International Journal of Mass Spectrometry 205 (2001) 1–6

Free Electron Molecule Interactions

Total electron-ionization cross sections of the NO_2 molecule

D. Lukić, G. Josifov, M.V. Kurepa*

Institute of Physics, P.O. Box 68, 11081 Beograd, Yugoslavia

Received 15 November 1999; accepted 22 February 2000

Abstract

Total cross sections of the NO_2 molecule by electron impact have been measured in the incident electron energy range from threshold to 1000 eV. To the author's knowledge this is the first experimental result of its kind. Cross section data from the experiment have been compared with recently calculated values. (Int J Mass Spectrom 205 (2001) 1–6) © 2001 Elsevier Science B.V.

Keywords: Ionization; Electron impact; Nitrogen dioxide

1. Introduction

Nitrogen dioxide (NO_2) is one of those molecules that appear in car and truck exhaust gases. Through reaction with water from the air, the HNO_3 acid is formed, which is highly chemically active, causing damage to metal constructions such as bridges, posts, etc.

The recent paper of Kim et al. [1] inspired us to measure the total ionization cross sections of the NO_2 molecule. They presented calculations for a few molecules using the BEB (binary–encounter–Bethe) model, which combines the binary encounter theory and the Bethe theory for electron impact ionization. Among others, they calculated total ionization cross sections for the NO_2 molecule, and stated that there was no experimental measurement available to which they could compare their calculations.

There are rather scarce data on electron impact ionization of the NO_2 molecule. Kandel [2,3] determined the appearance potential of NO_2^+ and NO^+ ions; Collin and Lossing [4] determined the appearance potentials of NO_2^+, O^+, and NO^+; as did Kiser and Hasatsine [5]. Newton and Sciamanna [6] investigated the dissociation of NO_2^+ and NO^+ ions by electron impact in a mass spectrometer. Franklin et al. [7] determined only the appearance potential of the NO_2^+ parent ion.

Stephan et al. [8] are the only ones so far, to the authors knowledge, to determine partial ionization cross sections. They measured formation of NO_2^+ and NO_2^{2+} ions, pointing out that they were able to analyze and collect in the mass spectrometer only these ions because they have, at the instance of formation, no excess kinetic energy.

* Corresponding author.

Dedicated to Professor Aleksandar Stamatovic on the occasion of his 60th birthday.

1387-3806/01/$20.00 © 2001 Elsevier Science B.V. All rights reserved
PII S1387-3806(00)00208-6

2. Experimental

The total ionization cross sections were measured using a parallel plate ionization chamber, basically the same as that described in detail by Kurepa et al. [9]. The interaction chamber ion collection part was the same, except that in front of the parallel plate assembly and behind it three pairs of split electrodes were introduced with decreasing gaps toward the center of the interaction chamber. This alteration was added in order to reduce the inhomogeneity of the electric field, as seen by the electron beam while entering and leaving the ion collection electrode region.

A second improvement made recently was the addition of a new eighth segment solenoid with a different number of winding, calculated and made following the approach of Overshott and Smith [10]. The magnetic field of the solenoid was carefully measured (Josifov et al. [11]). This increased the length of the homogeneous magnetic field inside which the trochoidal electron monochromator (Stamatović and Schulz [12]), the parallel plate interaction chamber with the three electron guard split-electrodes, and the primary electron beam collector are housed. The consequence of this was that the electron beam intensity could be kept constant in a very wide energy range.

Absolute target gas pressures were determined by a capacitance manometer (MKS, Model 170-6M) and a rotating ball manometer (MKS, Model SRG-2), both calibrated by the manufacturer, that claims the exact pressure values to be known within an error of $\pm 2\%$. Relative variations of the gas pressure were monitored by an ionization gauge (Granville Phillips, Model 307 Vacuum Gauge Controller). The gas purity was checked by a quadrupole mass filter (A.I.G., 50).

