IONIZATION CROSS-SECTIONS OF ATOMS AND MOLECULES BY ELECTRON IMPACT

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ABSTRACT. Apparent ionization cross-sections of several atoms and molecules for 70 ev electrons have been measured with the help of a mass spectrometer. By introducing a simple correction an attempt has been made to improve the method of Otvos and Stevenson for the calculation of the ionization cross-sections of atoms and molecules. With this correction, the additivity postulate for the molecular ionization cross-sections appears to hold better.

INTRODUCTION

The knowledge of ionization cross-sections of atoms and molecules has various practical applications in problems of physics and astro-physics. This is of particular interest and importance in the analytical applications of mass spectrometry. The ionization cross-section is intimately related to the electronic structure of atoms and molecules. However, till now reliable data on the ionization cross-sections are very scanty. The earliest absolute measurements of the ionization cross-sections are those of Bleakney (1930), Smith (1930) and Tate and Smith (1932). More recently, Otvos and Stevenson (1956), to be subsequently referred to as O and S, and Lampe, Franklin and Field (1957) subsequently referred to as L.F. and F have used mass spectrometers to obtain the total cross-sections of a large number of atoms and molecules using 75 ev electrons as the ionizing agent in the source of the mass spectrometer. The agreement between the two sets of data is not quite satisfactory. The methods available at present for the calculation of the ionization cross-sections are at best approximate. By considering their own experimental data O and S have suggested that the molecular ionization cross-sections can be calculated as a purely constitutive property of the gaseous substance. This suggestion of O and S has been critically analysed and compared by L. F. and F with their own experimental data. They have arrived at the conclusion that the seeming agreement between O and S calculated and experimental values is a consequence of compensating errors and therefore reservations have been expressed regarding the validity of additivity postulate for calculating molecular ionization cross-sections. The present state of our knowledge of ionization cross-sections of atoms and molecules has been reviewed by Haissinsky (1961). It is clear that further independent experimental measurements are needed to resolve the discrepancies between various sets of data

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which will also help in formulating a better theoretical method for the calculation of molecular ionization cross-sections. With this end in view we have measured the ionization cross-sections of several atoms and molecules by bombarding them with 70 ev electrons at the source of our MS3 mass spectrometer (manufactured by Messrs Associated Electrical Industries Ltd., U.K.).

In the second half of the paper, attempt has been made to introduce a simple correction and thereby improve the method of calculation of molecular ionization cross-sections as suggested by O and S. With this correction the additivity postulate for molecular ionization cross-section appears to hold better.

E X P E R I M E N T A L

In a mass spectrometer if 'i' is the electron current and 'i^+' is the positive ion current, N the number density of the atoms and 'l' the path length of the electrons then Massey (1956)

$$i^+/i = NlQ_i^{app} \qquad \qquad \dots \quad (1)$$

where Q_i^{app} is the apparent ionization cross-section which may be written as

$$Q_i^{app} = Q_i^{(1)} + 2Q_i^{(2)} + 3Q_i^{(3)} + \dots \qquad \dots \quad (2)$$

where $Q_i^{(1)}$, $Q_i^{(2)}$ .... are the cross sections for single, double ... etc. ionization. For effusive flow, if we determine total ion current as a function of the reservoir pressure in the mass spectrometer, a straight line should be obtained by plotting the total ion current i^+ against reservoir pressure, with the slope proportional to the ionization cross-section. By taking the absolute ionization cross section of a substance from some other source (e.g. Smith, 1930 and Tate and Smith 1932) as standard, one can find the apparent ionization cross-section Q_i^{app} for any other substance.

Experimental measurements were made with the MS3 mass spectrometer which is a 90°-sector type instrument, with a tube radius of 4 in. The ion source was run with 2kv ion accelerating voltage, 70 ev electron accelerating voltage, 3V ion repeller voltage and $85\mu A$ trap current. Peaks were tuned by magnetic scanning and very small variation of the ion accelerating voltage. The gas reservoir of the mass spectrometer was slightly modified to include a McLeod gauge for measuring the reservoir pressure accurately. The gases He, Ne, A, Kr, Xe, N_2 and O_2 were supplied by Messrs British Oxygen Co., as spectroscopically pure.

