

## Cross Sections for Ionization by Electrons. I. Absolute Ionization Cross Sections of Zn, Cd, and Te<sub>2</sub>. II. Comparison of Theoretical with Experimental Values for Atoms and Molecules\*

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Ionization cross sections for Zn, Cd, and Te<sub>2</sub> vapors have been measured by collection of the total positive ion currents produced from electron impact by 50-eV electrons in the specially designed ion source of a mass spectrometer. The results:  $\sigma_i(\text{Zn}) = 5.03 \pm 0.45 \times 10^{-16} \text{ cm}^2$ ,  $\sigma_i(\text{Cd}) = 8.54 \pm 0.33 \times 10^{-16} \text{ cm}^2$ ,  $\sigma_i(\text{Te}_2) = 17.46 \pm 0.48 \times 10^{-16} \text{ cm}^2$ . These results are combined with available data to set up a compilation of absolute ionization cross sections for 27 atoms. Very limited agreement is found with theoretical ionization cross sections: It is shown that ionization cross sections of molecules cannot be calculated reliably by summation of the ionization cross sections of the constituent atoms.

THE mass spectrometer is universally used to analyze reaction products that effuse from a thermal reactor. To calculate the partial pressures of species in the effusate (usually from a Knudsen cell), it is necessary to obtain the ionization efficiency factor for each species. This includes the cross section for ionization by electrons (50–75 eV) and other discrimination factors such as detector response. The latter can be taken into account by calibration, but the ionization cross sections must be obtained individually.

We define the ionization cross section of a species ( $\sigma_i$ ) as follows:

$$\sigma_i = (i_i/i_e)(T/274)(pL3.535 \times 10^{16})^{-1} \text{ cm}^2, \quad (1)$$

in which  $i_i$  is the total ion current for an ionizing electron current of  $i_e$  whose path length is  $L$  cm in a gas of pressure  $p$  Torr and temperature  $T^\circ\text{K}$ .  $i_i$  and  $i_e$  are expressed in the same units. The equation holds if  $i_e \gg i_i$ . This condition is fulfilled throughout the normally operating pressure range of a mass spectrometer ( $10^{-4}$  Torr or lower).

Because of the difficulties in obtaining experimental values of ionization cross sections, especially for refractory materials, most workers in this field have used relative ionization cross sections of atoms as calculated by Otvos and Stevenson<sup>1</sup> (O. and S.). These theoretical cross sections were based on an interpretation of the Bethe<sup>2</sup> relation for inelastic scattering of electrons by atoms. Recently Stevenson and Schissler<sup>3</sup> have pointed out that the theoretical ionization cross sections are more properly the sum of the cross sections for excita-

tion and ionization of the atoms. Agreement between theory and experiment would only be expected for atoms which have similar ratios of cross sections for excitation vs ionization. O. and S. also proposed the rule of additivity which states that the ionization cross section of a molecule is the summation of the cross sections of the constituent atoms. Recent experimental evidence<sup>3-6</sup> has shown this rule to be unreliable except for members of homologous series, such as the alkanes, and for some simple molecules.

The work reported in this paper was undertaken to obtain experimental values for ionization cross sections of some metal atoms; to correlate these with other reported measurements and obtain a tabulation of absolute ionization cross sections of atoms; and to compare these results with those calculated by O. and S.

### DETERMINATION OF IONIZATION CROSS SECTIONS

This section summarizes the most common techniques that are used to obtain experimental values for absolute and relative ionization cross sections.

#### A. Collection of All Positive Ions that Result from Passage of an Electron Beam through a Gas in Equilibrium with Its Surroundings

From Eq. (1),  $\sigma_i$  can be obtained directly and in absolute units. Relative  $\sigma_i$ 's can also be determined if  $p$  is unknown, by comparison of the total ion current with that of a reference material of known  $\sigma_i$ , provided that the relative pressure ratios are measured in some

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<sup>1</sup> J. W. Otvos and D. P. Stevenson, *J. Am. Chem. Soc.* **78**, 546 (1956).

<sup>2</sup> H. Bethe, *Ann. Physik* **5**, 352 (1930).

<sup>3</sup> D. P. Stevenson and D. O. Schissler, *The Chemical and Biological Action of Radiations*, edited by M. Haissinsky (Academic Press Ltd., London, 1961), Vol. 5, pp. 181–192.

<sup>4</sup> W. L. Fite and R. T. Brackmann, *Phys. Rev.* **112**, 1141 (1958).

<sup>5</sup> P. Goldfinger and M. Jeunehomme, *Trans. Faraday Soc.* **59**, 2851 (1963).

