# Electron scattering from $CH_3I$. Total cross section measurements

Czesław Szmytkowski and Andrzej M. Krzysztofowicz
*Department of Physics, Technical University of Gdańsk, ul. G. Narutowicza 11/12, 80-952 Gdańsk, Poland*

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Absolute electron-scattering total cross sections for methyl iodide have been measured at impact energies between 0.5 and 220 eV using a linear transmission method. The cross section increases rapidly as the energy becomes smaller than 1.5 eV, has a minimum ($50\times10^{-20}$ $m^2$) around 2.5 eV followed by a broad maximum ($58\times10^{-20}$ $m^2$) centered close to 6.5 eV, and monotonically decreases at higher energies.

## 1. Introduction

Accurate experimental data concerning electron–atom/molecule scattering are of importance in understanding phenomena in the earth and other planets' atmospheres, interstellar matter, radiation chemistry, gaseous discharge plasma and/or electron impact-induced reactions on surfaces. Among the scattering cross sections that can be measured the total cross section is the most reliable. Therefore it may serve as a standard value (upper limit) for the normalization of data for the individual scattering processes and/or as a test of theoretical models. However, in spite of the conceptual simplicity of the methods used for the determination of electron-scattering total cross sections and the efforts of many groups, remarkable differences still exist in magnitude and/or in shape of electron-energy dependencies of the measured total cross sections [1].

Most experiments on electron scattering from methyl iodide have considered low impact energies. Investigations of the dissociative electron attachment process leading to $I^-$ ion formation in $CH_3I$ were carried out at low energies by Spence and Schulz [2] and Stockdale et al. [3], at thermal energies by Alge et al. [4] and Shimamori and co-workers [5,6], and at subthermal energies only by Alajajian et al. [7]. Their results, obtained with quite different techniques, reveal a sudden increase in electron attachment rates as the projectile energy is decreased to zero. Spence [8], Benitez et al. [9] and Modelli et al. [10] looked for resonances employing an electron transmission technique. Feshbach resonances were found between 5 and 8 eV and no shape resonances were observed at low energies. Weak resonant effects have been noticed between 60 and 100 eV in electron-impact dissociative ionization cross sections by Mathur and Badrinathan [11]. Sushanin et al. [12] studied dissociative excitation of $CH_3I$ induced by electron impact at energies ranging from the threshold up to 600 eV. Further information on electron–methyl iodide interaction is available from the differential measurements of Volkmer et al. [13], in which electrons of energy 1 keV were elastically scattered from free, spatially oriented $CH_3I$ molecules.

The present work is part of a program which aims at the measurement of absolute total electron scattering cross sections for polyatomic molecules over a wide energy range.

## 2. Experimental

The linear transmission method has been used to measure the absolute total cross section for electron scattering from methyl iodide molecules. The transmission technique was described in detail by Bederson and Kieffer [14]. In the present experiment, the $CH_3I$ vapour sample in a scattering cell was irradiated by a quasimonoenergetic ($\Delta E=70$ meV, fwhm) electron beam and the attenuation of the

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electron current passing through the target volume was measured. Other quantities taken in the course of experiment are: an electron beam energy, $E$, target vapour pressure, $p$, its temperature, $T$, and length of the scattering volume, $L$. The total cross section $\sigma(E)$ was derived from the Bouguer–de Beer–Lambert relationship

$$I(E, n)/I(E, 0) = \exp[-nL\sigma(E)] ,$$

where $I(E, n)$ and $I(E, 0)$ are the electron beam currents transmitted through the scattering chamber with the target of number density $n$ ($=p/kT$) or in its absence, respectively; $k$ is the Boltzmann constant.

In the course of the experiment the sample vapour was allowed alternately into the scattering chamber and outer vacuum volume in such a way that the electron gun and whole electron optics were always exposed to the same partial pressure of the sample when $I(E, n)$ and $I(E, 0)$ were measured. We found that, due to this procedure, the intensity of the primary electron beam (at the entrance of the scattering cell) was approximately insensitive to the presence or absence of the target in the scattering volume.

The target vapour effusing from the sample cell might essentially influence the length over which scattering takes place. Therefore, at either orifice of the scattering cell we used a configuration of electron lenses to ensure efficient removal of the target flowing from the orifices and the electrostatic shielding of the electron beam as well. Using the effective scattering path-length calculations [15] we established that in the present experiment the effect of the density drop across the orifices is less than 0.5% and the geometrical distance (30.5 mm) between them can be adopted as the absorption length $L$.

The target vapour absolute pressure was measured with a capacitance manometer. Its head was thermally stabilized at $322 \pm 1$ K whilst the temperature of the scattering cell was typically a few degrees lower. This temperature difference was accounted for by applying the thermal transpiration [16].

