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Total cross sections for electron scattering by NH_3 molecules in the energy range 300–5000 eV

G García and F Manero
Centro de Investigaciones Energéticas Medioambientales y Tecnológicas (CIEMAT), Avenida Complutense 22, 28040 Madrid, Spain

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Abstract. Total cross sections for electron scattering by NH_3 molecules in the energy range 300–5000 eV have been measured with experimental errors of about 3%. The method was based on a transmission-beam technique and a detailed error-source analysis is included. Present results have been compared with available experimental and theoretical data. The dependence on electron energy of the total cross sections obtained shows an asymptotic behaviour, in agreement with the Born–Bethe approximation. In addition, an analytical formula is provided to extrapolate total cross sections to higher energies.

1. Introduction

There is continual interest in the study of total cross sections (σ_T) for electron scattering by atoms and molecules; accurate values for a wide range of energies will be useful for many scientific and technological applications. Recently, Jain and Baluja (1992) have summarized the results available in the literature for an important number of molecules. This compilation shows that experimental data for impact energies above 500 eV are scarce. However, this energy range has a special interest for the search for systematic relations between σ_T and other molecular parameters. For this reason, in the last few years the number of works devoted to σ_T measurements for impact energies ranging from 50 to 5000 eV has been increasing (Sueoka *et al* 1994, Zecca *et al* 1995, Karwasz 1995, Szmytkowski *et al* 1995, Szmytkowski and Krzysztofowicz 1995, García and Manero 1996).

For electron–NH_3 collisions, most of the previous σ_T measurements were performed at energies below 500 eV (Sueoka *et al* 1987, Szmytkowski *et al* 1989). Experimental data for energies above 500 eV can only be found in the work of Zecca *et al* (1992). These measurements were carried out by using a modified Ramsauer technique (Dalba *et al* 1981).

Concerning theoretical data, Jain (1988) has calculated σ_T values for NH_3 in the energy range 10–3000 eV by means of a complex optical model potential. As mentioned in that work, electron–NH_3 collisions are relevant in space physics and plasma chemistry, where they play an important role as a source of nitrogen atoms. However, there is a lack of theoretical and experimental information about electron scattering by NH_3, compared with other polyatomic molecules.

On the other hand, previous work (García *et al* 1988, 1990, Karwasz *et al* 1993, García and Manero 1996) on electron scattering by different molecules (N_2, CO, CO_2) has shown serious discrepancies in the energy dependence of σ_T given by the different authors for energies above 1500 eV. Therefore it is worthwhile investigating this situation for other molecules. These considerations have prompted the present work.

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In this work values of total cross sections are given for e^-–NH_3 collisions in the energy range 300–5000 eV. The measurements have been made by using a transmission-beam technique and the estimated experimental errors are approximately 3%. A detailed error-source analysis has been made, paying special attention to those arising from forward scattered electrons. The dependence of σ_T on electron energy has been compared with theoretical predictions and especially with the energy dependence derived from the Born–Bethe approximation (Inokuti 1971, Inokuti and McDowell 1974, Inokuti *et al* 1975). A simple formula to extrapolate cross section values to higher energies has been obtained by assuming an asymptotic behaviour of σ_T as a function of the energy, according to the Born–Bethe theory.

2. Experiment

2.1. Experimental set-up

The experimental set-up was the same as that described in previous work (García *et al* 1990, García and Manero 1996) and will be mentioned only briefly here. An electron beam 1 mm in diameter was generated by an electron gun operating at typical currents of 10^{-13} A. The pressure in the gun region was maintained at less than 10^{-5} Torr during the measurements. The primary beam was transported by an electrostatic three-element lens which controls the divergence of the beam. The collision chamber was defined by two apertures 1 mm in diameter, separated by a distance (L) that can be changed from 70 to 127 mm according to the experimental requirements. Possible changes in the beam trajectory during the measurements were detected and corrected by a deflection plate system placed just in front of the collision chamber. The gas pressure in the chamber was measured with an absolute capacitance manometer (MKS Baratron 127A). The energy of the emerging electrons from the gas cell was analysed by means of an electrostatic hemispherical spectrometer of 81.9 mm mean radius and 1 mm diameter entrance and exit apertures, operating in a constant resolution and transmission mode. The energy resolution was better than 1 eV (full width at half maximum) for incident energies in the range from 300–5000 eV. Transmitted electrons were finally detected by a channeltron electron multiplier operating in single-pulse mode. The pressure in the region of the energy analyser and detector was maintained at less than 10^{-5} Torr during the measurements.