<sup>6</sup> J. Berkowitz, H. A. Tasman, and W. A. Chupka, *J. Chem. Phys.* **36**, 2170 (1962).

part of the gas-handling system. This method has been widely used for materials that are sufficiently volatile at room temperature.<sup>1,7,8</sup>

### B. Quantitative Vaporization from a Knudsen Cell of Known Quantities of Two Elements or Compounds and Comparison of Integrated Ion Intensities

$$\frac{\sigma_i(A)}{\sigma_i(B)} = \frac{\sum i_A}{\sum i_B} \frac{n_B}{n_A} \frac{\Delta t_A}{\Delta t_B} \left( \frac{T_A M_B}{T_B M_A} \right)^{\frac{1}{2}} \quad (2)$$

In Eq. (2),  $\sum i_A$  and  $\sum i_B$  are the integrated ion intensities for Species A and B,  $n_A$  and  $n_B$  are the number of moles of A and B that are evaporated in times  $\Delta t_A$  and  $\Delta t_B$  for cell temperatures  $T_A$  and  $T_B$ , respectively.  $M_A$  and  $M_B$  are the molecular weights of A and B. The weight loss from the Knudsen cells must be corrected for volatile impurities and the ion currents are corrected for discrimination effects at the electron multiplier.<sup>9</sup>

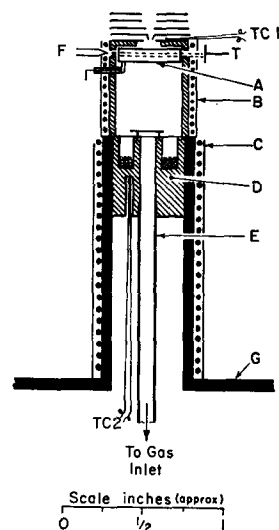
### C. Vaporization of a Compound which Evaporates Congruently by Decomposition

The ratio of pressures is then known from the vaporization process and the relative ion intensities lead directly to relative ionization cross sections—making allowance as above for ionic collection efficiencies. Similarly if the equilibrium constant is known for dissociation of a gaseous molecule, one can obtain ratios of ionization cross sections between the species present at known reactor conditions. A modification of this technique is the use of a constant-boiling system<sup>10</sup> in which the flux ratio of the component vapor species is the same as the composition ratio in the condensed phase.

### D. Vaporization from a Double-Oven Knudsen Cell

This technique was first proposed by Milne<sup>11</sup> for the estimation of relative  $\sigma_i$ 's for dimers and monomers  $\sigma_i(d)/\sigma_i(m)$ . The Knudsen cell is divided into two sections which can be maintained at different temperatures and are joined by a connecting channel. The sample is contained in the lower chamber at temperature  $T_1$ . This is held constant while the temperature of the upper chamber  $T_2$  is varied from  $T_2 = T_1$  to  $T_2 > T_1$ . If flow is molecular both in and out of the upper chamber, one can obtain  $\sigma_i(d)/\sigma_i(m)$  from the relative ion intensities  $i_d/i_m$ , according to the treatment by

FIG. 1. Mass-spectrometer ion source: A, ion-collection electrode; B, ion-source furnace; C, sample furnace; D, sample holder with metal sample; E, gas-inlet tube; G, mounting plate; F, filament; T, electron trap; TC<sub>1</sub>, source thermocouple; TC<sub>2</sub>, sample thermocouple.



Gorochov<sup>12</sup> and by Berkowitz *et al.*<sup>6</sup> This treatment has been extended to systems containing more than two components.<sup>13</sup>

### E. Modulation of a Molecular Beam of Products Effusing from a Reactor

A mass spectrometer is used to determine the degree of dissociation of the reagent and the relative ionization cross sections are obtained from the ratio of ion intensities of undissociated parent to the product species. This technique has been applied by Fite and Brackmann<sup>4,14</sup> and by others<sup>15,16</sup> to determine  $\sigma_i(d)/\sigma_i(m)$  for  $O_2$ ,  $H_2$ , and  $N_2$ .

## EXPERIMENTAL

Method A was chosen for measuring the ionization cross sections of Zn, Cd, and  $Te_2$  because of the uncomplicated nature of the technique and the availability of a mass spectrometer with a heated ion source that could be modified for this purpose. The source, Fig. 1, is that used by Mann and Tickner<sup>17</sup> with the following modifications: an electrode, parallel to the electron beam, was introduced to collect the total positive ion current, and was maintained a few volts negative with respect to the source walls. The distance from the electron beam to the electrode was approximately 2 mm,

<sup>12</sup> L. N. Gorochov, *Vestn. Mosk. Univ. Ser. II*, No. 6, 231 (1958).

<sup>13</sup> L. N. Siderov and P. A. Akishin, *J. Phys. Chem. (USSR)* **151**, 581 (1963).

<sup>14</sup> W. L. Fite and R. T. Brackmann, *Phys. Rev.* **113**, 815 (1959).

<sup>15</sup> E. W. Rothe, L. L. Marino, R. H. Neynaber, and S. M. Trujillo, *Phys. Rev.* **125**, 582 (1962).

<sup>16</sup> A. C. H. Smith, E. Caplinger, R. H. Neynaber, E. W. Rothe, and S. M. Trujillo, *Phys. Rev.* **127**, 1647 (1962).

<sup>17</sup> K. H. Mann and A. W. Tickner, *J. Phys. Chem.* **64**, 251 (1960).

<sup>7</sup> J. T. Tate and P. T. Smith, *Phys. Rev.* **39**, 270 (1932).