Temperature of the target gas was measured and monitored inside the interaction chamber by using a thermocouple thermometer, to within ± 0.5 K.

The whole apparatus was thoroughly calibrated with nitrogen (N_2) as a target gas before and after the final cross section measurement of NO_2. The reason for choosing nitrogen was that its cross sections are well known from accurate measurements by Rapp and Englander–Golden [13], Halas and Adamczyk [14], and Durić et al. [15]. That was corroborated by recent measurements of Josifov et al. [16] obtained with the apparatus used in the present experiment. Values agreed within $\pm 2\%$.

Cross section values have been determined in the energy range from threshold up to 1000 [eV], with a relative error of $\pm 5\%$.

3. Experimental results

Experimentally obtained total ionization cross sections are given numerically in Table 1, and presented graphically as a log–log diagram in Fig. 1. In the figure partial ionization cross section data for the formation of NO_2^+ ions by Stephan et al. [8] are also given for comparison. They state that in mass spectra, at 100 eV electron incident energy, the NO_2^+ ion contributes some 40% to the total ion signal, and that contributions of NO^+ and O^+ are approximately 10% and 2%, respectively. The diagrams in Fig. 2 of their paper certainly show that ion beams of fragment ions NO^+ and O^+ are broad when swept across the mass spectrometer entrance slit, proving that they have appreciable kinetic energies that prevent their total collection and represent their partial ionization cross sections. The authors are not aware of any systematic experiment reporting ion energy and angular distributions from dissociative ionization collisions of the NO_2 molecule, which could shed some more light on details of these processes.

Still, the total ionization cross section at 100 eV of $(3.80 \pm 0.20) \cdot 10^{-20}$ m^2, as measured in the present experiment, and the value of $6.25 \cdot 10^{-21}$ m^2 expected by the prediction of Stephan et al. [8], differ by about a factor of six. This difference is difficult to explain.

4. Calculated cross sections

In order to compare our experimentally obtained total ionization cross sections with some calculations, we chose empirical relations basically derived by Gryzinski [17] in the form

Table 1
Total ionization cross sections of the NO_2 molecule by electron impact, in units of 10^{-20} (m^2)

ϵ_0/(eV)	$\sigma_{i,\mathrm{tot}}$/ (10^{-20} m^2)	ϵ_0/(eV)	$\sigma_{i,\mathrm{tot}}$/ (10^{-20} m^2)	ϵ_0/(eV)	$\sigma_{i,\mathrm{tot}}$/ (10^{-20} m^2)
10	0.009	72	3.55	185	3.43
12	0.035	74	3.58	190	3.40
14	0.088	76	3.62	195	3.37
16	0.175	78	3.64	200	3.34
18	0.294	80	3.67	225	3.19
20	0.440	82	3.69	250	3.05
22	0.607	84	3.71	275	2.91
24	0.788	86	3.73	300	2.79
26	0.976	88	3.74	325	2.68
28	1.11	90	3.76	350	2.57
30	1.35	92	3.77	375	2.48
32	1.579	94	3.78	400	2.39
34	1.74	96	3.78	425	2.30
36	1.91	98	3.79	450	2.23
38	2.07	100	3.806	457	2.15
40	2.22	105	3.80	500	2.09
42	2.36	110	3.80	525	2.02
44	2.49	115	3.79	550	1.96
46	2.62	120	3.78	575	1.91
48	2.73	125	3.76	600	1.86
50	2.83	130	3.74	700	1.70
52	2.93	135	3.72	800	1.56
54	3.02	140	3.70	900	1.46
56	3.10	145	3.67	1000	1.35
58	3.18	150	3.65		
60	3.25	155	3.62		
62	3.31	160	3.59		
64	3.37	165	3.56		
66	3.42	170	3.53		
68	3.47	175	3.50		
70	3.51	180	3.47		

$$\sigma_{i,\mathrm{tot},G}(\epsilon) = \sum_n 4\pi a_0^2\, \xi_n \left[\frac{\mathrm{E}_i(\mathrm{H})}{\mathrm{E}_{i,n}}\right]^2 f(u) \qquad (1)$$

