

Electron collisions with trifluorides: BF_3 and PF_3 molecules

Czesław Szmytkowski, Michał Piotrowicz, Alicja Domaracka, Łukasz Kłosowski, Elżbieta Ptasinska-Denga, and Grzegorz Kasperski

Atomic Physics Group, Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, ul. G. Narutowicza 11/12, 80-952 Gdańsk, Poland

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Absolute total cross sections (TCSs) for electron scattering from boron trifluoride (BF_3) and phosphorus trifluoride (PF_3) molecules have been measured using a linear transmission method. The electron energy ranges from 0.6 to 370 eV for BF_3 and from 0.5 to 370 eV for PF_3 . The TCS energy dependence for BF_3 exhibits two very pronounced enhancements: resonantlike narrow feature located near 3.6 eV with the maximum value of $19.2 \times 10^{-20} \text{ m}^2$, and intermediate energy very broad enhancement with two humps, one centered around 21 eV ($18.8 \times 10^{-20} \text{ m}^2$ in the maximum) and the other near 45 eV ($19.5 \times 10^{-20} \text{ m}^2$). For PF_3 the TCS has quite different low-energy dependence: at 0.5 eV it has a high value of $70 \times 10^{-20} \text{ m}^2$ and decreases steeply towards higher energies. Beyond the minimum near 5.5 eV, the TCS reveals two distinct humps: the resonant one centered near 11 eV with the peak value of $32.9 \times 10^{-20} \text{ m}^2$ and the second one much broader around 35 eV ($27.9 \times 10^{-20} \text{ m}^2$). The present TCSs for trifluorides are compared to each other as well as to previous TCS data for selected perfluorides and to results for their perhydryd counterparts. The differences and similarities in the shape and magnitude of TCSs are pointed out. © 2004 American Institute of Physics. [DOI: 10.1063/1.1766297]

I. INTRODUCTION

The continuing interest in the investigation of the electron-molecule interactions arises from the contribution of electron-assisted processes towards understanding and modeling phenomena underlying many of today's advanced technologies.¹ In addition to the practical interest, electron-scattering data are of fundamental theoretical importance.²

The present work dealing with BF_3 and PF_3 molecules, is one in an extended series of our studies focused on determining the total electron-scattering absolute cross sections for perfluorinated compounds; they are widely used in electrical industries, plasma assisted fabrication of microcircuits, surface hardening, in agriculture, and medicinal fields. For example, BF_3 is primarily used in neutron counters,^{3,4} while more recently has been considered as the alternative agent for plasma doping⁵ and for metal surface treatment.⁶ PF_3 is suggested to be a useful reagent for the gas-phase synthesis and as a replacement for PH_3 applied to date in microelectronic technology.

Boron trifluoride has been studied previously in a variety of electron-impact experiments. They started with electron diffraction investigations.⁷ Later, the formation of positive ions^{8–16} and negative fragments^{11,13,14,16–21} in the electron beam and electron swarm measurements have been intensively studied. Much less work refers to electron-impact excitation of electronic¹⁹ and vibrational²² levels of BF_3 molecule. Spectrometric experiments provided information on the energy location and abundances of the ionic species; however, the obtained intensities of observed phenomena were mostly in relative units, which alone makes difficult their application for modeling of electron stimulated processes or comparison with theoretical calculations. Absolute

measurements were reported so far for electron transport and rate coefficients,^{13,16} electron-impact ionization,¹⁴ and dissociative electron attachment^{14,20,21} cross sections. Theoretical works on e^- - BF_3 processes are yet scarce and concern the calculations of the electron-impact ionization cross section using different formalisms^{23,24} and the study of the elastic electron scattering at low energies.²⁵

In contrast to BF_3 , the study of electron-impact from PF_3 molecule has received much less attention. Electron diffraction patterns were used for the study of PF_3 structure.²⁶ Later investigations concerned the formation of positive and negative ions from PF_3 in the gas phase.^{17,27,28} More recently, electron stimulated desorption of positive and negative ions from PF_3 adsorbed on metal surfaces has been also studied.^{29,30} Theoretical works on e^- - PF_3 scattering are yet not available in the literature.