<sup>8</sup> F. W. Lampe, J. L. Franklin, and F. H. Field, *J. Am. Chem. Soc.* **79**, 6129 (1957).

<sup>9</sup> H. E. Stanton, W. A. Chupka, and M. G. Inghram, *Rev. Sci. Instr.* **27**, 109 (1956).

<sup>10</sup> A. W. Searcy, W. S. Williams, and P. O. Schissel, *J. Chem. Phys.* **32**, 957 (1960).

<sup>11</sup> T. A. Milne, *J. Chem. Phys.* **28**, 717 (1958).

the length of the electrode being 1.14 cm. The same source body was used as before wherein the entrance and exit slits for the electron beam were  $0.7 \times 2.6$  mm. The electron beam was collimated by a 350-G magnetic field.

The sample holder was a cylinder of molybdenum,  $\frac{5}{8}$ -in. long  $\times$   $\frac{1}{2}$ -in. diam with a  $\frac{1}{8}$ -in. diam hole drilled through the center to admit gas directly into the source. A deflector plate covered the gas exit to prevent direct flow through the source. In addition, two semi-circular channels  $\frac{1}{8}$ -in. wide by  $\frac{1}{4}$ -in. deep were cut out of the cylinder to contain the metal samples. The sample holder was directly connected to the end plate of the source envelope by a bellows assembly. Compression of the bellows when reassembling provided sealing pressure for the top of the sample holder against a ridge inside the furnace. The temperatures of the sample holder and the ion source were measured with calibrated Chromel-Alumel thermocouples.

Further details of the operation of the furnace assembly and mass spectrometer are available from the earlier work.<sup>17</sup>

## RESULTS AND DISCUSSION

### A. Ionization Cross Sections of Zinc, Cadmium, and Tellurium

Mann and Tickner<sup>17</sup> have shown that equilibrium conditions between the solid metal and metal vapor are maintained for zinc and cadmium in the ion source used for this study. The vapor pressures reported in the literature are of excellent quality for both metals, and their vapors are monotomic. In addition the required vapor pressures ( $10^{-7}$  to  $10^{-4}$  Torr) are readily achieved in the operating range of our source, ( $100^{\circ}$ – $400^{\circ}$ C). The third material, tellurium, vaporizes to dimer molecules, and good vapor-pressure data are available.

In order to apply the method of saturated ion currents for the measurement of  $\sigma_i$ , it is necessary to determine the contributions of background ions to the total ion current. This was easily done in the present apparatus since the electron-impact chamber could be operated as the ion source of the mass spectrometer. In this mode, the ion collection electrode was connected to the source body by means of an external switch. The ion current due to background could be obtained relative to the metal-ion current by summation of individual ion peaks from the mass spectrum. By means of repeated temperature cycling of the system, it was possible to reduce background contributions to less than 15% of the total ion current for the three materials in this study.

The over-all operation of the system was checked by collecting the total ion currents for the rare gases; argon, krypton and xenon. They were admitted to the

ion source by means of a molecular leak from an exterior vacuum system. Ion currents were found to be linear with respect to the pressure of added gas as measured on the high-pressure side of the leak. The relative cross sections for ionization, calculated from the slopes of the ion current vs inlet pressure, agreed with the recent values of Asundi and Kurepa.<sup>18</sup> This was considered to offer sufficient proof that saturated ion currents were being measured and that the system could be used to obtain ionization cross sections.

Subsequently it was found that the trap current was fairly sensitive to the source temperature and, in addition, temperature drift occurred if attempts were made to maintain steady trap current by altering the filament controls. Therefore a rare gas (argon or xenon) was usually admitted after a measurement of the metal-ion current had been made, and the ion current of the rare gas was used to correct the metal-ion intensity to that which would result from a trap current of  $12.5 \mu\text{A}$ .

If we substitute in Eq. (1) the experimental values for  $i_e$  and  $L$ , we obtain:

$$\sigma_i = (i_i/p) (T/273) 1.985 \times 10^{-12} \text{ cm}^2. \quad (3)$$

The ionization cross sections for zinc, cadmium, and tellurium, calculated by means of Eq. (3) are summarized in Tables I, II, and III. The energy for the electrons was 50 eV. This value was chosen because the source was more stable in this condition than at higher voltages and the ion yields for unit trap current changed very little for electron energies between 50–75 eV.

The vapor pressures of zinc and cadmium were obtained from the tabulation by Nesmeyanov.<sup>19</sup> Dis-

TABLE I. Ionization cross section of Zn for 50-eV electrons.

$T(^{\circ}\text{K})$	$P(\text{Zn})$ (Torr)	$i^t(\text{Zn})$ ( $\text{A} \times 10^{-9}$ )	$\sigma_i(\text{Zn})$ ( $\text{cm}^2 \times 10^{16}$ )
486	$1.05 \times 10^{-6}$	1.68	5.65
487	1.13	1.50	4.66
489	1.28	1.73	4.81
487	1.13	1.40	4.39
488	1.20	1.61	4.76
492.5	1.60	2.26	5.06
492	1.55	2.05	4.73
493	1.64	2.38	5.20
495	1.86	2.57	4.97
495.5	1.92	2.67	5.01
505	3.45	5.62	5.98
506	3.68	5.10	5.10
			Mean $5.03 \pm 0.45$

<sup>18</sup> R. K. Asundi and M. V. Kurepa, *J. Electron. Control* **15**, 41 (1963).