where $\mathrm{E}_i(\mathrm{H})$ and $\mathrm{E}_{i,n}$ are energies for ionization of the hydrogen atom and the electron in the observed atom in nth subshell (binding energy), respectively. ξ_n is the number of equivalent electrons in the nth subshell, a_0 is the Bohr radius, and the function $f(u)$ is defined as

$$f(u) = \frac{1}{u}\left[\frac{u-1}{u+1}\right]^{3/2}\left\{1+\frac{2}{3}\left[1-\frac{1}{2u}\right]\ln\left[2,7 + (u-1)^{1/2}\right]\right\} \qquad (2)$$

u being the incident electron energy E_0 normalized versus the ionization energy of the respective quantum state from which the electron is rejected

$$u = \mathrm{E}_0/\mathrm{E}_{i,n} \qquad (3)$$

For comparison, cross section values calculated by Kim et al. [1] were used. Their results were obtained using the equation

$$\sigma_{\mathrm{BEB}} = \frac{S}{u+v+1}\left\{\frac{\ln(u)}{2}\left(1-\frac{1}{u^2}\right)+1-\frac{1}{u} - \frac{\ln(u)}{u+1}\right\} \qquad (4)$$

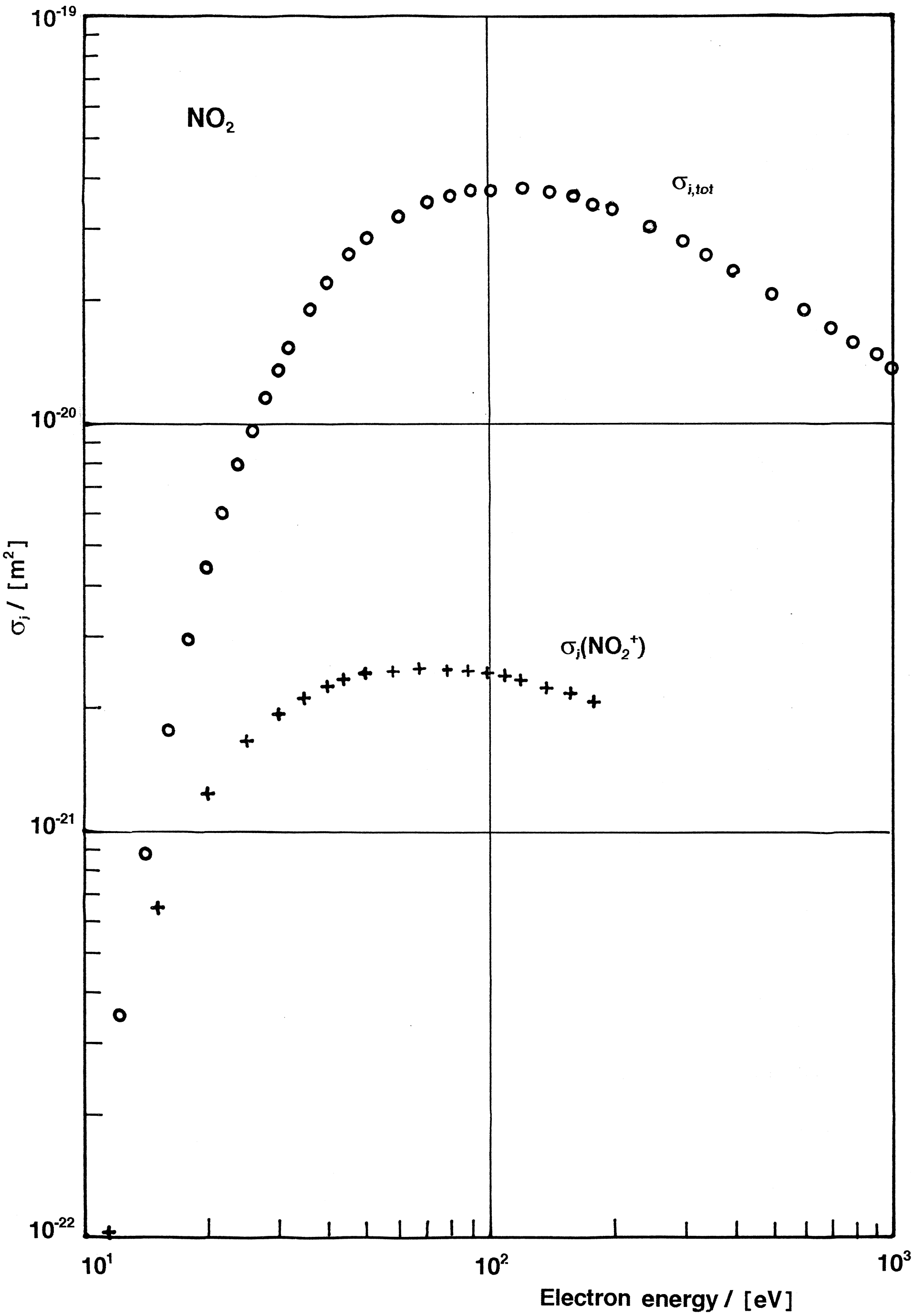

Fig. 1. Circles are present values of the NO_2 molecule electron impact total ionization cross sections; plus signs are partial ionization cross sections for the formation of the NO_2^+ parent ions by Stephan et al. [8].