2.2. Procedure

The method is based on the measurement of the electron beam attenuation through the gas cell. The recorded beam intensity (I) follows the law

$$I = I_0 \exp(-nL\sigma_T) \tag{1}$$

where I_0 is the intensity of the primary beam, L is the interaction region length, n is the molecular density and σ_T is the total cross section; n was obtained from the measurement of pressure and temperature in the gas cell. Each measurement was processed by plotting on a semilogarithmic scale the measured I/I_0 values as a function of pressure in the gas cell, at least for ten different values ranging from 2–70 mTorr. The experimental points obtained in this way lie on a straight line, the slope of which gives the total cross section.

2.3. Error-source analysis

The accuracy of the pressure measurements was assumed to be better than 1%, as stated by the manufacturer of the MKS-Baratron 127A. To ensure that pressure gradients did not contribute to the experimental errors, the pressure was measured at several points along the cell. Measurements have been carried out at electron currents ranging from 10^{-13} to 10^{-15} A. For this current range no dependence of σ_T on electron intensity has been found. Each measurement was repeated at least five times with the same experimental conditions, to ensure statistical uncertainties of less than 2%. We have made measurements with lengths in the collision chamber of 70 and 127 mm. The corresponding σ_T values were found to be in agreement within statistical uncertainties (namely 2%). This result indicates that our measured length (L) corresponds to the actual absorption length and that possible scattering outside the collision chamber as well as multiscattering effects are negligible for our experimental conditions.

Special attention was paid to avoiding errors arising from forward electron scattering. As has been pointed out by several authors (Blaaw *et al* 1980, Ma *et al* 1989), electrons scattered in the forward direction can be the main source of error at high impact energies if they are not efficiently discriminated.

Equation (1) represents the ideal case, in which the beam is infinitely narrow and the solid angle subtended by the detector is zero. Blaaw *et al* (1980) incorporated the small-angle scattering contribution to equation (1) giving the expression:

$$I = I_0 \exp\left(-nL\sigma_T + n\int_0^L \mathrm{d}x \int_0^{\Delta\Omega(x)} \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right) \mathrm{d}\Omega\right) \qquad (2)$$

where the corrective term represents the effect of the colliding electrons, at a distance x from the entrance of the gas cell, which are scattered into the solid angle subtended by the detector $(\Delta\Omega(x))$ and $(\mathrm{d}\sigma/\mathrm{d}\Omega)$ represents the sum of the elastic and inelastic differential cross sections.

A sketch of the scattering geometry used in the present experiment is shown in figure 1. In our experimental conditions, the maximum acceptance angle of the detector is defined by the distance D (150 mm) between the end of the collision chamber and the entrance aperture of the energy analyser.

The inelastic part of the corrective term in equation (2) is fully suppressed by the energy

