



# Electron scattering from methyl bromide. Absolute total cross section measurements

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## Abstract

The absolute total cross section for electron-CH<sub>3</sub>Br scattering has been measured in a wide energy range (from 0.4 to 250 eV) by the linear transmission method. At the lowest investigated energies the cross section increases rapidly when the energy decreases. A shallow minimum of the total cross section between 2.5 and 4.5 eV followed by a weak broad enhancement around 7 eV is observed. A comparison is made with available data.

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## 1. Introduction

Gaseous bromine-containing compounds play an important role in the delivery of bromine to the lower stratosphere. Model results [1] show that bromine is a potentially significant depleter of stratospheric ozone. Among the organobromine species, methyl bromide accounts for more than half of the current bromine content of the atmosphere [2].

Increasing interest in electron impact phenomena involving CH<sub>3</sub>Br molecules, evident from a number of works employing a variety of experimental techniques, began in the mid-sixties. Most of the studies on electron scattering from CH<sub>3</sub>Br molecules have dealt with thermal [3–15] and low [7,12,14,16–19] energies. The experimental methods applied in those studies are listed in ref. [13]. Electron attachment processes have been investigated by Lee [3], Johnson et al. [5], Wentworth et al. [6], Christodoulides and Christophorou [7], Bansal and Fessenden [8], Schindler [9], Mothes et al. [11], Stockdale et al. [12], Alge et al. [13], Petrović and Crompton [10], Wang and Lee [16] and Datskos et al. [14]. The rel-

atively large number of works devoted to the same problem was provoked by controversies concerning the value of electron attachment rate constants.

Furthermore, Spence and Schulz [15] and Stockdale et al. [12] were interested in the negative ion formation processes at low energies. Spence [17], Benitez et al. [18] and Modelli et al. [19] employed the transmission technique to look for resonances in electron-methyl bromide scattering.

In addition, there have been a few experiments at higher energies. They concern measurements of the electron-impact ionization cross section [20,21] and inner-shell excitation of CH<sub>3</sub>Br [22].

The only total absolute cross section available in the literature has been measured by Benitez et al. [18] for low energies (0.3–7.5 eV).

## 2. Experimental

In the reported experiment a linear transmission technique [23] has been applied. The apparatus used consisted of a source – a quasi-monoenergetic beam

of electrons ( $\Delta E = 70$  meV, fwhm), a cylindrical scattering cell 30.5 mm in diameter, and a retarding field analyzer followed by a Faraday cup.

A beam of electrons irradiates the investigated gas sample in the scattering chamber. The rate of attenuation of the electron current passing through the scattering volume when the target is present or absent in the scattering cell enables us to derive the total cross section  $\sigma(E)$  by use of the Bouguer–de Beer–Lambert law,

$$\sigma(E) = \frac{1}{nL} \ln \left( \frac{I_0(E)}{I(E)} \right), \quad (1)$$

where  $I_0(E)$  is the intensity of the incident beam of electrons of energy  $E$ , and  $I(E)$  is the intensity of the electron current transmitted through the target under study. Other quantities we should determine are: the length  $L$  through which the scattering processes take place and the density number  $n$  of target molecules. Because of the effusion of the target particles through the entrance and exit orifices of the scattering cell, the effective scattering length is always different from the geometric distance between the cell orifices. In spite of the applied geometry of the electron optics system, which ensures good pumping of the volume surrounding the gas chamber, some scattering events are unavoidable also outside the gas cell. The product  $nL$  in (1) should then be replaced with

$$(nL)_{\text{eff}} = \int n(x) dx, \quad (2)$$

where  $n(x)$  describes the distribution of gas density number and the integration is performed along the whole electron trajectory.

More detailed investigations, following the Nelson and Colgate calculations [24], show that in our case the effect of density drop across the orifices is almost compensated by the longer (in comparison to geometrical) scattering length. As a result, within the accuracy of 0.5%, we can assume that  $(nL)_{\text{eff}} = nL$ , where  $L$  is the geometric size (diameter) of the scattering cell and  $n$  is the average gas density number inside the scattering container.

The target absolute pressure in the gas cell was measured with a baratron. Since the temperature of the manometer head ( $T_m = 322$  K) is higher by about 10–14 K than the temperature  $T_t$  of the target (scattering cell), a correction of the pressure readings  $p$  is

necessary. Assuming applicability of the ideal gas law and taking into consideration the thermal transpiration effect [25] <sup>#1</sup> the gas density number  $n$  is given by

$$n = p/k\sqrt{T_t T_m}, \quad (3)$$

where  $k$  is the Boltzmann constant.