The total ion current was determined by adding up the specific intensities of the ions in the resolved mass spectra. The total mass spectral sensitivity, however, has not been corrected for the mass discrimination effect as this is minimised to a large extent by employing magnetic scanning in our mass spectrometer and whatever discrimination still remains will be more pronounced in case of fragment ions

with large initial kinetic energies formed as a result of dissociation of molecules. Thus the effect of neglecting mass discrimination in calculating the relative total ionization cross-section from the total mass spectral sensitivity data can be considered to be minor especially in the case of monatomic gases. The absolute ionization cross section of argon at 70 ev which is used as standard is taken to be 3.58×10^{-16} cm^2, which is the value of ionization efficiency of argon at 70 ev (12.75 positive ions/cm path/mm pressure at 0°C) as reported by Smith (1930) multiplied by the conversion factor 2.81×10^{-17} to get the cross section in cm^2 unit. The results thus obtained are shown in Table I. For the sake of comparison we have also given the value of 75 ev as obtained by O and S and L. F. and F with a slight correction. The value of the ionization cross section of argon at 75 ev has been taken as 3.62×10^{-16} cm^2 as reported by Smith (1930) and not 3.52×10^{-16} cm^2. The ionization cross section of other atoms and molecules have increased slightly due to this change in the value of the standard.

TABLE I

Ionization Cross Sections of Atoms and Molecules

$(Q_i \times 10^{-16}$ cm$^2)$

Substance	70 ev electrons		75 ev electrons		
	This work	Absolute measurement	Absolute measurements	O & S (1956) Expt.	L.F. & F. (1957) Expt.
He	0.309	0.312[a]	0.322[c]	0.299	0.397
Ne	0.553	0.593[a]	0.622[c]	0.579	0.633
A	3.58	3.58[a]	3.62[c]	3.62	3.62
Kr	5.17		—	5.55	5.33
Xe	6.68	–	.	—	7.53
N$_2$	2.47	2.67[b]	2.74[d]	2.72	2.96
O$_2$	2.51	2.63[b]	2.70[d]	2.34	2.58

a Smith (1930)

b Massey, H.S.W. and Burhop, E.A., *Electronic and Ionic Impact Phenomena*, p. 265, Oxford University Press, Oxford, 1952.

c Interpolated values from Smith (1930).

d Interpolated values from Tate & Smith (1932).

It may be seen that the agreement between our measurements and those of Tate and Smith (1932) is fairly good. For krypton and xenon no data are available for 70 ev electrons. It is possible that due to the presence of various electrostatic fields and secondary electrons in the source of the mass spectrometer

some uncertainty will occur in the determination of the ionization cross section by this method.

THEORETICAL CALCULATION OF THE IONIZATION CROSS-SECTIONS

Bethe's (1930) formula for the total ionization cross-section may be written as

$$Q_{nl}{}^i = \frac{2\pi e^4}{mv^2} \cdot \frac{c_{nl}}{E_{nl}} \cdot Z_{nl} \log\left(\frac{2mv^2}{C_{nl}}\right) \qquad \ldots \quad (3)$$

where e is the charge, m the mass and V is the velocity of the electrons. E_{nl} is the ionization potential and Z_{nl} the nuclear charge corresponding to the nl shell. C_{nl} is an energy of the order of the ionization potential and c_{nl} is given by

$$c_{nl} = (Z_{eff}{}^2/n^2 a_0{}^2) \int |x_{nl,k}|^2 dk. \qquad \ldots \quad (4)$$

$|x_{nl,k}|^2$ is one-third the mean square radius of the electron and dk corresponds to a range of energy such that k lies between k and $k+dk$. K is related to E_k, the energy of the level, by the relation,

$$E_k = k^2 h^2/8\pi^2 m. \qquad \ldots \quad (5)$$

However, it is not possible to apply Eq. (3) satisfactorily to atoms more complex than helium. In order to calculate the ionization cross-sections of atoms, O and S have modified Bethe's (1930) formula. According to the modified method, the ionization cross-section is calculated as the sum of the outer or valence electrons weighted by the mean square radii of those electron as calculated from hydrogenlike wave functions.