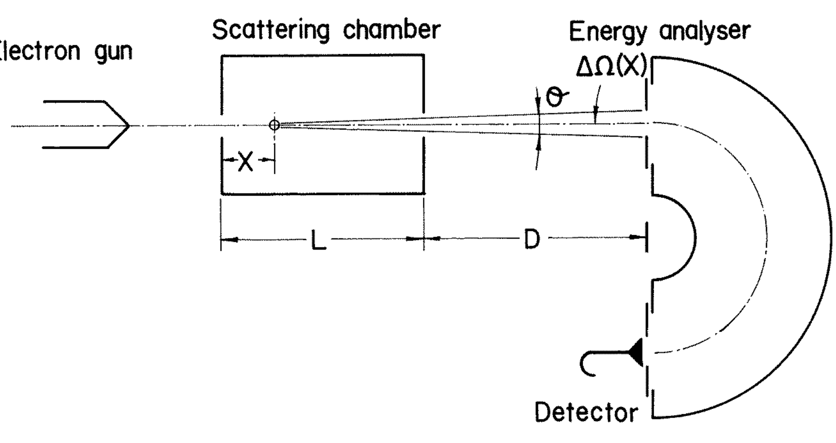

Figure 1. A sketch of the scattering geometry of the experimental set-up.

analyser. Figure 2 shows a typical energy spectrum at the detector for electrons of 2500 eV incident energy and 70 mTorr of NH_3 in the collision chamber. As can be seen in this figure, the energy resolution of the analyser allows one to eliminate the contribution of forward inelastic collisions.

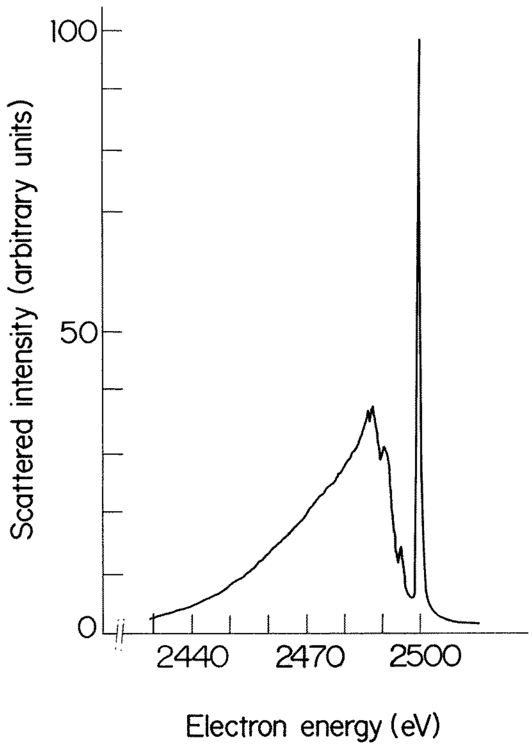

Figure 2. The energy spectrum at the detector for electrons of 2500 eV incident energy and 70 mTorr of NH_3 in the collision chamber.

The contribution of elastic scattering in the forward direction can be minimized by reducing the angular acceptance of the analyser. For the energy range considered, the angular distribution of the elastically scattered electrons has a maximum for small θ angles. For this reason, the elastic part of the integral expression in equation (2), satisfies (Blaaw *et al* 1980) the inequality

$$\int_0^L \mathrm{d}x \int_0^{\Delta\Omega(x)} \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\text{elastic}} \mathrm{d}\Omega \leqslant L\Delta\Omega \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\substack{\text{elastic}\\ \theta=0}} . \tag{3}$$

Differential elastic cross sections ($(\mathrm{d}\sigma/\mathrm{d}\Omega)_{\text{elastic}}$) for NH_3 have been measured by Harshbarger *et al* (1971) at 300, 400 and 500 eV for scattering angles ranging from 2–10°. Measurements at higher energy were published by Lahmam Bennani *et al* (1979) for 35 keV colliding electrons. Figure 3 shows a semilogarithmic plot of the differential elastic cross section given by the authors Harshbarger *et al* (1971) and Lahmam Bennani *et al* (1979) against the momentum transfer (K) for $K \leqslant 1$. As seen in the figure, the plot shows a linear behaviour for the region of small K. Hence elastic differential cross sections for zero angle can be extrapolated by fitting the experimental values to an exponential function. Values of $(\mathrm{d}\sigma/\mathrm{d}\Omega)_{\text{elastic},\theta=0}$ obtained in this way lie between 97 and 55 a_0^2 sr^{-1} for energies ranging from 0.3–35 keV, respectively. For this reason we have assumed 100 a_0^2 sr^{-1} as an upper limit for the energy range considered in this experiment (0.3–5 keV). Introducing this value in (3) and considering the maximum angular acceptance of the detector (3.5×10^{-5} sr), we obtain an error contribution for the elastic forward scattering of less than 0.2% for energies ranging from 300–5000 eV.