The effect constantly arising in transmission experiments, which tends to lower the measured cross sections, is the incomplete discrimination by the detector system of the electrons which are scattered through small angles in the forward direction. The uncertainty in the total cross section, related to this effect, increases with impact energy and is higher for targets with higher permanent electrical dipole moment. We have used a retarding potential field after the scattering chamber to discriminate against electrons which are scattered inelastically in the forward direction. The solid angle subtended at the Faraday cup detector by the exit scattering cell aperture is of 1 msr. In order to determine the extent to which small-angle scattering could affect the measured total cross section, quantitative data on the angular distribution of scattered electrons would be needed. However, the lack of pertinent information for $e^-$–$CH_3I$ scattering makes the correction of the obtained results impossible.

The energy scale was calibrated by reference to the 2.3 eV oscillatory resonant structure in $N_2$ admixing some amount of nitrogen to the sample vapour under study. The energy accuracy was estimated to be $\pm 60$ meV.

The electron energy dependence of the $CH_3I$ total cross section was measured in a series of runs with the selected impact energy. A standard procedure in every data run was to measure the total cross section with different target-vapour densities. The results in series were independent (in the limits of statistical uncertainties) of the target pressure applied in the scattering cell (60–120 mPa at low and 100–200 mPa at higher energies), the background pressure in the region of electron optics ($<0.2$ mPa), and the electron beam intensity ($\leqslant 100$ pA). The final total cross sections at particular energies are the weighted means of the average from different series.

Statistical uncertainties (one standard deviation of the weighted mean values) reach 2% at the lowest and the highest applied energies and do not exceed 1% for intermediate energies. Particular attention has been given to reduce systematic uncertainties in the present experiment. Nevertheless, the direct sum of all relevant individual potential systematic uncertainties is estimated to be up to 9% at the lowest applied energies where the energy dependence of the cross section is the strongest, 6% above 80 eV and about 4% elsewhere.

Liquid $CH_3I$ of 99% purity was degassed periodically using freeze–pump–thaw cycles before use.

## 3. Results

The present absolute total electron-scattering cross section measured in the 0.5–220 eV energy range for methyl iodide ($CH_3I$) is displayed in fig. 1. The experimental low-energy results of Benitez et al. [9] are included for comparison. Numerical values of total cross sections are given in table 1.

The most striking feature of the cross section obtained is its relatively large magnitude which can be related to the geometrical dimension of the molecule. Starting from the low-energy limit, one can observe a very strong monotonical decrease of the total cross section from about $90\times10^{-20}$ m$^2$ at 0.5 eV to almost $50\times10^{-20}$ m$^2$ at the minimum, around 2.5 eV. Such behaviour of low-energy electron-scattering total cross section is characteristic for polar molecules ($\mu_{CH_3I}=1.62$ D [17]) and is mainly explained in terms of direct processes. There are, however, some suggestions concerning the existence of resonant effects below 2 eV. From correlation investigations between electron transmission spectra and inner shell excitation spectra for a series of halogen-substituted

Table 1
Measured total cross sections (TCS) for electron impact of $CH_3I$ in units of $10^{-20}$ m$^2$

| Energy (eV) | TCS | Energy (eV) | TCS | Energy (eV) | TCS |
|---|---|---|---|---|---|
| 0.45 | 95.8 | 3.8 | 51.1 | 19 | 47.0 |
| 0.55 | 85.8 | 4.3 | 52.6 | 21 | 45.8 |
| 0.65 | 80.3 | 4.8 | 54.1 | 24 | 44.0 |
| 0.70 | 76.4 | 5.3 | 55.6 | 27 | 41.5 |
| 0.80 | 72.1 | 5.6 | 56.2 | 30 | 39.5 |
| 0.90 | 68.5 | 5.8 | 56.9 | 35 | 37.4 |
| 1.00 | 64.2 | 6.1 | 57.8 | 40 | 35.0 |
| 1.10 | 61.7 | 6.3 | 58.0 | 45 | 34.1 |
| 1.20 | 57.9 | 6.8 | 58.1 | 50 | 33.0 |
| 1.25 | 56.0 | 7.3 | 57.6 | 55 | 32.0 |
| 1.35 | 55.3 | 7.8 | 56.2 | 60 | 31.1 |
| 1.45 | 53.1 | 8.3 | 55.2 | 70 | 29.4 |
| 1.65 | 51.3 | 8.8 | 54.8 | 80 | 28.0 |
| 1.85 | 50.2 | 9.3 | 54.2 | 90 | 26.4 |
| 2.0 | 49.7 | 9.8 | 53.8 | 100 | 24.0 |
| 2.2 | 50.0 | 10.3 | 53.2 | 120 | 22.4 |
| 2.4 | 49.8 | 10.8 | 52.3 | 140 | 20.2 |
| 2.6 | 50.0 | 12 | 51.9 | 160 | 18.5 |
| 2.8 | 49.7 | 13 | 51.1 | 180 | 16.9 |
| 3.0 | 49.5 | 15 | 50.0 | 200 | 15.7 |
| 3.3 | 50.4 | 17 | 48.7 | 220 | 14.8 |