In order to calculate molecular ionization cross-sections, O and S have used the additivity postulate according to which the ionization cross-section is the sum of the cross-sections of the constituent atoms. In a subsequent publication L.F. and F have analysed their own data on the ionization cross-sections of a large number of atoms and molecules as well as those of O and S. Their analysis shows that the agreement between the experimental and the theoretical values of the total ionization cross-sections calculated by the O and S method is not satisfactory and the additivity postulate does not hold well.

A look at Table II shows that for the atoms the difference between the calculated and the experimental values of the total ionization cross-section increases with the increase of the atomic number Z. It has also been pointed out by O and S that due to the method of calculation, the values of the mean-square radius become too large for the outer or valence electrons for higher Z values. This error in calculating the mean-square radii results in too high values of the ionization cross-sections calculated by the O and S method,

TABLE II

Experimental and calculated atomic ionization cross sections,
($Q_i \times 10^{16}$ cm^2)

Substance	Z	O & S (1956) (Expt.)	O & S (1956) (Calc.)	Deviation
He	2	0.299	0.347	+0.048
Ne	10	0.579	0.875	+0.296
A	18	3.62	5.45	+1.83
Kr	36	5.55	8.70	+3.15
Xe	54	7.53[a]	12.1	+4.57

[a]Expt. value of L.F. & F (1957)

In order to test the validity of the additivity postulate for calculating molecular ionization cross-sections, it is essential to have correct atomic ionization cross-sections. For this we assume the difference between the calculated and the experimental values of the atomic ionization cross-sections to be function of Z only i.e.,

$$Q_{i_{corr}} = Q_{i_{calc.}} - C(Z) \tag{6}$$

where $C(Z)$ is the correction factor.

In Fig. 1, we have plotted the difference between the calculated and the experimental values of O and S of the total ionization cross-section ($Q_{i_{calc}}$
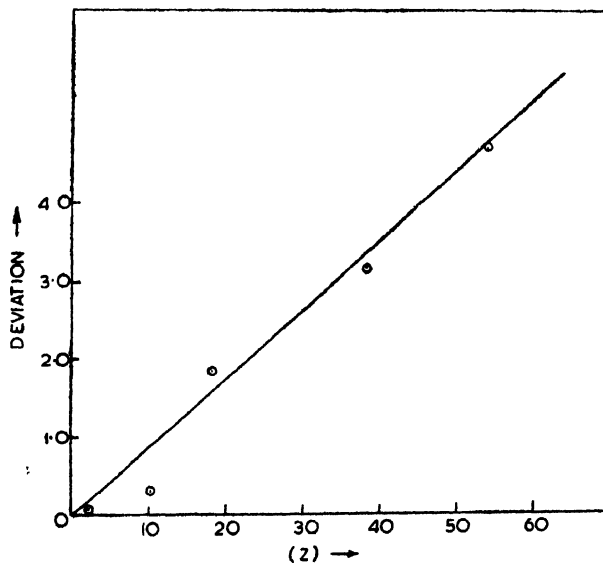

Fig. 1. Difference of the O & S (1956) calculated and experimental values of the total ionization cross-section, as a function of Z.

$Q_{i_{expt}}$) as a function of Z. There is some uncertainty in the calculated values for Ne, consequently, we have considered only the point for He, A, Kr and Xe. It will be seen that the plot is a straight line passing through the origin and therefore $C(Z)$ may be represented as

$$C(Z) = AZ \qquad \qquad \dots \ (7)$$

with $A = 0.09$.

