J. Phys. B: At. Mol. Phys. **15** (1982) L175–L178. Printed in Great Britain

LETTER TO THE EDITOR

Total cross section measurement for e–SF_6 scattering down to 0.036 eV

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Received 3 December 1981

Abstract. Absolute total cross sections in the range 0.036 to 1.0 eV were determined in a transmission experiment performed with a time-of-flight spectrometer. Above 0.5 eV, where other measurements are available the agreement is excellent. At lower energies our results can be compared with electron attachment cross sections derived from swarm as well as threshold photoelectron attachment experiments. Extrapolation of our data to energies below 0.02 eV permits comparison with the scattering behaviour of the weakly bound electrons in highly excited (Rydberg) atoms.

The interaction between low-energy electrons and sulphur hexafluoride (SF_6) has been investigated extensively (cf Massey 1976). Special attention has been paid to the experimental study of electron attachment in SF_6, because it is widely used as a scavenger for slow electrons and has gained importance as a gaseous dielectric. The attachment cross section has a sharp resonance at zero energy, the main features of which were established in experiments by Hickam and Fox (1956), and which was later studied in a considerable number of experiments using swarm, beam and other techniques (cf Christophorou 1971).

From swarm experiments only the electron attachment cross section has been determined. There has been little work on measurement of the total cross section.

Up to now data on the total cross section below 0.5 eV have not been available. With our time-of-flight (TOF) electron spectrometer we determined the total e–SF_6 cross section at low energies, starting at 1.0 eV to obtain overlap with published data and ending at 0.036 eV, the energy below which diminishing electron intensity prevented further measurements. Apparatus and procedure were the same as described previously (Ferch *et al* 1980, 1981). Additional experimental difficulties with SF_6 arose from the extremely high cross section at low energies ($>10^{-14}$ cm^2) and the high molecular weight. The former led to very low target pressures which are difficult to measure absolutely and the latter was responsible for the slow gas flow through narrow pipes connecting gas bottle, target and manometer, requiring waiting times of 10 min and more after pressure changes. The reproducibility of the data under a variety of experimental conditions (electron optics, target pressure) was not as good as for our measurements with He and H_2 (Ferch *et al* 1980). The experimental error was determined from averaging different measurements, taking two standard deviations of the mean and adding to that the estimated systematic errors common to all measurements (e.g. the uncertainty in manometer calibration). For our e–SF_6 total cross sections shown in figure 1 the error is ±7% above 0.2 eV and ±9% below.

0022-3700/82/050175+04$02.00

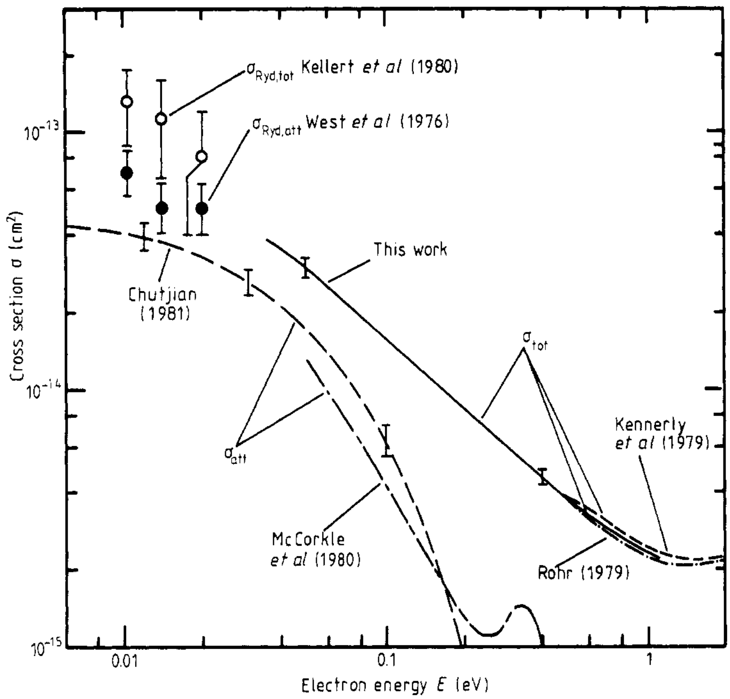

Figure 1. Comparison of our data with other e–SF_6 cross sections. σ_{tot} is the total cross section, σ_{att} the electron attachment cross section, $\sigma_{Ryd,tot}$ and $\sigma_{Ryd,att}$ are the total and attachment cross sections for quasi-free electrons of Rydberg atoms computed from rate constants measured in collisions of highly excited xenon atoms with SF_6.

The other data on SF_6 with which our results can be compared are also shown in figure 1. The total cross section (σ_{tot}) above 0.5 eV was measured by Kennerly *et al* (1979), also employing a TOF technique, and by Rohr (1979), who integrated his differential cross section data. The agreement between the different σ_{tot} measurements is excellent.

The total e–SF_6 cross section is the sum of all partial cross sections for the open reaction channels. At low energies the electron attachment cross section σ_{att} provides the largest contribution to σ_{tot}.

The recent measurements of σ_{att} shown in figure 1 lie below the σ_{tot} values as expected. The curve of McCorkle *et al* (1980) was obtained from a re-evaluation of swarm data of Christophorou *et al* (1971, 1972). An interesting feature is the resonance peak at 0.35 eV attributed to dissociative electron attachment leading to SF_5^-+F. In order to extract structures like that from swarm data the electron energy distribution must be known very accurately. An earlier evaluation with a slightly different distribution function gave a peak twice as high at 0.3 eV (cf Christodoulides *et al* 1979). The reduced peak height obtained by McCorkle *et al* (1980) with an improved distribution function is the best result available but its error margin is not known. If the peak in the dissociative attachment cross section is not compensated by a dip in another partial cross section it should also be visible in σ_{tot}. In our measurement special attention was paid to the shape of σ_{tot} in this energy region but no structure was observed. The peak shown in σ_{att} of figure 1 superimposed on an otherwise smooth $\sigma_{tot}(E)$ curve would barely exceed the error of our measurement.

