ELSEVIER

International Journal of Mass Spectrometry and Ion Processes 171 (1997) L1–L5

International Journal of Mass Spectrometry and Ion Processes

Short Communication

# Electron impact ionisation of molecules at high energies

Vandana Saksena[a], M.S. Kushwaha[a], S.P. Khare[b,*]

[a]*Department of Applied Physics, Institute of Technology and Science, Gwalior—474 005, India*
[b]*Department of Physics, Chaudhary Charan Singh University, Meerut—250 004, India*

Received 26 November 1996; accepted 19 January 1997

Ionisation cross-sections of molecules find their applications in a number of fields [1]. However, their theoretical evaluation is a difficult task. At low impact energy (less than about 50 eV) one is required to solve a set of coupled integro-differential equations. In an ionisation process the final channel contains two free electrons and the molecules are multi-centred objects. Hence a solution of the coupled integro-differential equations becomes extremely difficult. At intermediate energies at least the distortion of the wave function of the incident electron is to be considered. Thus along with the first Born, higher terms of the Born series are to be included. At impact energy greater than about ten times the ionisation potential, the first Born approximation (FBA) is expected to be valid. This approximation requires the continuum generalised oscillator strengths (CGOS). Due to the multi-centred nature of the initial and final wave functions of the molecule, the generation of the CGOS becomes quite difficult. Hence there seems to be no calculation of the molecular ionisation cross-sections even in the FBA. Most of the theoretical calculations have combined the contributions of the soft collisions (given by the Bethe cross-section) with that of the hard collisions (given by the Mott cross-sections) in some suitable manner to obtain the total ionisation cross-sections [2–4]. The experimental cross-sections are analysed with the help of the Fano plot obtained from the Bethe formula for the ionisation cross-sections [5].

In the present investigation we have started from the FBA, including relativistic corrections the longitudinal interaction through the static, unretarded Coulomb field and the transverse interaction through emission and the reabsorption of the virtual photons [6]. In this approximation the total ionisation cross-section $\sigma_T$ of a molecule due to the impact of an electron of velocity $v$ and kinetic energy $E$ is given by [6]

$$\sigma_T = \frac{8\pi a_0^2 R}{mv^2}\left[\int_I^E \int_{\ln Q_{min}}^{\ln Q_{max}} \frac{R}{W}\frac{df(W,Q)}{dW} d(\ln Q) dW - M^2\{\ln(1-\beta^2)+\beta^2\}\right] \quad (1)$$

where $m$, $a_0$, $R$, $I$, $W$ and $Q$ are the rest mass of the electron, the Bohr radius, the Rydberg energy, the ionisation potential energy, the energy lost by the incident electron in the ionisation process and the recoil energy of the residual ion, respectively. $\beta$ is the ratio of the velocity $v$ and the velocity of light $c$ and $(df(W,Q))/(dW)$ is the continuum generalised oscillator strength (CGOS). For ionisation $M^2$ is equal to the total dipole matrix squared measured in the units of $a_0^2$.

* Corresponding author.


*PII* S0168-1176(97)00016-5

It is also given by [5]

$$M^2 = \int_I^\infty \frac{R}{W}\frac{df(W,0)}{dW}dW \quad (2)$$

where $(df(W,0))/(dW)$ is the continuum optical oscillator strength (CGOS). At the relativistic velocities $Q_{max,min}$ are given by

$$Q_{max,min} = \frac{1}{2mc^2}(\{E(E+2mc^2)\}^{1/2} \pm \{(E-W)(E-W+2mc^2)\}^{1/2})^2 \quad (3)$$

In Eq. (1) the term under the integral is due to the longitudinal interaction and the second term is due to the transverse interaction [6]. The latter term is of significance only at ultra relativistic velocities. The occurrence of the CGOS in this equation makes the evaluation of $\sigma_T$ for the molecules difficult.