We are unaware of any total electron-scattering cross-section measurements or calculations for either BF_3 or PF_3 . That deficiency of quantitative cross sections for the electron scattering from BF_3 and their complete scarcity in the case of PF_3 molecule motivated us to measure the absolute total electron-impact cross sections for both aforementioned targets. It would be also interesting to examine how the difference in the structure of these target molecules is reflected in the shape and magnitude of their TCS energy dependence. The *grand* total cross section measured in this work is the sum of the integral cross sections for all scattering channels, therefore the subtle features visible in the energy dependence of cross sections for particular channels are in the TCS energy function apparently smoothed out or even blur. However, the TCS can be measured without any normalization procedure, and among variety of quantities describing the scattering, is one of the most reliable. In consequence, it can

be used as quantitative test of theoretical models and/or computational procedures. Accurate TCS data can be also useful for normalization or estimation of the upper limit of cross sections obtained for specific electron-induced processes in relative units only or for those difficult to obtain. The regularities and structures discerned in the TCS energy function may be also a stimulus for further more detailed investigations. Moreover, due to their accuracy, reliable sets of TCS data, especially those obtained in the same laboratory, can be helpful in comparative studies and may give some insight into mechanisms of the scattering.

II. EXPERIMENT

To determine electron-scattering TCS we have used the transmission method in a linear configuration which relates cross section at given energy to the transparency of the gas target at a given pressure for a beam of electrons.³¹ The experimental procedure and apparatus used in the present work have been described in detail earlier.³² In brief, the electron beam of desired energy E , with an energy spread of 80–90 meV (full width at half maximum), is formed in an electron optics system with a cylindrical electrostatic deflector as monochromator and then injected into scattering chamber. Electrons leaving the reaction volume are energetically discriminated and eventually detected by a Faraday cup. The attenuation of the incident electron current, passing through the volume filled with the target molecules, as measured at the detector is related to the total cross section $Q(E)$ using the Bouguer–de Beer–Lambert (BBL) formula

$$I(E, n) = I(E, 0) \exp(-Q(E)nl),$$

where $I(E, n)$ and $I(E, 0)$ are the transmitted electron intensities measured in the presence and absence of the target molecules in the scattering cell. The other measured quantities necessary for TCS derivation are the effective path length l of impact electrons through the target and absolute target number density n obtained from the ideal gas law based on absolute measurements of the target pressure in reaction volume and the target temperature; the pressure readings were corrected for the thermal transpiration effect.³³ The target pressure in the scattering cell ensures the single-collision conditions. The experimental energy scale was calibrated by reference to the oscillatory structure observed in the transmitted current around 2.3 eV after the admixture of N_2 .

The measurements at given energy were carried out in a series (4–13) at different target pressures. It was found that the TCSs obtained in different series at the same energy were, within the statistical experimental variations, independent of the intensity of the electron beam (0.1–40 pA) and the applied target pressure (50–200 mPa). The mean TCS values from different series of individual runs (6–10 in a series) at the same energy were averaged and weighted according to their uncertainties, giving the final total cross section value. The TCS uncertainty of a random nature (one standard deviation of the weighted mean value) is found to be about 1%–2% for BF_3 and does not exceed 1% for PF_3 over the whole energy range used. The accuracy of the resulting TCS is mainly determined by the possible systematic

uncertainties of the experimental procedure which may affect the measurements of quantities in BBL formula. These uncertainties are difficult to estimate and even difficult to recognize. Therefore, the conceptually simple problem of determining a TCS through direct measurements of a few physical quantities becomes a difficult task when one wishes to obtain the TCS of great accuracy. There are two principal sources of uncertainty in determining the TCS magnitude using the transmission method. One of the serious problems arises from the inability to discriminate against electrons which are scattered elastically through small angles in the forward direction. The lack of such discrimination tends to lower measured cross sections; the effect increases for polar molecules and/or at higher electron energies. The value by which the present TCS may be too low can be estimated if the angular distribution (experimental or theoretical) of elastically scattered electrons is known. Differential cross sections (DCSs, theoretical) are available only for BF_3 molecule at low energies from 5 to 40 eV.²⁵ Based on these data we found that underestimation of e^- - BF_3 TCS obtained in the present experiment does not exceed 0.8% below 40 eV and, we believe it should be underneath 2% at the highest energies applied. No such DCS data (experimental or theoretical) are as yet available for PF_3 molecule. Rough estimation, based on respective data available for other weakly polar targets, gives value 1%–2% at low impact energies and about 2%–4% at high energy. The present TCS data are not corrected for this effect. Another uncertainty, encountered in the transmission experiment, is related to determination of the factor nl in the BBL formula. The effusion of the target particles through orifices of the scattering cell leads to inhomogeneity of target-molecules distribution in the reaction volume, and also to a notable presence of molecules outside the cell apertures. However, calculations (adopted from Ref. 34) show that the end effects in the present experiment are nearly balanced and do not exceed 1%; the resulting uncertainty of the factor nl is about 2%. The overall systematic uncertainty in the measured TCSs, estimated as a direct combination of potential systematic errors of measured individual quantities used for TCS derivation, amounts to about 7%–8% below 1.5 eV, decreasing to 4%–5% between 5 and 100 eV, and increasing to 6%–7% at the highest energies applied. The increase of uncertainty at the lowest applied energies is partly related to the electron current drift.