<sup>19</sup> A. N. Nesmeyanov, *Vapor Pressure of the Chemical Elements*, edited by R. Gary (Elsevier Publishing Company, Inc., New York, 1963).

crepancies were noted between the original vapor pressure data of solid tellurium by Korneyeva *et al.*<sup>20</sup> and the tabulation by Nesmeyanov<sup>19</sup> that is based on this data. The original work was therefore used as the source for the vapor pressures of tellurium in Table III.

### B. Comparison of Experimental with Theoretical Ionization Cross Sections of Atoms

The relative ionization cross sections of atoms calculated by Otvos and Stevenson<sup>1</sup> for 75-eV electrons have been converted to units of square centimeters by relating the individual cross sections to that of argon, for which  $\sigma_i = 3.62 \times 10^{-16}$  cm<sup>2</sup>. The resultant values are compared to the available experimentally determined ionization cross sections in Table IV. The experimental methods by which these cross sections have been obtained are given in the second-last column; the letters refer to the enumeration of techniques in the Introduction. Parentheses are used to designate values that have been estimated by methods other than those described above. The sources for the experimental cross sections given in Table IV are described in further detail below.

#### Hydrogen, Oxygen, Nitrogen

Ionization cross section were obtained by Method E, whereby the degree of dissociation was determined for molecular beams of these gases effusing from reactors. The ratios of the ionization cross sections for dimers to

TABLE II. Ionization cross section of Cd for 50-eV electrons.

T (°K)	P(Cd) (Torr)	$i^+(\text{Cd})$ ( $\text{\AA} \times 10^9$ )	$\sigma_i(\text{Cd})$ ( $\text{cm}^2 \times 10^{16}$ )
414	$5.81 \times 10^{-6}$	1.60	8.29
426	$1.44 \times 10^{-5}$	4.06	8.76
432.5	$2.30 \times 10^{-5}$	6.49	8.87
434	$2.55 \times 10^{-5}$	7.33	9.07
406.5	$3.20 \times 10^{-5}$	0.92	8.54
412	$5.00 \times 10^{-5}$	1.39	8.32
419	$8.52 \times 10^{-5}$	2.16	7.72
420.5	$9.55 \times 10^{-5}$	2.46	7.88
421.5	$1.03 \times 10^{-4}$	2.78	8.28
422	$1.07 \times 10^{-4}$	2.93	8.39
425	$1.35 \times 10^{-4}$	3.59	8.22
428.5	$1.73 \times 10^{-4}$	4.84	8.72
430	$1.94 \times 10^{-4}$	5.32	8.57
433	$2.38 \times 10^{-4}$	6.40	8.46
417	$7.33 \times 10^{-5}$	2.24	9.26
430	$1.94 \times 10^{-4}$	5.32	8.56
431.5	$2.15 \times 10^{-4}$	6.08	8.90
432.2	$2.24 \times 10^{-4}$	6.44	9.03
Mean			$8.54 \pm 0.33$

<sup>20</sup> N. V. Korneyeva, A. S. Pashenkin, A. V. Novoselova, and Yu. A. Priselkov, *Zh. Neorgan. Khim.* **2**, 1720 (1958).

TABLE III. Ionization cross section of Te<sub>2</sub> for 50-eV electrons.

T (°K)	P(Te <sub>2</sub> ) (Torr)	$i^+(\text{Te}_2)$ ( $\text{\AA} \times 10^9$ )	$\sigma_i(\text{Te}_2)$ ( $\text{cm}^2 \times 10^{16}$ )
530.5	$2.68 \times 10^{-6}$	12.40	17.86
525	1.90	8.67	17.42
518	1.25	5.76	17.35
525	1.90	8.67	17.42
526	2.03	9.03	17.00
530	2.61	11.86	17.51
525.5	1.98	8.57	16.54
529	2.45	11.45	17.98
521	1.50	7.14	18.03
Mean			$17.46 \pm 0.48$

monomers were measured and related to the absolute ionization cross sections for the molecular gases.<sup>7</sup>

#### Rare Gases: Helium, Neon, Argon, Krypton, and Xenon

All values were taken from the recent work of Asundi and Kurepa<sup>18</sup> who determined absolute ionization cross sections by means of a Lozier apparatus.<sup>21</sup>

#### Beryllium

The ratio  $\sigma_i(\text{Be})/\sigma_i(\text{O}) = 2.1$ , reported by Theard and Hildenbrand<sup>22</sup> was combined with  $\sigma_i(\text{O}) = 0.70 \times 10^{-16}$  cm<sup>2</sup>. In the same paper the authors also measured  $\sigma_i(\text{O}_2)/\sigma_i(\text{O}) = 1.4$ , in good agreement with the data of Fite and Brackmann.<sup>14</sup> Chupka *et al.*<sup>23</sup> reported  $\sigma_i(\text{Be})/\sigma_i(\text{O}) = 0.2$ , but if their experimental ratio  $\sigma_i(\text{O}_2)/\sigma_i(\text{O}) = 0.60$  is brought into agreement with that of Fite and Brackmann, the result  $\sigma_i(\text{Be}) = 2.50 \times 10^{-16}$  cm<sup>2</sup> is obtained.