According to the semi-phenomenological model of Mayol and Salvat [7] the CGOS is approximately given by

$$\frac{df(W,Q)}{dW} = \frac{df(W,0)}{dW}\theta(W-Q) + h(Q)\delta(W-Q) \quad (4)$$

where $\theta$ and $\delta$ are the step function and the Dirac delta function, respectively, and $h(Q)$ is equal to the integral of $df(W, 0)dW$ over $W$ from $I$ to $Q$. Putting Eq. (4) in Eq. (1) and integrating over $Q$ we get

$$\sigma_T = \frac{8\pi a_0^2 R^2}{mv^2}\left[\int_I^E \left\{\frac{1}{W}\frac{df(W,0)}{dW}\ln\left(\frac{W}{Q_{min}}\right) + \frac{h(W)}{W^2}\right\}dW - \frac{M^2}{R}\left\{\ln(1-\beta^2)+\beta^2\right\}\right] \quad (5)$$

where $h(W)$ is again equal to the integral of $(df(W', 0))/(dW')$ over $W'$ but from $I$ to $W$. Now the evaluation of $\sigma_T$ from Eq. (5) requires only COOS. Using the experimental and the theoretical values of COOS [8,9], the total ionisation cross-sections for $H_2$, $N_2$, $O_2$ and $H_2O$ due to electron impact in the energy range of 1 keV to 3 MeV are calculated.

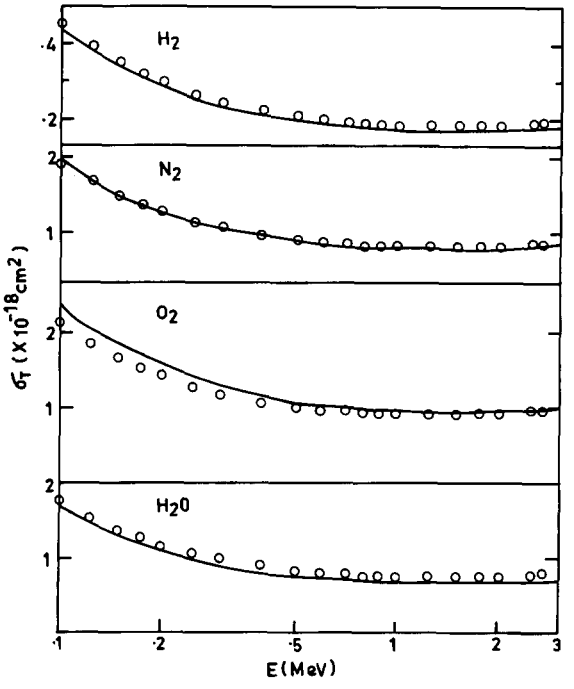


Fig. 1. Total ionisation cross-sections of $H_2$, $N_2$, $O_2$ and $H_2O$ due to electron impact in the energy range 0.1 to 3 MeV. Solid curves show the present results and open circles are the experimental data of Rieke and Prepejchal [10].

Fig. 1 shows $\sigma_T$ in the energy range of 0.1 to 3 MeV. It is found that the relativistic effect increases $\sigma_T$ by a factor of about 1.2 at 0.1 MeV but at 3 MeV the increase in $\sigma_T$ due to this effect is by a factor of about 9. As expected the contribution of the transverse interaction to $\sigma_T$ at 0.1 MeV is small (less than 0.5%) but it increases with $E$ and it is about 20% at 3 MeV. Due to this interaction $\sigma_T$ is found to increase with $E$ for $E$ greater than about 1.5 MeV.

The figure also shows the experimental cross-sections $\sigma_{RP}$ of Reike and Prepejchal [10], available in the energy range 0.1 to 2.7 MeV. They have expressed their cross-sections in terms of parameters $C_{RP}$ and $M^2$ (see Eq. (3) of their paper). A nice agreement between $\sigma_T$ and $\sigma_{RP}$ is noticed for $N_2$ over the whole energy range. For $H_2$ and $H_2O$ $\sigma_T$ are slightly less than $\sigma_{RP}$ but for $O_2$ the situation is reversed. However, the difference between $\sigma_T$ and $\sigma_{RP}$ is less than

about 10%. Thus the agreement between the theory and the experiment is good.

