Intermediate-energy total cross sections for electron scattering on WF$_6$

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Total cross sections for electron scattering on WF$_6$ molecules have been measured in the 75–3500-eV energy range by an absolute transmission method. The data are compared to other heavy gases, SF$_6$, Xe, and GeH$_4$. Apparently different energy dependencies for these gases can be described by the same, simple four-parameter formula. A study of atomic total-cross-section parameters in the keV energy range for 15 atoms from H to W is presented.

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Studies of electron scattering on heavy targets at intermediate energies are important for modeling thin-film deposition, plasma etching and doping in the semiconductor industry [1], and electron implantation processes [2]. In particular, tungsten hexafluoride (WF$_6$) is used as source of W atoms for tungsten [3] and tungsten silicide films [4]. To our knowledge, no electron-scattering cross sections have been measured for WF$_6$ or W. As far as we know, only electron-impact ionization of W^{q+} ions, with $q=1,...,10$, has been studied [5]. We are not aware of any theoretical calculation for the WF$_6$ total cross section (TCS).

Another reason to study heavy targets by electron scattering is a search for possible scaling laws for cross sections vs atomic number Z [6,7] or polarizability [8]. The lack of experimental data hinders validation of those models. To our knowledge, TCS measurements for heavy atoms in the gas phase are limited to Xe for energies up to 4000 eV [9] and Hg up to 300 eV [10]. To our knowledge, few calculations of TCS for targets like Pb and Ge exist [11].

In our previous work [12] for ten molecular targets we showed how the atomic TCS can be estimated from experimental molecular cross sections via an additivity rule [13]. Therefore, measurements on WF$_6$ would possibly determine the atomic-tungsten TCS or, at least, define an upper limit on it. As many as 33 targets measured in our laboratory on the same apparatus prompted systematic comparisons. In this paper we present experimental data for WF$_6$ at 75–3500 eV and a comparative analysis of TCS for different targets in the keV energy range.

A modified Ramsauer-like apparatus, described previously [14], has been used to perform the present measurements. A beam-attenuation technique in the scattering cell has been adopted. The total cross section σ vs collision energy E has been evaluated from the de Beer–Lambert formula

$$\frac{I_{C1}}{I_{C1}+I_{S1}} = \frac{I_{C2}}{I_{C2}+I_{S2}}\exp[-\sigma(E)L(N_1-N_2)], \qquad (1)$$

where $I_{C1,2}$ and $I_{S1,2}$ are, respectively, the collector and the scattering currents measured at two different pressures, L is the path length of electrons in the scattering chamber, and

$N_{1,2}$ are the gas densities corresponding to these pressures. Both the scattering cell and collector currents (I_S and I_C) were measured in order to reduce any beam instability effects. The total cross section in a run was determined from $\ln(I_{C,i})/\ln(I_{Ci+1})$ ratios and from a slope coefficient of $\ln(I_C)$ vs p for 6–8 pressure values. The Baratron head temperature was tracing the gas cell temperature within 0.1 °C, a single electrometer was used to measure both currents, and several other measures were taken to assure good beam stability and repeatability of runs. Due to the highly corrosive nature of WF$_6$, only two to eight runs were performed at each energy. This has led to a somewhat higher statistical error bar of the present data (typically 4%) compared to our earlier measurements [15]. The overall systematic uncertainty, apart from the angular resolution error, was within 3%. The pressure meter calibration and nonlinearity of the current meter are potentially the main sources of the systematic error.

Special attention has to be devoted to the handling of the highly poisonous and corrosive WF$_6$ gas. All the apparatus and the gas line were constructed of stainless steel. Nevertheless, some solid deposits were spotted after measurements inside gas-dosing valves. The rotary pumps were ballasted with N$_2$ during the measurements and this prevented damage. However, one of the turbo pumps, equipped with ceramic bearings, underwent a failure shortly after the WF$_6$ measurements. The reduced pump life has been attributed to the action of the gas on the bearings.

An intrinsic error of the attenuation method causes an underestimation of the measured total cross sections at high energies. The error is due to forward scattering into small angles within the angular acceptance of the detector. The average angular acceptance of the present apparatus is 0.34 m sr. At a given energy in the Born-approximation range [16], a required correction is higher for light gases and polar molecules and its relative value rises linearly with energy. To estimate the magnitude of the angular resolution error and the consequent correction, the differential cross sections of the target molecule should be known. We are not aware of any theoretical or experimental differential cross sections for WF$_6$, therefore, we have not corrected our measured data for the angular resolution error.

