, Phys. Rev. A **41**, 5861 (1990).

[3]T. R. Hayes, R. C. Wetzel, F. A. Baiocchi, and R. S. Freund, J. Chem. Phys. **88**, 823 (1988).

[4]R. J. Shul, T. R. Hayes, R. C. Wetzel, F. A. Baiocchi, and R. S. Freund, J. Chem. Phys. **89**, 4042 (1988).

[5]T. R. Hayes, R. J. Shul, F. A. Baiocchi, R. C. Wetzel, and R. S. Freund, J. Chem. Phys. **89**, 4035 (1988).

[6]S. C. McNevin and G. E. Becker, J. Appl. Phys. **58**, 4670 (1985).

[7]M. S. Ameen and T. M. Mayer, J. Appl. Phys. **63**, 1152 (1988).

[8]W. L. O'Brien, C. M. Paulsen-Boaz, T. N. Rhodin, and L. C. Rathbun, J. Appl. Phys. **64**, 6523 (1988).

[9]R. C. Wetzel, F. A. Baiocchi, T. R. Hayes, and R. S. Freund, Phys. Rev. A **35**, 559 (1987).

[10]Colutron Research Corp., Boulder, CO 80301; L. Wahlin, Nucl. Instrum. Methods **27**, 55 (1964).

[11]K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

[12]E. M. Bulewicz, L. F. Phillips, and T. M. Sugden, Trans. Faraday Soc. **57**, 921 (1961).

[13]A. G. Gaydon, *Dissociation Energies* (Chapman and Hall, London, 1953).

[14]D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K.L. Churney, and R. L. Nuttall, J. Phys. Chem. Ref. Data **11**, Suppl. 2 (1982).