At present no experimental cross-section seems to be available in the energy range of 20 keV to 0.1 MeV. Hence $\sigma_T$ in the above energy range is not presented.

Table 1 shows ionisation cross-sections in the energy range 1.2 to 20 keV. It is evident from the table that $\sigma_T$ are greater than the experimental cross-sections of Schram et al. [11] for $H_2$, $N_2$ and $O_2$ and those of Schutten et al. [12] for $H_2O$ over the whole energy range.

However, the differences between the theoretical and experimental cross-sections are less than 3% for $H_2$, 10% for $N_2$, 13% for $O_2$ and 15% for $H_2O$. For $H_2$ the semi-empirical cross-section of van Wingerden et al. [13] available at 2 keV is about 15% higher than $\sigma_T$. For $H_2O$ $\sigma_T$ are slightly lower than the theoretical cross-sections of Kim and Rudd [4] and the experimental data of Bolorizadeh and Rudd [14].

At 1 keV a number of experimental cross-sections are available. They are shown in Table 2. At this energy $\sigma_T$ for $N_2$ and $O_2$ are in good agreement with $\sigma_{RE}$, the measured cross-sections of Rapp and Englander-Golden (having experimental errors equal to $\pm$ 7% for $N_2$ and $\pm$10% for $O_2$) [15], but are higher than those given by Schram et al. [11]. This is a correct trend, because according to de Heer and Inokuti [5] $\sigma_{RE}$ for $H_2$, $O_2$ and $N_2$ (measured up to 1 keV) are most likely right within stated limits of errors but the cross-sections of Schram et al. are too low. At 1 keV the cross-section of Krishnakumar and Srivastava [16] for $O_2$ is in nice agreement with $\sigma_{RE}$ but for $N_2$ their cross-section is about 14% higher than $\sigma_{RE}$. For $H_2$ the present $\sigma_T$ is in good agreement with the cross-section of Schram et al. [11] even at 1 keV but is less than $\sigma_{RE}$ (with experimental error equal to $\pm$ 4.5%), the semi-empirical cross-section [13] and the theoretical cross-section [4] by about 20%. Thus for this molecule the theory underestimates the cross-sections. The reason for this underestimation is not clear at present. Experimental determination of the ionisation cross-sections for