A rough estimate of the angular resolution error can be made only by comparison with other gases, for which the correction is known. For CH$_4$ we estimated the possible angular resolution error as 1% in the elastic channel and a few
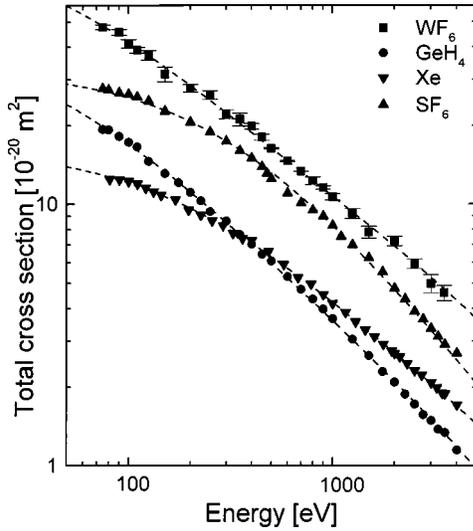
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FIG. 1. Total cross sections for electron scattering on heavy targets. Present experimental data for WF_6: error bars correspond to one standard deviation of the mean value; Xe [9]; GeH_4 [24]; SF_6 [18]; broken lines, present semiempirical fit [Eq. (3)]; parameters given in Table I.

percent in the inelastic channel at 3000 eV [17]. In SF_6 measurements [18] we evaluated the error due to the elastic scattering to be less than 0.5% at 700 eV. An indirect evaluation of our angular resolution error can be done by comparison with other experiments. In SF_6 at 500 eV our data was 7% higher than that of Dababneh *et al.* [19] measured with an angular resolution roughly one order of magnitude poorer than the present one. On the other side, the best angular resolution (4×10^{-5} sr for elastic scattering) is achieved by the apparatus of García, Arqueros, and Campos [20]. The discrepancy between measurements made with the present apparatus and those of Garcia and collaborators amounted to 5% in Ar [14,20] and 10% in N_2 [21,22] at 3000 eV. Probably, the largest part of this discrepancy is to be attributed to inelastic scattering, more important in light targets than in heavy ones [23]. For the heavy, nonpolar WF_6 molecule a possible correction of our data for the angular resolution error should be closer to the one for Ar than for N_2. Therefore, we believe that the overall angular resolution corrections of the present data at 3000 eV should be less than 10%.

The present results for WF_6 together with their statistical errors are shown in Fig. 1. The WF_6 cross section falls by one order of magnitude in the investigated energy range from about 47×10^{-20} m^2 at 75 eV to 4.6×10^{-20} m^2 at 3500 eV. No shoulder or resonant structures can be distinguished outside the statistical error bar in the monotonic fall of the cross section. In Fig. 1 we present also our previous results for other heavy gases, SF_6 [18], GeH_4 [24], and Xe [9]. At low energies the WF_6 cross section exceeds that of GeH_4 by a factor of roughly 2.5; this ratio rises to more than three at 3 keV. On the other hand, the relative difference between WF_6 and Xe diminishes between 75 eV and 3 keV. In the high-energy limit the slopes of the total-cross-section curves $\sigma(E)$ for Xe and WF_6 become similar. The SF_6 total cross section at 75 eV is 70% smaller than the one of WF_6. This difference

is as little as 30% at 1000 eV and rises again to 60% at 3500 eV. Apparently, the four gases considered show different dependencies of TCS on energy.

We have proved previously [15,18] that a simple formula

$$\sigma = \frac{\sigma_0 b}{b + \sigma_0 E} \qquad (2)$$

can be useful for the parametric description of the TCS energy dependence at intermediate energies. The σ_0 parameter in Eq. (2) is a low-energy constant-value $\sigma(E \to 0) = \sigma_0$ cross section and b is the proportionality coefficient in the asymptotic high-energy dependence $\sigma(E \to \infty) = b/E$. Formula (2) allows us to approximate TCS well above, roughly, 30–100 eV for hydrides [15], diatomic [21], and triatomic [25] molecules. For some targets, like heavier noble gases Kr and Xe [26] or chlorofluoromethanes [27] two additional parameters should be used, yielding the relation

$$\sigma = \frac{1}{A(B+E)} + \frac{1}{C(D+E)}$$

$$+ \frac{2}{E}\left(\frac{BD}{AC}\right)^{1/2} \frac{1}{|B-D|} \left| \ln \frac{\frac{E}{D}+1}{\frac{E}{B}+1} \right|. \qquad (3)$$

A logarithmic term in Eq. (3) appears in analogy to the elastic cross section for scattering on a double Yukawa potential in the Born approximation [28].