The target absolute pressure in the scattering cell was in the range 70–130 mPa at low impact energies and 100–200 mPa at higher energies. These values were sufficiently low to ensure that multiple-scattering processes were negligible. The background pressure (outside the scattering cell – in the electron optics region) was about three orders of magnitude lower than the pressure in the collision chamber. The target gas was let alternatively into the scattering cell and into the outer vacuum in such a way that the background pressure was kept constant whether the gas was in the scattering cell or not. This enabled us to minimize the influence of the gas, effusing from the scattering cell into the region of the electron optics, on the intensity of the primary electron beam ( $I_0$ ) and, in consequence, on the measured total cross section. The base pressure, while the gas was absent in the apparatus, was within the order of 20  $\mu$ Pa.

Eq. (1) is based on the assumption that no electron which undergoes scattering with target particles reaches the collector. In an actual experiment, however, due to the finite angular resolution of the detector system (in the present experiment  $\approx 1$  msr), the detector can accept electrons scattered in the small-angle forward direction. The retarding field analyzer provides discrimination only of the inelastically scattered electrons which leave the scattering chamber through the exit orifice. The effect of incomplete discrimination systematically reduces the value of the measured total cross section and may cause serious experimental error [23]. A direct estimation of this error in the present experiment is impossible, as no angular distribution of electrons scattered on  $\text{CH}_3\text{Br}$  is available. It is well known that for polar molecules, especially at higher energies, the amount of electrons scattered in the forward direction tends to increase with the increase in the electric dipole moment of the target. Because the dipole moments of the water mol-

<sup>#1</sup> For the validity of the approximation see ref. [26].

ecule and the molecule under study are very close ( $\mu_{\text{H}_2\text{O}} = 1.85 \text{ D}$  and  $\mu_{\text{CH}_3\text{Br}} = 1.82 \text{ D}$  [27]) the differential cross sections for  $\text{H}_2\text{O}$  [28,29] have been used for a rough error estimation (see Table 1). The validity of such an approach was recently approved by Petrović and Crompton [10]. In the absence of other data, they have used the  $\text{H}_2\text{O}$  molecule parameters to estimate the energy dependence of the  $e^-/\text{CH}_3\text{Br}$  momentum transfer cross section at very low energies. The resulting momentum transfer cross section at 0.4 eV ( $61.6 \times 10^{-20} \text{ m}^2$ ) agrees surprisingly well with our experimental total cross section ( $62.6 \times 10^{-20} \text{ m}^2$ ) at the same energy.

The energy calibration procedure, aiming at eliminating the energy shift, was performed with reference to the oscillatory resonance structure in  $\text{N}_2$  near 2.3 eV, using a mixture of the gas sample under study and nitrogen. The accuracy of the energy scale was estimated to be  $\pm 60 \text{ meV}$ .

Measurements at a given energy were carried out in 2–12 series typically consisting of 10–20 single runs. It was established that the total cross sections obtained in different series at the same energy were independent, within the limits of statistical uncertainties, of applied sample pressures and electron beam intensities ( $\leq 10 \text{ pA}$ ). The final values of the total cross section at particular energies are weighted means of the average from different series of individual runs taken at the same energy.

The values of systematic and statistical uncertainties (one standard deviation) at selected energies are presented in Table 1. The overall, rather pessimistic, experimental error was calculated as the direct sum of all possible uncertainties.

Commercially available  $\text{CH}_3\text{Br}$  (Merck-

Schuchardt) was used without further purification. Due to a suggestion [10] concerning greater than nominal contents of impurities, a mass spectroscopy analysis of the gas in the cylinder was carried out. No significant impurities were detected. The analysis proved that the gas had the 99.5% purity guaranteed by the supplier.

### 3. Results

The absolute total cross section obtained in the present experiment for energies ranging from 0.4 to 250 eV is presented in Fig. 1. Comparison with the absolute experimental data of Benitez et al. [18], the only available in the literature, has been made. No significant differences either in magnitude or in shape have been found in the overlapping region of energies used in the compared experiments. The results agree well within the limits of stated uncertainties. Table 2 contains the present results in numerical form.

For the lowest applied energies the total cross section sharply decreases from about  $60 \times 10^{-20} \text{ m}^2$  at 0.4 eV to about  $40 \times 10^{-20} \text{ m}^2$  at 2.5 eV. Such behaviour of the cross section in the low-energy region is characteristic for polar molecules and can be mainly explained in terms of direct scattering processes.