Table 1
Total ionisation cross-sections in units of $10^{-18}$ cm$^2$

| $E$ (in keV) | $H_2$ | | $N_2$ | | $O_2$ | | $H_2O$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | P | Sr | P | Sr | P | Sr | P | Su | KR | BR |
| 1.2 | 17.2 | 16.8 | 75.0 | 68.0 | 91.4 | 79.1 | 66.0 | – | – | 70 |
| 1.4 | 15.1 | 14.9 | 67.5 | 60.7 | 80.4 | 70.6 | 58.0 | – | 62 | 58[a] |
| 1.6 | 13.5 | 13.2 | 60.0 | 54.7 | 71.9 | 63.4 | 51.9 | – | – | – |
| 1.8 | 12.3 | 12.0 | 55.0 | 49.9 | 65.2 | 57.7 | 47.1 | – | – | – |
| 2.0 | 11.2 | 10.9<br>13.3[b] | 50.1 | 45.9 | 60.0 | 53.1 | 43.1 | 37.5 | 47 | 44 |
| 3.0 | 7.97 | 7.81 | 35.6 | 32.8 | 42.6 | 38.6 | 30.6 | 26.1 | 34 | – |
| 4.0 | 6.24 | 6.10 | 27.9 | 26.2 | 33.4 | 30.5 | 24.0 | 22.0 | 28 | – |
| 5.0 | 5.16 | 5.04 | 23.1 | 21.8 | 27.7 | 25.7 | 19.8 | 18.3 | 21 | – |
| 6.0 | 4.41 | 4.34 | 19.8 | 18.7 | 23.7 | 22.0 | 17.0 | 16.0 | 19 | – |
| 8.0 | 3.44 | 3.39 | 15.5 | 14.9 | 18.5 | 17.5 | 13.3 | 12.3 | 15 | – |
| 10.0 | 2.84 | 2.80 | 12.8 | 12.3 | 15.3 | 14.6 | 10.9 | 10.1 | 11 | – |
| 12.0 | 2.43 | 2.39 | 10.9 | 10.6 | 13.1 | 12.5 | 9.34 | 8.8 | – | – |
| 14.0 | 2.13 | 2.11 | 9.57 | 9.33 | 11.5 | 11.0 | 8.19 | 7.8 | 8 | – |
| 16.0 | 1.90 | 1.88 | 8.55 | 8.39 | 10.2 | 9.95 | 7.31 | 6.4 | – | – |
| 18.0 | 1.72 | 1.71 | 7.74 | 7.70 | 9.26 | 9.13 | 6.62 | 5.8 | – | – |
| 20.0 | 1.57 | 1.58 | 7.08 | 7.03 | 8.48 | 8.42 | 6.06 | 5.4 | 5.9 | – |

[a] At $E$ = 1.5 keV.
[b] Semi-empirical value from [13].
The sources of the above cross-sections are P, present; Sr, [11]; Su, [12]; KR, [4] (the values are read from their Fig. 11); BR, [14].

Table 2
Total ionisation cross-sections in the units of $10^{-18}$ cm$^2$ at $E$ = 1 keV

| | Present | [4] | [11] | [12] | [13] | [14] | [15] | [16] | [17] |
|---|---|---|---|---|---|---|---|---|---|
| $H_2$ | 20.2 | 24[a] | 19.6 | – | 23.9 | – | 24.0 | – | – |
| $N_2$ | 89.1 | – | 78.1 | – | – | – | 92.3 | 107.7 | – |
| $O_2$ | 106 | – | 90.6 | – | – | – | 105 | 105.4 | – |
| $H_2O$ | 76.7 | 79[a] | – | 62.2 | – | 79 | – | – | 102.6 |

[a] Read from the Figs. 7 and 11 of [4].

$H_2O$ is difficult because of the uncertainty involved in the absolute measurement of the pressure. At 1 keV $\sigma_T$ of $H_2O$ is lower than the cross-section of Rao et al. [17] by about 25%, higher than that of Schutten et al. [12] by about 20% but shows nice agreement with the data of Bolorizadeh and the cross-section of Kim and Rudd [4]. The cross-sections of Khare and Meath [2] (not shown) are also in good agreement with $\sigma_T$. But their method requires parameters $C_i$ and $\epsilon_{0i}$ in addition to the CGOS as input (see Eq. (5) of their paper) and an evaluation of $C_i$ requires the CGOS [5]. Khare and Meath took $C_i$ to be same as derived from the experimental total ionisation cross-sections measured by Reike and Prepejchal [10] at very high energies and took $\epsilon_{0i}$ equal to 70 eV.

Considering the differences between $\sigma_T$ and the various experimental cross-sections along with their percentage of errors, it may be stated that between 1 and 5 keV the present method is expected to yield cross-sections with an accuracy better than 15%. Further investigations are needed for a more definite statement. At present no sum rule for the ionisation-cross sections is available to access the accuracy of the calculated and the measured cross-sections.

Total ionisation cross-sections for energies between threshold of ionisation and 1 keV are available for a good number of molecules. De Heer and Inokuti [5] have tabulated the molecules for which ionisation cross-sections were measured between 1966 and 1982. They have also given a table showing the data centres that treat ionisation cross-sections. Mark [18] has listed di- and tri-atomic molecules whose ionisation cross-sections are available. For some of the molecules ionisation cross-sections are tabulated by Keiffer [19]. An up-to-date table of the ionisation cross-sections is desirable.