Parametrization of TCS allows us to reduce the statistical spread of data. It also permits us to extrapolate TCS towards high, experimentally nonaccessible energies. As discussed before, for the four targets in Fig. 1, at arbitrarily chosen energies the TCS dependencies show different slopes. Therefore, analysis of the cross-section parameters should potentially give more insight than comparisons of measured or calculated values at separate points [29]. Obviously, the choice of the approximating formulas is arbitrary and the derived parameters depend on this choice. In Table I we give the parameters obtained by fitting Eq. (3) to the data for the four targets presented in Fig. 1. The parameters of the fit were obtained by minimizing the sum of squares of these differences. Minimizing the relative differences has the advantage of giving correct statistical weight to cross sections at low- and high-impact energies. The cross-section values calculated with Eq. (3) and Table I lie very close to the measured values. The mean percentage differences amount to 1.0% for Xe and 2.5% for WF_6 and remain within the experimental uncertainties. The SF_6 molecule necessitates only two fitting parameters [18].

Using formula (3), the high-energy coefficient equivalent to b in Eq. (2) and the low-energy saturation value σ_0 read, respectively,

$$b = \frac{1}{A} + \frac{1}{C} + \frac{2}{|B-D|}\left(\frac{BD}{AC}\right)^{1/2}\left| \ln \frac{B}{D} \right|, \quad \sigma_0 = \frac{1}{AB} + \frac{1}{CD}. \qquad (4)$$

TABLE I. Semiempirical parameters A, B, C, and D of the fit Eq. (3) for heavy gases, and asymptotic values b and σ_0 calculated from the fit parameters using the formula (4). Cross sections are taken in 10^{-20} m^2 and energies in keV. Parameters of the fit for Xe and SF_6 are from Refs. [26] and [18], respectively. In the last column the mean relative difference between the experimental values and the fit is reported.

Gas	A	B	C	D	b (m^2 keV)	σ_0 (10^{-20} m^2)	Mean difference
WF_6	0.520	0.028	0.076	1.72	20.5	76.8	2.5%
GeH_4	0.956	0.031	0.429	1.16	5.3	35.3	1.1%
Xe	0.407	0.219	0.101	20.2	16.8	11.7	1.0%
SF_6	0.091	0.334			11.0	33.2	2.1%

The values of σ_0 and b for the four targets presented in Fig. 1 are given in Table I. In the preceding work [12] we compared the ''low-energy'' σ_0 parameter to the molecular polarizability α. A direct dependence of the σ_0 parameter on the molecular polarizability is confirmed also by the measurements for WF_6 (see Table I). A quantitative comparison [12] is not possible anyway, as we are not aware of the exact polarizability value for WF_6. At high energies the electrostatic interaction dependent on the atomic number Z dominates over dynamic (polarizability) effects. Therefore, the high-energy parameter b should be suitable for studies of any possible Z-scaling law.

In the following we will give a discussion of the Z dependence of the b parameters for 15 atoms. Atomic cross sections were obtained from direct measurements performed in our laboratory (noble gases) or by applying an inverted additivity rule [12] to measured molecular cross sections. The choice of using the data measured in our laboratory has been dictated by the need to have a homogeneous data set. One of the simplest theoretical calculations of atomic cross sections, giving an explicit Z scaling, is the one describing the elastic scattering in the Born approximation within the Thomas-Fermi atomic model [30]:

$$\sigma_{el} = 7.14\pi \frac{Z^{4/3}}{k^2}. \tag{5}$$

In Eq. (5) the cross section is expressed in atomic units a_0^2, $k^2 = 2E/m$, and m is the electron mass.