By combining the partial error components mentioned above, we have a total error of 3% for the present measurements.

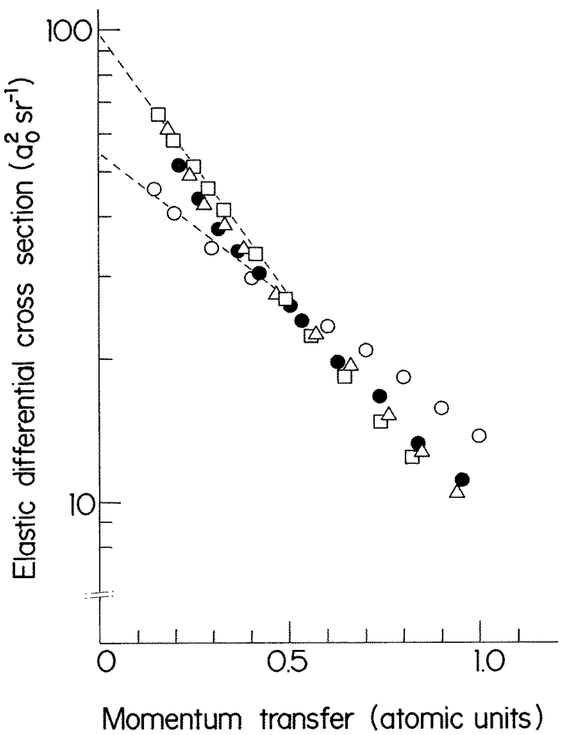

Figure 3. The elastic differential cross sections for e^-–NH_3 scattering versus momentum transfer at: □, 300 eV; △, 400 eV; ●, 500 eV (Harshbarger *et al* 1971) and ○, 35 000 eV (Lahmam Bennani *et al* 1979).

3. Results

The measured total cross sections for electron scattering by NH_3 molecules in the energy range 300–5000 eV are given in table 1, together with the experimental values of Zecca *et al* (1992) and Sueoka *et al* (1987) for comparison. The results obtained by Sueoka *et al* (1987) at 300 and 400 eV impact energies are about 8% lower than the present ones. Data from Zecca *et al* (1992) show, in general, a good agreement (within 2%) with the present results for energies between 300 and 1200 eV. However, for energies above 1200 eV they are systematically lower than ours, reaching discrepancies of about 28% at 4000 eV.

Theoretical results available in the literature are also included in table 1. Jain (1988) has reported calculations obtained by means of semi-empirical complex optical potentials which include different terms (static, exchange, polarization and absorption). Following the

Table 1. Experimental and theoretical total cross sections (in units of a_0^2) for electron scattering from NH_3.

Energy (eV)	Experimental values			Theoretical data Jain (1988)	
	This work	Zecca *et al* (1992)	Sueoka *et al* (1987)	SEPa1	SEPa0
300	15.0	15.2	13.9	16.9	12.0
400	12.4	12.4	11.4	14.0	9.64
500	10.3	10.5		12.0	8.11
600	9.02	8.96		10.5	7.00
800	7.13	7.11		8.46	5.57
1000	5.84	5.75		7.11	4.64
1250	5.00	4.67			
1500	4.38	3.93		5.11	3.11
1750	3.88	3.35			
2000	3.51	3.05		3.96	2.54
2500	2.98	2.43		3.25	2.07
3000	2.58	1.98		2.79	1.75
3500	2.26	1.66			
4000	2.05	1.47			
4500	1.86				
5000	1.70				

notation used by Jain (1988) in his work, we have labelled his results as SEPa1 and SEPa0 to distinguish between the models in which the absorption term either includes or does not include target charge distortion effects, respectively. The SEPa0 set of data gives lower values than the present measurement (about 30%), but the SEPa1 data are slightly higher than ours at low energies, showing a reasonable agreement for higher energies (within 8% at 3000 eV).