For the molecule investigated in this paper the FBA is expected to be valid for $E > 150$ eV (more than ten times the ionisation potential). However, we have noticed that the present method overestimates the cross-sections even at a few hundred electron volts. This indicates either the failure of Eq. (4) or the FBA itself.

Finally we conclude that the present formalism is successful in the calculation of $\sigma_T$ for the molecules for the impact energies greater than about 1 keV. This indicates that Eq. (4) is a reasonable approximation and a knowledge of the CGOS or $C_i$ is not essential for a successful evaluation of the ionisation cross-sections. To the best of our knowledge this is the first calculation of the molecular ionisation cross-sections covering such a wide energy range with only COOS and $I$ as inputs.

An extension of the present approach to other molecules, to the partial ionisation and to the low values of $E$ is of interest.

## Acknowledgements

Financial assistance to two of us (VS and SPK) by the Council of Scientific and Industrial Research, India is gratefully acknowledged. Thanks are due to Dr R.D. Gupta for his encouragement to VS and MSK.

## References


[1] W. Lindinger, F. Howorka, J.M. Shull, A.V. Phelps, E.C. Zipf, Y.K. Kim, J.H. Futrell, in: T.D. Mark, G.H. Dunn (Eds.), Electron Impact Ionization, Springer, Berlin, 1985.

[2] S.P. Khare, W.J. Meath, J. Phys. B 20 (1987) 2101.

[3] J.H. Miller, W.E. Wilson, S.T. Manson, M.E. Rudd, J. Chem. Phys. 86 (1987) 157.

[4] Y.K. Kim, M.E. Rudd, Phys. Rev. A 50 (1994) 3954.

[5] F.J. de Heer, M. Inokuti, in: T.D. Mark, G.H. Dunn (Eds.), Electron Impact Ionization Springer, Berlin, 1985.

[6] U. Fano, Ann. Rev. Nucl. Sci. 13 (1963) 1.

[7] R. Mayol, F. Salvat, J. Phys. B 23 (1990) 2117.

[8] L.W. Gallagher, C.E. Brion, J.A.R. Samson, P.W. Langhoff, J. Phys. Chem. Ref. Data 17 (1988) 9.

[9] G.D. Zeiss, W.J. Meath, J.C.F. MacDonald, D.J. Dawson, Radiat. Res. 63 (1975) 64; Can. J. Phys. 55 (1977) 2080.

[10] F.F. Rieke, W. Prepejchal, Phys. Rev. A 6 (1972) 1507.

[11] B.L. Schram, F.J. de Heer, M.J. van der Wiel, J. Kistemaker, Physica, 31 (1965) 94.

[12] J. Schutten, F.J. de Heer, H.R. Moustafa, A.J.H. Boerboom, J. Kistemaker, J. Chem. Phys. 44 (1966) 3924.

[13] B. van Wingerden, R.W. Wagenaar, F.J. de Heer, J. Phys. B 13 (1980) 3481.

[14] M.A. Bolorizadeh, M.E. Rudd, Phys. Rev. A 33 (1986) 882.

[15] D. Rapp, P. Englander-Golden, J. Chem. Phys. 43 (1965) 1464.

[16] E. Krishnakumar, S.K. Srivastava, J. Phys. B 23 (1990) 1893; Int. J. Mass Spectrum. Ion Processes 113 (1992) 1.

[17] M.V.V.S. Rao, I. Iga, S.K. Srivastava, J. Geo. Res. Planet. 100 (1995) 421.

[18] T.D. Mark, in: T.D. Mark, G.H. Dunn (Eds.), Electron Impact Ionization, Springer, Berlin, 1985.

[19] L.J. Keiffer, JILA Inf. Cent. Rep. No. 13, 1973.