In Fig. 2 we compare the b parameters for 15 atoms. Note a nonlinear abscissa axis, corresponding to the $Z^{4/3}$ scaling. The broken line in Fig. 2 corresponds to the theoretical dependence of the b parameter on $Z^{4/3}$ given by Eq. (5). For H, C, F, Si, S, and Cl atoms the b values obtained in [12] are used. The parameters for noble gases have been extensively discussed in Ref. [26]. The b values for N (1.09×10^{-20} m^2 keV) and O (1.18×10^{-20} m^2 keV) have been determined through the additivity rule [12] starting from the NH_3 and H_2O cross sections [15], respectively. The b parameter of the WF_6 molecule amounts to 20.5×10^{-20} m^2 keV and can be considered as an upper limit for the b parameter for the W atom. An asymmetric error bar of about $+20\%$ and -10% has to be associated with this value. This error is due to the overall experimental uncertainty (the angular resolution included) and in part is influenced by the limited energy

range of the present measurements. Applying our additivity rule to the WF_6 parameter, i.e., subtracting the value of $6b_F = 8.1 \times 10^{-20}$ m^2 keV [12] of the six fluorine atoms, one gets $b_W = 12.4 \times 10^{-20}$ m^2 keV, i.e., the lower limit for the W atom. The lower limit for the Ge b value, 4.34×10^{-20} m^2 keV, has been obtained from GeH_4 measurements [24] using the b value for H [12]; the upper one is determined by the GeH_4 b value.

Note that at low Z, the b parameters for the 11 atoms presented (in the range from H to Ar) lie approximately on a straight line, quite close to the Thomas-Fermi dependence, Eq. (5). The Xe b value, and also the upper limit for the W atom are placed near the Thomas-Fermi elastic-cross-section line. The Ge and Kr atoms lie below this dependence, out-
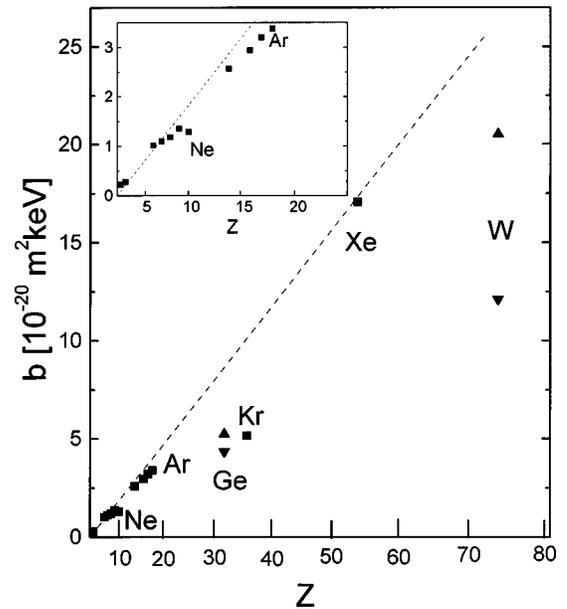

FIG. 2. Study of the Thomas-Fermi dependence for total cross sections. The high-energy parameter b [Eq. (4)] is plotted vs atomic number Z. Full points, atoms; noble gases, Ref. [26]; for other atoms the cross section parameter b has been obtained via the additivity rule [12] from experimental molecular cross sections—H_2 (unpublished, see [23]), CH_4, NH_3, H_2O, SiH_4, H_2S [15], CF_4, CCl_4 [27]. Triangles and inverted triangles: upper (molecular) and lower (additivity rule) limits, respectively, for Ge [24] and W (present results). Broken line, theoretical Thomas-Fermi Born dependence for elastic cross section, Eq. (5). Note a nonlinear abscissa scale, corresponding to $Z^{4/3}$.

side the uncertainty limits of the present analysis. This is somewhat surprising, as these rather heavy atoms should be well described by the statistical, Thomas-Fermi model. We can guess that the dependence of b on Z could be nonmonotonic but more experimental data between Ge and W are needed to validate this supposition. Note additionally some incongruity with possible partitioning schemes for TCS: the points in Fig. 2 lie close or even below the Thomas-Fermi line. Taking into account that inelastic scattering constitutes $\frac{1}{3}$ or more of TCS in the keV energy range [23], Fig. 2 suggests that the Thomas-Fermi model overestimates atomic elastic cross sections, as probed by electron scattering.

The present discussion of possible scaling laws for TCS is limited by the low number of targets for which TCS data is available. In order to achieve a narrower confidence bar on this type of analysis, several improvements would be required. From the experimental side, extending measurements to higher energies, lowering the angular resolution error, and enlarging the molecular database by performing experiments on such targets as SbH_4, TeH_2, and CH_3I are desirable. This in turn should allow formulation of more accurate models.

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