Although at present it is not possible to explain quantitatively the increase of the correction factor $C(Z)$ with increasing Z, a qualitative explanation may however, be given. The expression for the mean square-radius of the electron (n, l) may be written as.

$$\bar{r}^2_{nl} = a^2_0 \, n'^4 (Z - S_{nl})^{-2} - 1 + \tfrac{3}{2} \left(1 - \left\{ \frac{l(l+1) - 1/3}{n'^2} \right\} \right). \qquad \dots \ (8)$$

where a_0 is the Bohr radius, n' the effective quantum number and S_{nl} the Slater's screening constant. In the ionization process the screening is complete only when the energy of the ejected electron is less than the energy of the scattered electron, Bates (1962). As the atomic number Z increases, the ionization potential of the outermost electrons decreases with a consequent increase of energy of the ejected electron. Hence, the probability of the energy of the ejected electron to be higher than the energy of the scattered electron increases with increasing Z. This means that the values of S_{nl} should be taken less than Slater's value as Z increases, which will result in lower values of $\bar{r}^2_{nl}$. In the O and S method the effect of incomplete screening has not been considered in calculating the value of $\bar{r}^2_{nl}$, and hence difference between the calculated and experimental values of ionization cross-section increases with increasing Z. Another probable source of error in the method of O and S as pointed by Haisinsky (1961) is their association of the ionization cross-section Q_i with $\Sigma <r^2>$. Actually $\Sigma <r^2>$ is proportional to the sum of the ionization cross-sections and the excitation cross-section Qe, i.e.

$$Q_i + Q_e \, \alpha \Sigma <r^2>$$

or

$$Q_i = K \Sigma <r^2> \cdot Q_e$$

Thus the success of $\Sigma <r^2>$ in correlating the observed ionization cross-sections depends on the constancy of the proportion of inelastic collision which results in excitation. If the proportion of Q_e increases with inceasing Z the difference between the experimental and the values of Q_i as calculated by the O and S method will also increase.

By using Eqs. (6) and (7) it is possible to correct the calculated values of the atomic ionization cross-sections arrived at by O and S method. We have then calculated the molecular ionization cross-sections as the sum of the corrected

constituent atomic ionization cross-sections. The results for some inorganic and hydrocarbon molecules are shown in Table III. It may be seen that the agreement between the experimental values of O and S and their calculated values after correction is reasonably good thereby supporting the view that the total ionization cross-section of molecules are constitutive molecular properties. This is also in agreement with the quantum mechanical calculations of Watanabe (1961), who showed that for impinging electrons having energy greater than 80 ev the additivity postulate should hold within 20%.

TABLE III

Molecular ionization cross-sections (Q_i)

$$Q_i(H_2) = 1$$

Molecule	O & S (1956) Calc.	O & S (1956) Expt.	O & S (1956) corrected calc.
N_2	3.84	2.64	2.58
O_2	3.29	2.20	1.85
CO	3.73	2.66	2.47
CO_2	5.37	3.46	3.39
H_2S	7.40	4.23	5.78
HCl	6.40	3.68	4.78
CH_4	4.08	2 84	3 18
C_2H_4	6.16	4 17	4.72
C_2H_6	7.15	4 91	5.53
C_3H_6	9.24	6.20	7.08
C_3H_8	10.2	6.85	7.86
$i-C_4H_8$	12.3	8.37	9.42
$n-C_4H_{10}$	13.3	8.91	10.24
$i-C_5H_{10}$	15.4	10.1	11.80
$n-C_5H_{12}$	16.4	11.1	12.62
C_6H_6	15.5	10.8	11.72
$Cyclo-C_6H_{12}$	18.5	11.5	14.18
$n-C_6H_{14}$	19.5	12.8	15.00
CH_3Cl	9.48	5.26	7.14

In conclusion we may state that reasonably good values of the molecular ionization cross-sections can be obtained quite simply by applying the correction suggested by us to the values obtained by O and S method and using additivity postulate.

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