#### Boron, Titanium, Chromium, Tin, Gold, Uranium

In various investigations, experimental ratios of ionization cross sections have been obtained between members of this group and between this group and Ag, Cu, or Si. The relative values have been expressed in absolute units by conversion of the O. and S. relative  $\sigma_i$ 's for Ag, Cu, and Si to units of square centimeters and by using the experimental ratios of ionization cross sections which involve members of this group. Thus the ratio  $\sigma_i(\text{B})/\sigma_i(\text{Ag}) = 0.15 \pm 0.05$ <sup>24</sup> was used to obtain  $\sigma_i(\text{B}) = 1.74 \times 10^{-16}$  cm<sup>2</sup>. This value, combined with

<sup>21</sup> B. A. Tozer and J. D. Craggs, *J. Electron. Control* **8**, 103 (1960).

<sup>22</sup> L. P. Theard and D. L. Hildenbrand, *J. Chem. Phys.* **41**, 3416 (1964).

<sup>23</sup> W. A. Chupka, J. Berkowitz, and C. F. Giese, *J. Chem. Phys.* **30**, 827 (1959).

<sup>24</sup> G. Verhaegen and J. Drowart, *J. Chem. Phys.* **37**, 1367 (1962).

TABLE IV. Comparison of experimental with theoretical ionization cross sections of atoms for 75-eV electrons.

Atom	Theoretical		Experimental		
	Relative $\sigma_i$ (O. and S.) <sup>1</sup>	$\sigma_i$ (cm <sup>2</sup> ×10 <sup>16</sup> )	$\sigma_i$ (cm <sup>2</sup> ×10 <sup>16</sup> )	Method	Reference
H	1.00	0.332	0.70	E	(4)
He	0.935	0.311	0.32	A	(18)
Be	6.31	2.10	3.15	C	(22)
			2.50	C	(23)
B	5.02	1.67	1.74±0.05	B	(24)
C	4.16	1.38	(2.07±0.05)	...	...
N	3.84	1.28	1.41	E	(16)
O	3.29	1.09	1.50	E	(14)
Ne	1.75	0.581	0.590	A	(18)
Na	14.3	4.75	(8.6)	...	(32)
Si	14.4	4.78	...	...	...
S	12.8	4.25	4.63	B	(5)
Cl	11.8	3.92	(4.15)	...	...
Ar	10.9	3.62	3.62	A	(18)
K	38.8	12.89	(9.6)	...	(32)
Ti	36.8	12.22	13.2±2.6	C	(10)
Cr	28.1	9.33	17.4±3.5	B	(27)
Zn	16.0	5.31	5.03±0.45	A	(this work)
Se	18.5	6.14	7.18	B	(5)
Kr	17.4	5.78	5.5	A	(18)
Rb	58.4	19.39	(9.6)	...	(32)
Ag	34.8	11.56	...	...	...
Cd	22.1	7.34	8.54±0.33	A	(this work)
			(7.24)	A	(33)
Sn	25.8	8.57	20.9	B	(28)
Te	25.6	8.50	10.46	A, B	(this work) (34)
			10.47	A, B	(this work) (34)
Xe	24.1	8.00	7.6	A	(18)
Cs	73.5	24.41	(11.2)	...	(32)
Au	...	...	11.6	B	(25)
			11.6	B	(26)
Hg	27.4	9.10	(10.45)	A	(33)
U	55.7 <sup>(a)</sup>	18.50	16.6	B	(29)
			11.3	C	(31)

<sup>a</sup> Reference 30.

$\sigma_i(\text{Ti})/\sigma_i(\text{B})=7.6\pm1.5$  by Searcy *et al.*,<sup>10</sup> led to the tabulated  $\sigma_i(\text{Ti})$ . In two separate investigations,

$$\sigma_i(\text{Au})/\sigma_i(\text{Cu})=1.90^{25}$$

and

$$\sigma_i(\text{Au})/\sigma_i(\text{Si})=2.43^{26}$$

Both lead to  $\sigma_i(\text{Au})=11.6\times10^{-16}$  cm<sup>2</sup>, demonstrating the consistency between theoretical and experimental ratios for these ionization cross sections. The ratio  $\sigma_i(\text{Cr})/\sigma_i(\text{Au})=1.5\pm0.4$ <sup>27</sup> results in  $\sigma_i(\text{Cr})=17.4\times10^{-16}$  cm<sup>2</sup>, a value which is almost a factor of 2 greater than the theoretical  $\sigma_i(\text{Cr})$ . Ackerman *et al.*<sup>28</sup> have measured the ratios of ionization cross sections of Sn