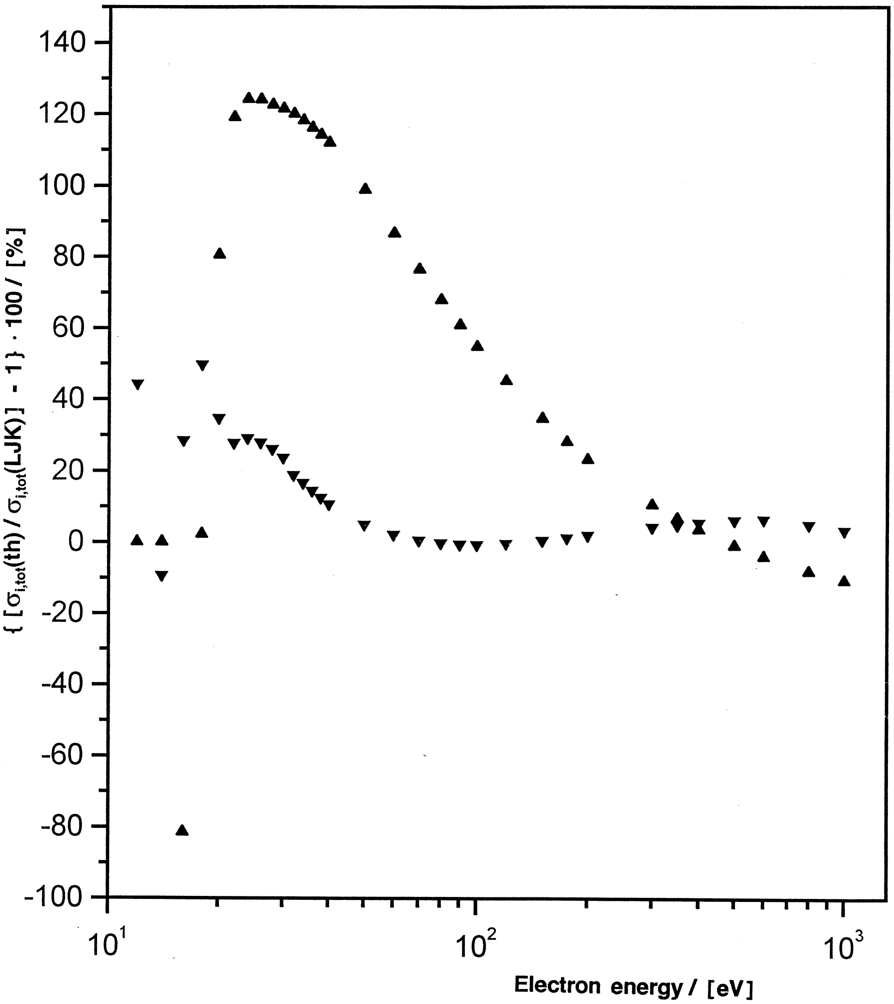

Fig. 2. Comparison of present experimentally obtained values for the NO_2 molecule total ionization cross sections with theoretically calculated values, in the form of differences in percentage triangles pointing up are with values obtained by the Grizinsky equation [17]; triangles pointing down are with values calculated by Kim et al. [1] using the BEB theory.

with $u = (E_0/E_{i,n})$, $v = (U/E_{i,n})$, $S = (4\pi a_2^2\ \xi_n R^2)/E_{i,n}^2$, and $R = 13.62$ eV. Here U is the kinetic energy of the electron in the orbital (in eV).

The present experimentally obtained total ionization cross sections are compared in Fig. 2 with calculated values in the form of differences in percentage. As one can see, agreement with the values of Kim et al. [1] is very good for incident electron energies higher than 30 eV within ±10%. On the contrary, values calculated by the Gryzinsky [17] equation differ substantially, even reaching a factor of two at lower energies.

Acknowledgements

The authors express their gratitude to Iztok Čadež for many fruitful discussions and advice, and to Miodrag Šmelcerović for his help in maintaining the apparatus in perfect working condition.

This work was supported by the Ministry of Science and Technology, Republic of Srbija.

References