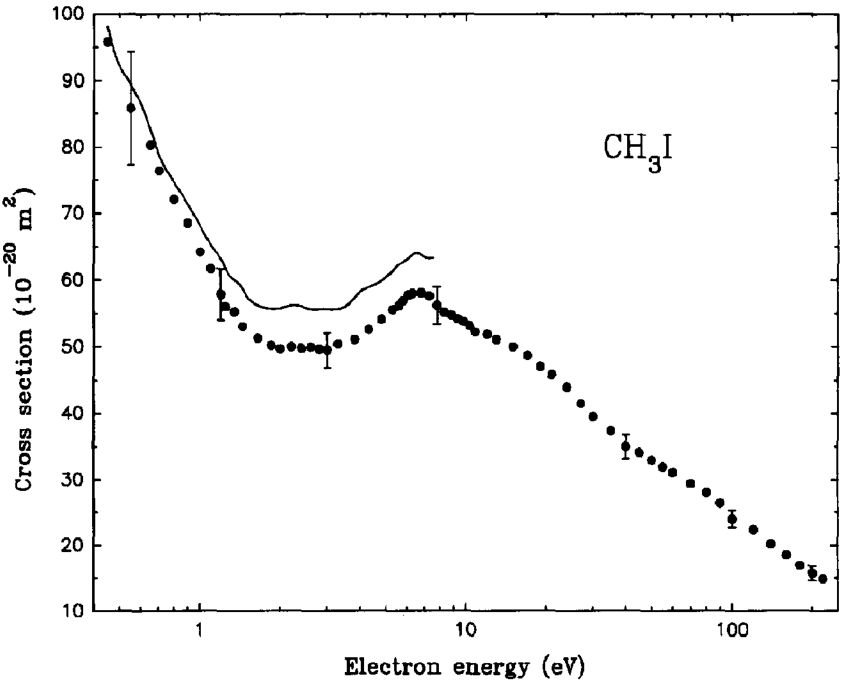


Fig. 1. Absolute e$^-$–$CH_3I$ scattering total cross sections. (●) Present; (——) ref. [9]. The error bars correspond to the overall experimental uncertainties at some selected energies.

compounds Benitez et al. [9] deduced the presence of shape resonance in $CH_3I$ slightly below 1 eV but they did not find any evidence for it in their electron transmission experiment. Moreover, Modelli et al. [10] predicted a weak low-energy resonant $\sigma^*(a_1)$ $CH_3I^-$ state by means of bound and continuum multiple scattering $X\alpha$ calculations at 1.44 and 1.22 eV, respectively. Their calculations demonstrated, however, that an intensity of this resonance is too weak to be observed. It was then confirmed by their experimental high sensitive transmission spectra [10], in which no resonant-like structure was observed between 1 and 2 eV.

Far below the energies studied in the present work, Alajajian et al. [7] measured electron attachment cross sections of $CH_3I$ using a threshold photoionization technique. Low-energy electrons attach to $CH_3I$ via repulsive negative ion state(s) $(CH_3I^-)^*$ which may decay to $I^-$ and $CH_3$. This process appears to be effective at low energies and cross sections for $I^-$ formation amounts about $200\times10^{-20}$ $m^2$ at 10 meV falling drastically to $10\times10^{-20}$ $m^2$ near 150 meV. Experiments of Stockdale et al. [3] and Shimamori et al. [6] indicate that cross sections for $I^-/CH_3I$ formation decrease further by more than one order of magnitude as the energy increases from near-thermal energies to 1 eV and that at energies studied in the present work $CH_3I$ attaches electrons weakly.

Above 3 eV the total cross section slowly increases with impact energy and reaches a maximum of $58\times10^{-20}$ $m^2$ centered around 6.5 eV. Transmission experiments of Spence [8], Benitez et al. [9], and Modelli et al. [10] give convincing evidence of Feshbach resonances in the region of the maximum formed by the binding of the extra electron to the Rydberg states of the molecule. These resonant effects are, however, weak and cannot explain the observed increase of the total cross section. The presence of such broad maxima, more or less appreciable near 10 eV in total cross sections for other targets, is most probably related in part to a variety of direct processes accessible at these energies and to numerous broad weak shape resonances [18] which cannot be distinguished either in transmission spectra or even much less in the electron-energy dependence of the total cross section.

An additional observation is that for impact energies of more than 10 eV the total cross section again monotonically decreases with energy to the value of $16\times10^{-20}$ $m^2$ near 200 eV.

A comparison of the present results with the only available data of Benitez et al. [9] (fig. 1) shows that the general shapes of both curves with respect to energy are very similar. The visible difference in magnitudes (on an average 7%) is, however, well within the combined declared uncertainties of each separate experiment.

Recently, Modelli et al. [10] calculated the total section for $e^-/CH_3I$ scattering at low energies and published the only derivative of the cross section which cannot be directly compared with the present results.

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