with respect to Cu, Ag, and Au. The authors report experimental ratios which lead to a relative  $\sigma_i(\text{Sn})=63$  (O. and S. units). We obtain  $\sigma_i(\text{Sn})=20.9\times10^{-16}$  cm<sup>2</sup> by conversion of the relative units. This result is more than twice the theoretical value. De Maria *et al.*<sup>29</sup> obtained  $\sigma_i(\text{U})/\sigma_i(\text{Ag})=1.436$ , giving  $\sigma_i(\text{U})=16.6\times10^{-16}$  cm<sup>2</sup> in good agreement with the theoretical value which was calculated by Gingevich and Lee<sup>30</sup> by the method of O. and S. Cater *et al.*<sup>31</sup> determined  $\sigma_i(\text{U})/\sigma_i(\text{S})=2.44$  which results in  $\sigma_i(\text{U})=11.3\times10^{-16}$  cm<sup>2</sup> if we use the experimental  $\sigma_i(\text{S})$ . The discrepancy between the two experimental values for  $\sigma_i(\text{U})$  possibly exceeds the measurement errors and may result from an erroneous  $\sigma_i(\text{Ag})$ .

<sup>25</sup> M. Ackerman, F. E. Stafford, and J. Drowart, J. Chem. Phys. **33**, 1784 (1960).

<sup>26</sup> P. Goldfinger, Report No. AF61 (052)-225, February 29, 1960.

<sup>27</sup> M. Ackerman, F. E. Stafford, and G. Verhaegen, J. Chem. Phys. **36**, 1560 (1962).

<sup>28</sup> M. Ackerman, J. Drowart, F. E. Stafford, and G. Verhaegen, J. Chem. Phys. **36**, 1557 (1962).

<sup>29</sup> G. DeMaria, R. P. Burns, J. Drowart, and M. G. Inghram, J. Chem. Phys. **33**, 1373 (1960).

<sup>30</sup> K. A. Gingevich and P. K. Lee, J. Chem. Phys. **40**, 3520 (1964).

<sup>31</sup> E. D. Cater, E. G. Rauh, and R. J. Thorn, J. Chem. Phys. **35**, 619 (1961).

### Sodium, Potassium, Rubidium, and Cesium

Brink<sup>32</sup> measured the absolute ionization cross sections of these alkali atoms by electron impact on molecular beams of their vapors that issued from a graphite furnace. A surface ionization detector established the beam density, and positive ions from electron impact by a crossed electron beam were collected to obtain  $\sigma_i$ 's. The experimental  $\sigma_i(\text{Na})$ ,  $\sigma_i(\text{K})$ ,  $\sigma_i(\text{Rb})$ , and  $\sigma_i(\text{Cs})$  in Table IV are those reported by Brink for electron energies corresponding to the maximum ion yields. This occurs below 75 eV for the alkali atoms so that the  $\sigma_i$ 's at an electron energy of 75 eV would be lower than those tabulated. In general, poor agreement is found with theoretical expectations and is most likely the result of the high cross sections for excitation of the alkali atoms.

### Sulfur, Zinc, Selenium, Cadmium, Tellurium, Mercury

The tabulated  $\sigma_i(\text{Zn})$  and  $\sigma_i(\text{Cd})$  are those obtained in this investigation. Dushman<sup>33</sup> reported relative ion yields for a number of atoms and compounds based on the response of a VG-1 ion gauge to vapors of these materials. The numbers in brackets for  $\sigma_i(\text{Cd})$  and  $\sigma_i(\text{Hg})$  were calculated from Dushman's data by relating the ion yields to  $\sigma_i(\text{Ar}) = 3.62 \times 10^{-16} \text{ cm}^2$ . The agreement with the other experimental as well as with the theoretical values is very good.

The relative ratios:  $\sigma_i(\text{S})/\sigma_i(\text{Cd})$ ,  $\sigma_i(\text{S})/\sigma_i(\text{Zn})$ , and  $\sigma_i(\text{S})/\sigma_i(\text{Hg})$  obtained by Goldfinger and Jeunehomme,<sup>5</sup> combined with the experimental values for  $\sigma_i(\text{Cd})$ ,  $\sigma_i(\text{Zn})$ , and  $\sigma_i(\text{Hg})$  yield  $\sigma_i(\text{S}) = 4.63 \pm .40 \times 10^{-16} \text{ cm}^2$ . If the ratio  $\sigma_i(\text{Te}_2)/\sigma_i(\text{Te}) = 1.68$ <sup>34</sup> is com-

bined with the experimental  $\sigma_i(\text{Te}_2)$  of this investigation the result:  $\sigma_i(\text{Te}) = 10.46 \times 10^{-16} \text{ cm}^2$  is obtained. Similarly the ratio  $\sigma_i(\text{Zn})/\sigma_i(\text{Te}) = 0.48$ <sup>34</sup> taken with the experimental  $\sigma_i(\text{Zn})$  leads to  $\sigma_i(\text{Te}) = 10.47 \times 10^{-16} \text{ cm}^2$ . Goldfinger and Jeunehomme<sup>5</sup> also reported  $\sigma_i(\text{Se})/\sigma_i(\text{Cd}) = 0.84$ . The resultant  $\sigma_i(\text{Se}) = 7.18 \times 10^{-16} \text{ cm}^2$  is derived from this ratio and our experimental  $\sigma_i(\text{Cd})$ .

