

LETTER TO THE EDITOR

Absolute electron-scattering total cross section measurements for methanethiol molecule, CH₃SH, from 0.6 to 250 eV

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Abstract. The absolute total cross section for electron scattering on CH₃SH molecules has been measured in a linear electron-transmission experiment for impact energies between 0.6 eV and 250 eV. No theoretical or experimental total cross section data are available for comparison. The obtained total cross section has an energy dependence which is typical for polar molecules. Static electric dipole polarizability of methanethiol has been estimated using a correlation of electron-scattering total cross section with target polarizability. The polarizability of CH₃SH thus obtained is in good agreement with values derived by empirical methods.

Cross section data for electron scattering on methanethiol, which is one of the most important products of degradation of organic matter, are interesting in view of its presence in Earth's atmosphere (Hines and Morrison 1992) and in interstellar space (Kaifu 1990). However, experiments of electron scattering on CH₃SH have so far been incidental, while theoretical studies are altogether lacking. The only information about electron impact interaction with methanethiol is available from the dissociative attachment experiment of Jäger and Henglein (1966), investigations of positive-ion formation by Amos *et al* (1969) and more recent low-energy transmission measurements of Dezarnaud *et al* (1991).

The objective of the present work is to supplement the data hitherto obtained for the e⁻-CH₃SH scattering performing absolute total cross section measurements for electron impact in the low to higher-intermediate energy range.

The experiment reported here was carried out with an electron spectrometer working in the transmission mode (Bederson and Kieffer 1971). Essentially, the method is based on the measurements of the projectile particles' intensity after they have penetrated the interaction region. In the present experiment, a quasimonoenergetic electron-beam (FWHM = 70 meV) was produced with an electron gun followed by a cylindrical electrostatic deflector and a system of electron lenses. It was then fired on the gas-target filling a scattering cell of length L . Electrons which escaped the scattering volume through the exit orifice were energetically discriminated with a retarding field element and then detected by Faraday cup.

The total cross section, $Q(E)$, at a given energy E was derived by measuring intensities of the electron beam, with (I_p) and without (I_0) the target in the scattering chamber, and applying the Bouguer-de Beer-Lambert relationship

$$Q(E) = \frac{1}{nL} \ln \frac{I_0(E)}{I_p(E)}. \quad (1)$$

The absolute number density n of the target gas was determined from absolute measurements of the gas-target pressure and its temperature, taking into the account the thermal transpiration effect (Knudsen 1910). The electron-energy scale was calibrated with reference to the well-known oscillatory resonant structure in nitrogen, around 2.3 eV. The purity of gas employed in the experiment was 99.5% (Aldrich). More detailed description of the used experimental setup and technique can be found elsewhere (e.g. Krzysztofowicz and Szymkowski 1995).

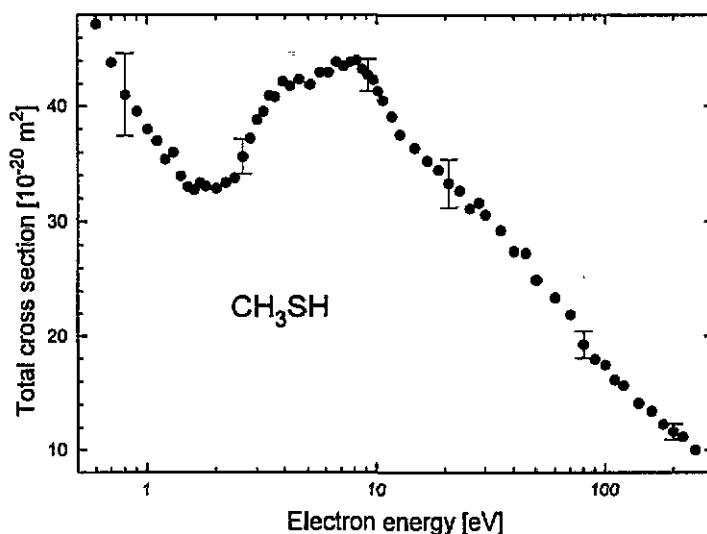


Figure 1. Absolute electron-CH₃SH scattering total cross sections: (●), present. The error bars correspond to overall experimental uncertainties estimated at selected points.

The total cross sections measured in the present experiment are listed in numerical form in table 1 and shown in figure 1. The presented results are the weighted means of the average cross sections obtained in different independent series (4–9) of individual runs (8–15 in series) for the same energy. No measurements and calculations are available for comparison.

The general character of changes in the total cross section as a function of energy (as shown in figure 1) is typical for polar molecules ($\mu_{\text{CH}_3\text{SH}} = 1.52$ D, Lide 1993–94). According to the features observed in the measured total cross section function, the whole of the investigated energy range can be divided into three regions.