[1] Y.K. Kim, W. Hwang, N.M. Weinberger, M.A. Ali, M.E. Rudd, J. Chem. Phys. 106 (1997) 1026.
[2] R.J. Kandel, Phys. Rev. 91 (1953) 436.
[3] R.J. Kandel, J. Chem. Phys. 23 (1955) 84.
[4] J. Collin, F.P. Lossing, J. Chem. Phys. 28 (1958) 900.
[5] W. Kiser, I.C. Hisatsune, J. Chem. Phys. 65 (1961) 1444.
[6] A.S. Newton, A.F. Sciamanna, J. Chem. Phys. 44 (1966) 4327.
[7] J.L. Franklin, J.G. Dillard, H.M. Rosenstock, J.T. Herron, K. Draxl, F.H. Field, NSB Ref. Data 26 (1969) 118.
[8] K. Stephan, H. Helm, Y.-B. Kim, G. Seykora, J. Ramler, M. Grössl, R. Märk, T.D. Märk, J. Chem. Phys. 73 (1980) 303.
[9] M.V. Kurepa, I.M. Čadež, V.M. Pejčev, Fizika (Zagreb) 6 (1974) 185.
[10] K.J. Overshott, I.S. Smith, J. Sci. Instrum. 40 (1961) 507.
[11] G. Josifov, M. Minić, D. Lukić, Proceedings of the IX Congress of Yugoslav Physicists, Petrovac na moru, 1995, in Serbian.
[12] A. Stamatović, G.J. Schulz, Rev. Sci. Instrum. 48 (1969) 219.
[13] D. Rapp, P. Englander–Golden, J. Chem. Phys. 42 (1965) 633.
[14] St. Halas, B. Adamczyk, Int. J. Mass Spectrom. Ion Phys. 10 (1972) 157.
[15] N. Durić, I. Čadež, M. Kurepa, Int. J. Mass Spectrom. Ion Processes 83 (1988) R7.
[16] G. Josifov, N. Durić, I. Čadež, M. Kurepa, Proceedings of the XVI Symposium of the Physics of Ionized Gases, Beograd, 1993, Contributed Papers, p. 28.
[17] M. Gryzinski, Phys. Rev. A 138 (1965) 305. supply.