### Carbon and Chlorine

The value,  $\sigma_i(\text{C}) = 2.07 \pm 0.05 \times 10^{-16} \text{ cm}^2$  was calculated from the experimental ionization cross sections for hydrocarbons, reported by Lampe *et al.*,<sup>8</sup> omitting the high value for cyclohexane, and assuming  $\sigma_i(\text{H}) = 0.70 \times 10^{-16} \text{ cm}^2$ .  $\sigma_i(\text{Cl})$  was similarly obtained by subtracting  $\sigma_i(\text{H})$  from  $\sigma_i(\text{HCl})$ .<sup>8</sup> Data by Lampe *et al.*<sup>8</sup> were normalized to  $\sigma_i(\text{Ar}) = 3.62 \times 10^{-16} \text{ cm}^2$ .

### C. Ionization Cross Sections of Molecules: The Additivity Rule

In the previous section,  $\sigma_i(\text{C})$  was obtained by application of the additivity rule to hydrocarbons and, indeed, the data are self-consistent. However, in many recent investigations, it has been pointed out that the ratios of ionization cross sections for dimers to monomers,  $\sigma_i(d)/\sigma_i(m)$ , is always less than the predicted value of 2. The available data are summarized in Table V.

As shown in the table, only for oxygen and nitrogen does this ratio approach 2; all others are considerably lower, and in several instances are less than 1.

Recently, Stevenson and Schissler<sup>3</sup> have compared the theoretical with experimental ionization cross sections of a number of volatile compounds. Little correlation is found between the two sets of numbers except for some simple gases. Discrepancies of as high as a factor of 6 are found for the halomethanes.

The discrepancies between calculated and experimental molecular ionization cross sections are also apparent in recent results that have been obtained from mass-spectrometric analyses (Methods B, C, D) of Knudsen-cell effusates. Siderov and Akishin<sup>18</sup> found  $\sigma_i(\text{NaF})/\sigma_i(\text{ZrF}_4)/\sigma_i(\text{NaZrF}_6) = 1.0/1.8/2.5$ . Colin and Drowart<sup>35</sup> reported  $\sigma_i(\text{S}_2)/\sigma_i(\text{In}_2\text{S}) = 1.04$ , and Sommer *et al.*<sup>36</sup> obtained  $\sigma_i(\text{Zn})/\sigma_i(\text{BS}_2)/\sigma_i(\text{B}_2\text{S}_2)/\sigma_i(\text{B}_2\text{S}_3) = 1/1.5/2.0/2.0$ . In all instances, these ratios are lower than the calculated ratios using the rule of additivity. White *et al.*<sup>37</sup> measured the relative pressures of  $\text{Li(g)}$  and  $\text{Li}_2\text{O(g)}$  and by calibration of the mass spectrometer were able to determine  $\sigma_i(\text{Li})/\sigma_i(\text{Li}_2\text{O}) = 1.6 \pm .3$ . This ratio is almost a factor of four higher than the calculated ratio of 0.42.<sup>1</sup> Similarly, Berkowitz and

TABLE V. Experimental ratios for ionization cross sections of dimer relative to monomer.

Monomer	$\sigma_i(d)/\sigma_i(m)$	Method	Reference
H	1.44	E	(4)
N	1.93	E	(16)
O	1.80	E	(14)
S	1.44	B	(5)
Se	1.64	B	(5)
Te	1.68	B	(34)
LiCl	1.15	D	(6)
	0.83	D	(6)
LiBr	1.42	D	(6)
	1.84	D	(6)
LiI	1.04	D	(6)
NaF	1.24	D	(6)
NaCl	1.58	D	(6)
NaI	0.86	D	(6)
KF	1.27	D	(6)
KCl	1.57	D	(6)
KI	1.66	D	(6)
RbCl	1.43	D	(6)

<sup>32</sup> G. O. Brink, Phys. Rev. **134**, A345 (1964).

<sup>33</sup> S. Dushman, *Vacuum Technique* (John Wiley & Sons, Inc., New York, 1949).

<sup>34</sup> (a) R. Colin, P. Goldfinger, and M. Jeunehomme, paper presented at the ASTM Conference on Mass Spectrometry, Chicago, Illinois, June 4-9, 1961; (b) R. Colin, Ind. Chim. Belge. **26**, 51 (1961).

<sup>35</sup> R. Colin and J. Drowart, Report No. WADD-60-682, September, 1963.

<sup>36</sup> A. Sommer, P. N. Walsh, and D. White, J. Chem. Phys. **33**, 296 (1960).

<sup>37</sup> D. White, K. S. Seshadri, D. F. Dever, D. E. Mann, and M. I. Linevsky, J. Chem. Phys. **39**, 2463 (1963).