For a number of molecules, resonant processes proceeding via formation of transient negative-ion states play an important role in the scattering at low energies [30]. Benitez et al. [18], basing on the inner shell electron energy loss spectroscopy results [22] and their own measurements, suggested the presence of a shape resonance near 1 eV, though they have not found their experimental results sufficient

Table 1

Effect of main experimental errors on the measured total cross section at selected energies (in percent)

	Energy (eV)				
	$\leq 0.7$	1.6	6.0	35	180
statistical uncertainties	1		<0.5	1	1.5
forward scattering	1		<0.5		1.5
electron energy uncertainty	2.5	0.2	<0.1	<0.1	<0.1
beam intensity measurements	2	1.5	1	0.5	0.4
pressure determining			2.5		
sum (maximum error)	10	6	5.5	5.5	6.5

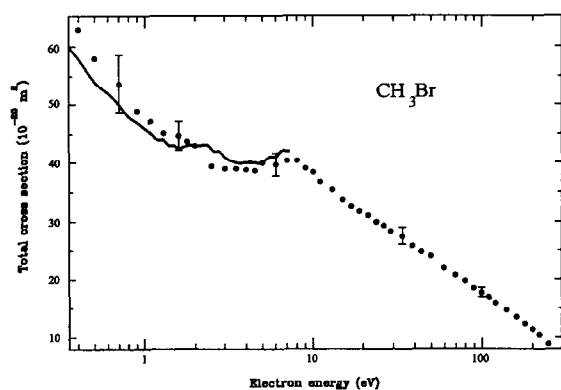


Fig. 1. Absolute electron- $\text{CH}_3\text{Br}$  scattering total cross sections: (●) present; (—) ref. [18]. The error bars correspond to the overall experimental uncertainties at selected energies.

Table 2

Measured total cross sections (TCS) for electron impact of  $\text{CH}_3\text{Br}$  in units of  $10^{-20} \text{ m}^2$  versus energy in eV

Energy	TCS	Energy	TCS
0.4	62.6	17	32.5
0.5	58.0	19	31.7
0.7	53.6	22	31.0
0.9	48.9	24	29.9
1.1	47.1	26	29.2
1.3	45.4	30	28.3
1.6	45.0	35	27.4
1.8	43.8	40	26.2
2.0	43.0	45	25.5
2.5	39.4	50	24.3
3.0	39.0	60	22.6
3.5	39.0	70	21.3
4.0	38.8	80	20.4
4.5	38.6	90	19.0
5.0	40.0	100	18.0
6.0	39.7	110	17.1
7.0	40.4	120	16.1
8.0	40.4	140	15.0
9.0	39.0	160	13.9
10	38.4	180	13.0
11	36.7	200	12.0
13	35.4	220	11.2
15	33.6	250	9.75

evidence. Furthermore, Modelli et al. [19] predicted a weak resonant  $\sigma^*(a_1) \text{CH}_3\text{Br}^-$  state near 2 eV using bound and continuum multiple scattering  $X\alpha$  calculations. These results were then confirmed in their high sensitivity transmission experiment which showed a resonant structure near 2.4 eV, much too

weak, however, to be observed in the total cross section.

Experiments [12,14,16] show that the value of the cross section for the dissociative attachment of an electron to the  $\text{CH}_3\text{Br}$  molecule is very low and near 0.4 eV, at its maximum, amounts to  $10 \times 10^{-22} \text{ m}^2$ . The contribution of this indirect process to the total cross section at the whole applied energies is relatively small.

In the 2.5–4.5 eV energy range the cross section has a wide shallow minimum. For higher energies, near 7 eV, a very weak broad structureless hump is observed. Near 7 eV and close to 9 eV Stockdale et al. [12] observed maxima in the  $\text{Br}^-/\text{CH}_3\text{Br}$  current. In the same energy region Spence [17] observed, and assigned configurations to, Feshbach resonances, formed by the binding of an extra electron to the Rydberg states of the  $\text{CH}_3\text{Br}$  molecule. Similar resonant structures were recently confirmed in transmission spectra by Benitez et al. [18] and Modelli et al. [19]. However, the intensities of these processes are too weak to explain the observed increase in the total cross section. It is most likely that the enhancement of the cross section around 7 eV should be mainly attributed to numerous overlapping direct processes accessible in this energy range, although a small contribution from the weak resonance is also possible.

Taking the higher energies into account, we can notice that as the impact energy increases the total cross section again monotonically decreases down to about  $8 \times 10^{-20} \text{ m}^2$  near 250 eV. In this energy range the ionization phenomena play an increasing role in the electron-scattering processes and the total ionization cross section near 70 eV was estimated to be from one third [20] to about a half of the total cross section [21].

No theoretical calculations of the absolute cross sections for electron- $\text{CH}_3\text{Br}$  scattering are available for comparison with the experimental data.

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