The energy range considered in this work is of special interest for checking the suitability of the calculations based on the Born–Bethe approximation (Inokuti 1971, Inokuti and McDowell 1974, Inokuti *et al* 1975). According to this theory, σ_T can be expressed as

$$\frac{E_0}{R}\frac{\sigma_T}{a_0^2} = \pi\left[A_{el} + B_{el}\frac{R}{E_0} + C_{el}\left(\frac{R}{E_0}\right)^2 + \cdots\right] + 4\pi\left[M_{TOT}^2 \ln\left(4C_{TOT}\frac{E_0}{R}\right) + \cdots\right] \tag{4}$$

where E_0/R is the incident energy in Rydberg units and a_0 is the Bohr radius. The constants A_{el}, B_{el}, C_{el}, M_{TOT} and C_{TOT} are related to internal dynamic properties of the targets (Inokuti 1971, Inokuti and McDowell 1974, Inokuti *et al* 1975). In these works, calculations of the mentioned parameters are given for some atoms. In the case of NH_3 molecules, direct calculations of these constants from molecular wavefunctions are not available in the literature. However, for energies high enough that the independent atom model of Mott and Massey (1987) applies, and by introducing the optical theorem for the forward scattering amplitude, total cross sections for molecular targets can be expressed, to a good approximation, in terms of those of their constituent atoms (Joshipura and Patel 1994, Sun *et al* 1994, Jiang *et al* 1995). Accordingly, the Born–Bethe total cross sections (σ_{BB}) for electron scattering by NH_3, evaluated by means of the atomic data given by Inokuti and McDowell (1974) and Inokuti *et al* (1975) follows the expression:

$$\frac{\sigma_{BB}}{a_0^2}\frac{E_0}{R} = 312 + 74.1\ln\frac{E_0}{R} - 159\frac{R}{E_0} + \cdots. \tag{5}$$

In order to study the dependence of the total cross section on the electron energy for the energy range of this experiment, we have made a Bethe plot $((E_0\sigma_T)/(R\,a_0^2)$ versus $\ln(E_0/R))$ which includes the present results and all the experimental and theoretical values available in the literature (see figure 4). As can be seen, the dependence of σ_T on the electron energy agrees for all the experimental values given for energies less than 1200 eV. For higher energies the values of Zecca *et al* (1992) show a clearly different behaviour from ours.