Marquart<sup>38</sup> obtained  $\sigma_i(\text{S}_8)/\sigma_i(\text{S}_2)=2.0$ , whereas the additivity rule predicts a ratio of 4. Finally, Ackermann *et al.*<sup>39</sup> obtained  $\gamma\sigma_i(\text{ThO})/\gamma\sigma_i(\text{ThO}_2)=3.5$ , in which  $\gamma$  is the ion-collection efficiency factor. This factor would not be greatly different for these two molecules so that the resulting  $\sigma_i(\text{ThO})/\sigma_i(\text{ThO}_2)$  would be of the order of 3, a value that is more than three times that predicted.

We conclude from these results that the additivity rule cannot be applied generally to obtain reliable values for ionization cross sections of molecules. It will continue to be necessary to measure such cross sections directly or to use empirical correlations<sup>5</sup> which may apply to particular groups of molecules.

<sup>38</sup> J. Berkowitz and J. R. Marquart, *J. Chem. Phys.* **39**, 275 (1963).

<sup>39</sup> R. J. Ackermann, E. G. Rauh, R. J. Thorn, and M. C. Cannon, *J. Phys. Chem.* **67**, 762 (1963).

## CONCLUSIONS

The results of this study have been combined with available data to set up a tabulation of experimental ionization cross sections of atoms. Although the O. and S. method for calculating ionization cross sections of atoms has been shown to possess limited applicability,<sup>3</sup> surprisingly good agreement is found between theory and experiment for most of the tabulated atoms. However, large errors occur for many of the atoms listed and agreement is particularly poor for those atoms in which most of the energy of the electron would result in excitation of discrete levels, e.g., the alkali atoms.

Additional experimental evidence shows that the concept of additivity for calculation of ionization cross sections of molecules is inapplicable, except for alkanes and some simple compounds.

## Vibrational Spectra of Trioxane and Trioxane-*d*<sub>6</sub>\*

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The infrared spectra of trioxane and trioxane-*d*<sub>6</sub> have been measured in the region from 4000 to 300 cm<sup>-1</sup> on the gaseous, solution, liquid, and solid samples. Polarized spectra have been taken on the oriented thin layer of crystal grown between NaCl or KBr plates. Group-theoretical analyses were made for a free molecule (point group *C*<sub>3v</sub>) and the crystal (site group *C*<sub>3</sub> and space group *R*3*c*-*C*<sub>3v</sub><sup>6</sup>). The symmetry species of the observed bands were determined on the basis of the polarized spectra of the crystal. The normal vibrations of a free molecule were calculated according to Wilson's **GF** matrix method by use of the Urey-Bradley potential field. The observed bands have been interpreted reasonably based on the calculated results. The band shapes of the gaseous spectra were found to be consistent with the dichroism of the polarized spectra of the crystal by taking into account the Coriolis interactions.

## INTRODUCTION

IN a previous paper,<sup>1</sup> the normal vibrations of polyoxymethylene (POM),  $(-\text{CH}_2\text{O}-)_n$  and its deuteroderivative,  $(-\text{CD}_2\text{O}-)_n$ , were calculated. The POM molecule contains nine chemical units and five turns in the fiber identity period 17.3 Å, and has a dihedral symmetry, the internal rotation angle around the C-O bond being 77°23' (nearly *gauche*).<sup>2</sup> Trioxane is a cyclic trimer of the same chemical unit. Its molecular structure has been examined by the method of

x-ray<sup>3-5</sup> and electron<sup>6,7</sup> diffraction, infrared<sup>8</sup> and microwave<sup>9,10</sup> spectroscopy, and dipole-moment measurements.<sup>11,12</sup> The structure was found to be a chair form with alternate sequences of internal rotation angles 60° and -60°. The conformational difference between

<sup>3</sup> N. F. Moerman, *Rec. Trav. Chim.* **56**, 161 (1937).

<sup>4</sup> V. Busetti, G. Carazzolo, and M. Mammi, *Gazz. Chim. Ital.* **92**, 1362 (1962).

<sup>5</sup> V. Busetti, M. Mammi, and G. Carazzolo, *Z. Krist.* **119**, 310 (1963).

<sup>6</sup> S. Kimura and K. Aoki, *J. Chem. Soc. Japan, Pure Chem. Sec.* **72**, 169 (1951).

<sup>7</sup> W. Shand, *Acta Cryst.* **3**, 54 (1950).

<sup>8</sup> D. A. Ramsay, *Trans. Faraday Soc.* **44**, 289 (1948).

<sup>9</sup> E. Amble, *Phys. Rev.* **83**, 210 (1951).

<sup>10</sup> T. Oka, K. Tsuchiya, S. Iwata, and Y. Morino, *Bull. Chem. Soc. Japan* **37**, 4 (1964).

<sup>11</sup> A. A. Maryott and S. F. Acree, *J. Res. Natl. Bur. Std.* **33**, 71 (1944).

<sup>12</sup> B. A. Arbousow, *Bull. Soc. Chim. France* **1960**, 1311.

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<sup>1</sup> H. Tadokoro, M. Kobayashi, Y. Kawaguchi, A. Kobayashi, and S. Murahashi, *J. Chem. Phys.* **38**, 703 (1963).

<sup>2</sup> H. Tadokoro, T. Yasumoto, S. Murahashi, and I. Nitta, *J. Polymer Sci.* **44**, 266 (1960).