(Note the logarithmic scale of σ in figure 1.) On the other hand, it is not certain that the peak would show up in σ_{tot}. If the resonance lies in the branching ratio of outgoing channels for the decay of the excited intermediate negative ion

$$(SF_6^-)^* \begin{array}{l} \nearrow SF_5^- + F \\ \searrow SF_6 + e^- \end{array}$$

it will not be visible in σ_{tot}.

The σ_{att} results of Chutjian (1981) were obtained with low-energy monoenergetic electrons produced in a $Xe + SF_6$ mixture by photoionising the Xe. The electron energy, equal to the excess photon energy, was varied between 0 and 0.2 eV. A comparison with our data shows that at energies of 0.04 to 0.06 eV the attachment accounts for 60% of the total cross section.

Both Chutjian's σ_{att} data and our curve of σ_{tot} extrapolated to lower energies can be compared with the results obtained in scattering highly excited (Rydberg) atoms from SF_6. A Rydberg atom consists of a very weakly bound electron and an ionic core. Theoretical work on the interaction of Rydberg atoms (Fermi 1934, Flannery 1970, 1980, Matsuzawa 1972a, b, and others) showed that the scattering behaviour of such an atom is, to a good approximation, given by the sum of the electron and core–ion scattering cross sections. The weakly bound electron with its orbital velocity v_o is considered as 'quasi-free' having the same cross section as a free electron of the same velocity. For the interaction of the quasi-free electron with a target molecule the relevant velocity is the vector sum of $\boldsymbol{v}_o$ and $\boldsymbol{v}_T$, the latter being the translational velocity of the Rydberg atom with respect to the target molecule. The determination of the corresponding free-electron velocity v_e is easiest in the two extreme cases where the ratio of v_T/v_o is either very small or very large compared with unity. First experimental confirmation of this theoretical prediction came from the measurements of Koch (1979), who studied collisions of fast, highly excited D atoms with N_2 molecules. In that case, $v_T/v_o \gg 1$; D atoms of energies around 9 keV have velocities equal to free electrons around 2.5 eV, the energy range of the well known e–N_2 resonances. Their characteristic structure was observed in Koch's experiment.

The comparison made here concerns the other extreme of $v_T/v_o \ll 1$. The free-electron velocities $v_e = v_o$ correspond to low energies on the order of 10^{-2} eV. Collisions of highly excited xenon atoms in the nF state ($n = 26$, 31, 36) with SF_6 were studied by the Rice University group (West *et al* 1976, Kellert *et al* 1980), measuring the rate constant for ionisation of the Rydberg atoms (which is energetically possible only by SF_6^- formation) as well as for collisions which led to depletion of the originally excited nF state. The latter can be considered as the Rydberg-electron analogue of free-electron total scattering.

From the rate constants for depletion of the Xe atoms in the nF state, $k_d(n)$, (Kellert *et al* 1980) we calculated a Rydberg-electron total cross section by using the following relations:

$$\sigma_{Ryd,tot}(E) = k_d(n)/v_e \qquad (1)$$

$$E = 13.6\ \text{eV}/(n - 0.055)^2 \qquad (2)$$

$$v_e = \bar{v}_o = (2\ mE)^{1/2} \qquad (3)$$

Equation (1) is the relation between rate constant and cross section where v_e is the relative velocity of the colliding particles. Equation (2) gives the binding energy of the electron in the nF states of xenon where 0.055 is the quantum defect of the F series at high n values (computed from the tables of Moore (1971)). The binding energy E equals the average kinetic energy of the orbiting electron. Equation (3) gives v_e as the root mean square velocity of the orbiting electron. Similarly we used the ionisation rate constants k_i, measured by West *et al* (1976), to compute the Rydberg-electron attachment cross section,

$$\sigma_{\mathrm{Ryd,att}}(E) = k_i(n)/v_e. \tag{4}$$

Since the Xe(nF) states have a very broad distribution of v_o (like all states for which $l \ll n$), the relative velocity of Rydberg electron and target molecule varies accordingly. The use of a single velocity v_e in equations (1) and (4) is an approximation. The computed cross sections are averages over a rather broad kinetic-energy distribution and this has to be borne in mind when they are compared with cross sections of monoenergetic free electrons.

Both Rydberg-electron cross sections are plotted in figure 1. The $\sigma_{\mathrm{Ryd,att}}$ values (dots) have to be compared with Chutjian's σ_{att} curve and the $\sigma_{\mathrm{Ryd,tot}}$ values (circles) with the extrapolation of our σ_{tot} curve. In view of the experimental errors and the approximation contained in equations (1)–(4) the agreement is satisfactory, confirming the assumption that the Rydberg electron interacts with a molecule very much like a free electron of comparable kinetic energy.

For stimulating and clarifying discussions we thank Professor R F Stebbings and Dr K A Smith (Rice University), Dr R M Hill (SRI), Professor P M Koch (Yale University), Dr A Chutjian (Jet Propulsion Lab.) and Dr S R Hunter (ORNL). This work was supported by the University of Bielefeld and the Deutsche Forschungsgemeinschaft.

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