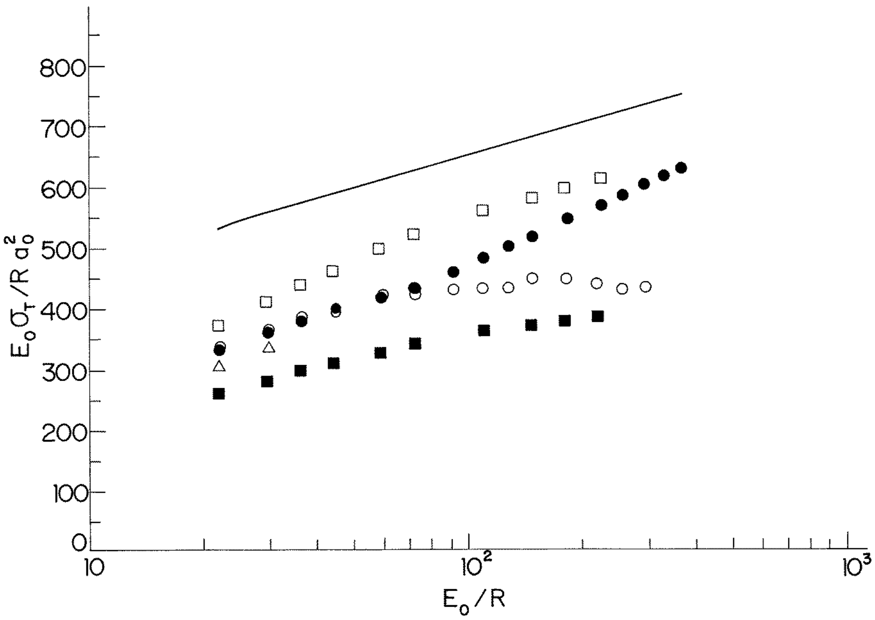

Figure 4. $E_0\sigma_T$ in units of $R\,a_0^2$ plotted versus E_0 in units of R. ●, represents the experimental results. △, represents the data from Sueoka *et al* (1987). ○, represents the experimental values of Zecca *et al* (1992). The calculations of Jain (1988) are represented by □ including distortion effects in the absorption term of the potential; ■, represents the calculations of Jain (1988) without this correction. ——, represents the Born–Bethe approximation in the framework of the independent atom model.

Concerning theoretical data, the SEPa1 calculations of Jain (1988), obtained by including charge distortion effects in the absorption term of the potential, tend to be close to ours at high energy. The SEPa0 data, calculated without this correction to the absorption term, show a different behaviour to the present measurements when the energy increases.

4. High-energy behaviour

The valid energy range of the Born–Bethe approximation can be checked by studying the relative difference between σ_{BB} values and the corresponding experimental ones as a function of energy. Figure 5 is a semilogarithmic plot of $(\sigma_{BB} - \sigma_T)/\sigma_{BB}$ versus E_0/R for energies above 1500 eV, obtained by using the present σ_T values and those of Zecca *et al* (1992) for comparison. As can be seen in this figure, while the relative differences with the Born–Bethe calculation decrease for our values with increasing energies, for those of Zecca *et al* (1992) they increase when the energy increases. Our data lie on a straight line which can be fitted by the following exponential function:

$$\frac{\sigma_{BB} - \sigma_T}{\sigma_{BB}} = 0.32 \exp\left[-\frac{1}{525}\frac{E_0}{R}\right]. \tag{6}$$

Thus total cross sections for high electron energies ($E_0 > 1500$ eV) can be obtained by

$$\sigma_T = \left[1 - 0.32 \exp\left(-\frac{1}{525}\frac{E_0}{R}\right)\right]\sigma_{BB} \tag{7}$$

where σ_{BB} is given by (5). This expression reproduces to a good approximation the present experimental results for electron energies from 1500–5000 eV, and can be used to extrapolate σ_T values to higher energies.

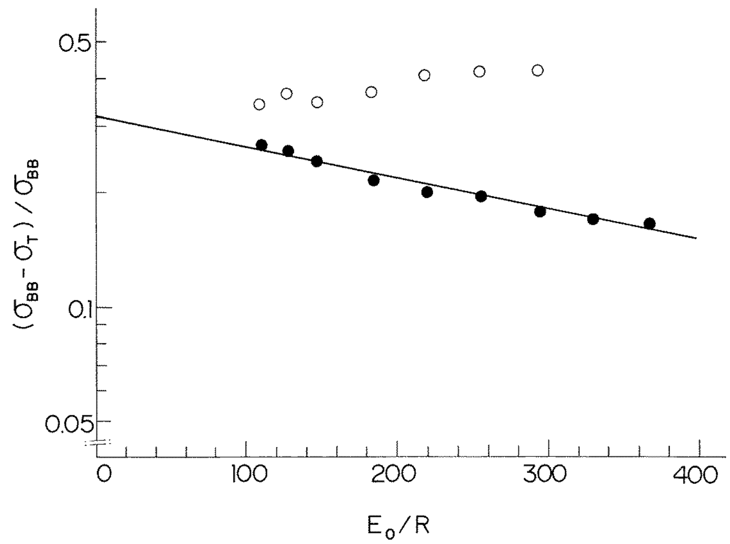

Figure 5. The relative difference between the experimental total cross sections (σ_T) and those predicted by the Born–Bethe approximation (σ_{BB}) versus electron incident energy (in Rydberg units); ●, considering the present values; ○, considering the results of Zecca *et al* (1992).