In the first, ranging from 0.6 to 1.6 eV, the cross section sharply decreases from $47 \times 10^{-20} \text{ m}^2$ to $33 \times 10^{-20} \text{ m}^2$ with increase of impact energy. In this energy range, Jäger and Henglein (1966) recorded CH₃S[−], CH₂S[−] and S[−] ions. These anions are mainly created via temporary capture of the impinging electron into empty molecular orbitals with formation of transient negative-ion resonant states of the parent molecule and subsequent decay into the observed negative ion and a radical. The negative ion formation turned out to be the most effective at 0.68 eV (CH₂S[−]) and 1 eV (CH₃S[−]), but the relative contribution of the dissociative attachment processes to e[−]-CH₃SH scattering is rather small and amounts to no more than about 2.5% of the total cross section at 0.68 eV and nearly 2% at 1 eV (Jäger and Henglein 1966). In this energy range, no resonant features were detectable in the electron transmission spectra of CH₃SH (Dezarnaud *et al* 1991). In the light of the above and according to the current understanding of the dipole molecule–electron scattering

Table 1. Absolute total cross sections (TCS) measured for electron impact of CH₃SH molecule in units of 10⁻²⁰ m².

Energy (eV)	TCS	Energy (eV)	TCS	Energy (eV)	TCS
0.60	47.22	3.9	42.19	25	31.14
0.70	43.87	4.2	41.81	28	31.63
0.80	41.05	4.6	42.37	30	30.61
0.90	39.56	5.2	41.92	35	29.27
1.0	38.03	5.6	42.99	40	27.49
1.1	37.02	6.1	42.99	45	27.29
1.2	35.45	6.6	43.92	50	25.00
1.3	36.04	7.1	43.53	60	23.45
1.4	33.99	7.6	43.89	70	21.92
1.5	33.06	8.1	44.05	80	19.26
1.6	32.78	8.6	43.26	90	17.96
1.7	33.37	9.1	42.73	100	17.46
1.8	33.09	9.6	42.31	110	16.14
2.0	32.89	10.0	41.34	120	15.67
2.2	33.39	10.5	40.53	140	14.13
2.4	33.81	11.5	39.10	160	13.45
2.6	35.66	12.5	37.55	180	12.29
2.8	37.23	14	36.40	200	11.64
3.0	38.84	16	35.30	220	11.18
3.2	39.54	18	34.51	250	10.00
3.4	40.95	20	33.33		
3.6	40.85	23	32.67		

(e.g. Christophorou *et al* 1982), one may believe, that the observed behaviour of the cross section below 1.5 eV is mainly due to direct scattering processes. The strong decrease of the cross section is followed by a flat minimum centred near 2 eV.

The second energy region, starting from 2.5 eV, is characterized by the very broad enhancement of the cross section. The shape of the hump between 2.5 and 20 eV, with the half width of nearly 10 eV, suggests that it consists of two weakly differentiated peaks, a weaker one around 4 eV and a more prominent one near 8 eV. To investigate e⁻-CH₃SH scattering resonances at low energies, Dezarnaud *et al* (1991) have analysed derivatives of the registered electron-transmission spectra. In the region of the first maximum they have succeeded in discerning a broad shape-resonance centred at 2.85 eV and suggested that the extra electron is temporarily trapped in σ^* molecular orbitals localized on the C-S-H linkage. However, their results do not allow us to estimate the absolute contribution of this resonant effect to the scattering. Jäger and Henglein (1966) found evidence of further very weak resonant features in the registered negative ion current, throughout the whole range of the broad total cross section enhancement. The energy range of the Dezarnaud *et al* experiment did not extend to the second maximum at 8 eV. The observed enhancement of the cross section may thus be related to a variety of direct processes accessible in the energy range, with a contribution of numerous overlapping weak resonances.

From the 8 eV maximum, all the way to the highest applied energy of 250 eV, total cross section decreases monotonically with increasing impact energy and for energies above 50 eV, the cross section changes as $E^{-\beta}$, where $\beta \simeq 0.5$. Such behaviour of the total cross section is in accordance with the theoretical results obtained by Vogt and Wannier (1954) for the pure polarization potential.

The relationships between electron-scattering cross sections and target parameters have

been investigated for some time now. On the one hand, such relationships should help us to understand the possible role of target properties in the scattering process, while on the other hand, they can also be employed in estimating the hitherto undetermined target parameters. Good correlation of electron-scattering total cross sections with static electric dipole polarizabilities of targets established earlier by Szmytkowski (1989) encourage its use for estimation of polarizability α of methanethiol. Basing on the present total cross section measurements and making use of the regression formula, we have found that $\alpha_{\text{CH}_3\text{SH}}$ lies between $5.0 \times 10^{-30} \text{ m}^3$ and $5.4 \times 10^{-30} \text{ m}^3$, which agrees well with the values of $5.31 \times 10^{-30} \text{ m}^3$ and $5.62 \times 10^{-30} \text{ m}^3$ obtained by empirical additivity methods (see Miller 1990), namely group polarizability and atomic hybrid component polarizability, respectively.

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