This result implies that, according to (5), σ_T varies with energy as a sum of E^{-1} and $E^{-1}\ln E$ terms, for energies ranging from 1.5–5 keV. However, the energy dependence proposed by Zecca *et al* (1992) for this energy range was proportional to E^{-1}. If we compare the extrapolated σ_T value at 5 keV given by the E^{-1} formula of Zecca *et al* (1992) with that deduced from the present results (equation (7)), there is a discrepancy of the order of 40%, the origin of this discrepancy is not known. However, if we assume that the addition rule used by Josipura and Patel (1994), Sun *et al* (l994) and Jiang *et al* (1995) is a reasonable approximation for these energies, approximated values of total cross section can be obtained from electron data libraries. Values commonly used in Monte Carlo electron transport simulations at high energies are those of Perkins *et al* (1991) for electron interaction cross sections from 10 eV to 100 GeV, for elements $Z = 1$–100. Total cross sections for e^-–NH_3 obtained in this way are shown in figure 6 for energies ranging from 1–5 keV. In this figure the present experimental results are also plotted together with the curve obtained from (7). The experimental results of Zecca *et al* (1992) are included as well, together with the curve derived from their energy-dependent formula (Zecca *et al* 1992). As can be seen in this figure, values deduced from the Evaluated Electron Data

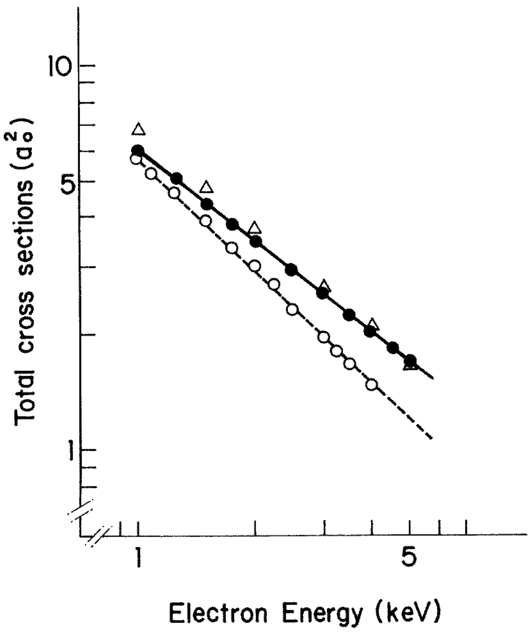

Figure 6. The energy dependence of total cross sections from 1–5 keV. ●, present experimental values. ○, experimental results of Zecca *et al* (1992). △, the values deduced from the tables of Perkins *et al* (1991). ——, the energy dependence given by (7). – – –, the energy dependence deduced by Zecca *et al* (1992).

Library (Perkins *et al* 1991) agree well with the present results, while data from Zecca *et al* (1992) deviate from them as the energy increases. It is difficult to estimate the accuracy of the values derived from the atomic data for the energy range considered, but it seems clear that the trend of the σ_T values above 1.2 keV must be coherent with the behaviour at higher energy (about 1 MeV), where the atomic cross section data are more accurate (Perkins *et al* 1991) and the independent atom model (Mott and Massey 1987) is valid.

5. Conclusions

Total electron scattering cross sections for the NH_3 molecule have been measured in the energy range from 300–5000 eV. The experimental values obtained agree well, within the experimental errors, with previously published values in the energy range from 300–1200 eV. Above 1200 eV the only previously published measurements of Zecca *et al* (1992) deviate from the present ones by more than the quoted error limit, the discrepancy being larger for increasing energies. Theoretical data of Jain (1988) show a reasonable agreement with the present results in the case where charge distortion of the absorption potential is taken into account. On the other hand, the energy dependence above 1 keV deduced from the present σ_T values is in agreement with the results of the Born–Bethe theory in the framework of the independent atom model and with the values deduced from atomic cross section tables (Perkins *et al* 1991).

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