Commercially supplied from Aldrich samples of BF_3 (99.5%) and PF_3 (99%) were used without further purification.

III. RESULTS AND DISCUSSION

In this section we present our total electron scattering cross sections for the boron trifluoride (BF_3) and for phosphorus trifluoride (PF_3) molecules. The TCSs were measured in the transmission experiment over energy range from 0.6 to 370 eV for BF_3 and between 0.5 and 370 eV for PF_3 . We are not aware of any reports on the measurements or calculations of TCS for the targets studied. Similarities and differences of TCS energy functions are also pointed out and discussed.

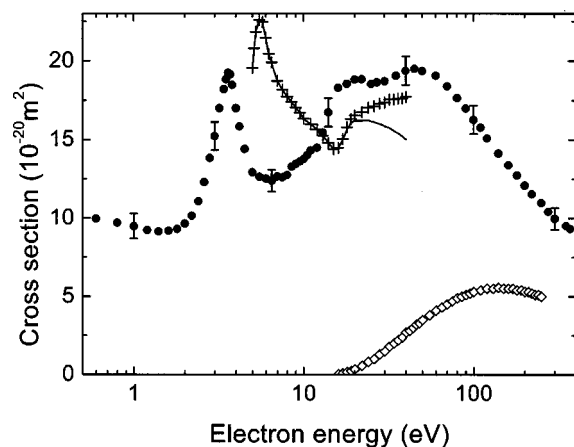


FIG. 1. Cross sections for e^- - BF_3 scattering. Experimental data: present TCS (closed circles), error bars denote overall (systematic plus statistical) uncertainties; ionization total cross section from Ref. 14 (open diamonds). Calculated integral elastic cross section, Ref. 25 (full line). The crosses (+) represent the sum of elastic and ionization cross sections used for comparison with the present experimental TCS.

A. Boron trifluoride, BF_3

Figure 1 shows absolute total cross section for electron scattering from BF_3 measured at energies from 0.6 to 370 eV. As other electron-impact TCS data for BF_3 are not available, for comparison the sum (“total” cross section) of calculated elastic integral cross section²⁵ and experimental electron-impact ionization total cross section¹⁴ is presented. As seen from Fig. 1, the overall energy dependence of the “total” cross section is quite similar to the present experimental TCS.

The magnitude of TCS for BF_3 is relatively low and varies from about $9 \times 10^{-20} \text{ m}^2$ at both ends of energy range applied to nearly $20 \times 10^{-20} \text{ m}^2$ at the TCS maxima. Two prominent enhancements in the TCS energy function, of similar magnitude but quite different in their extent on the energy scale, are visible. The first resonantlike enhancement is peaked near 3.6 eV with the value of $19.2 \times 10^{-20} \text{ m}^2$. This narrow ($\Delta E \sim 1.6 \text{ eV}$) structure can be related to formation of the temporary parent anion state (resonance) when the impinging electron of proper energy is accommodated to the lowest virtual molecular orbital. The resonant state decays either throughout dissociation, involving the formation of neutrals and negative fragment, or via competitive autodetachment channel which leaves the parent molecule in one of its vibrational states. Support for the resonant origin of the 3.6 eV peak comes from the experiment of Tronc *et al.*²² in which they observed a distinct out-of-plane deformation and stretching of BF_3 molecule, stimulated by near 3.8 eV electrons. Such pronounced vibrational excitation of the parent molecule is primarily related to differences in geometry of the BF_3 molecule and its transitory anion (BF_3^-)*; while the parent molecule has a planar symmetric geometry in its electronic ground state, the anion is rather trigonal pyramid. The appearance of low-energy resonant phenomenon results also from elastic calculations of da Costa *et al.*²⁵ The resonant maximum in the calculated cross section (Fig. 1) is, as a matter of fact, shifted by almost 2 eV to higher energy (about

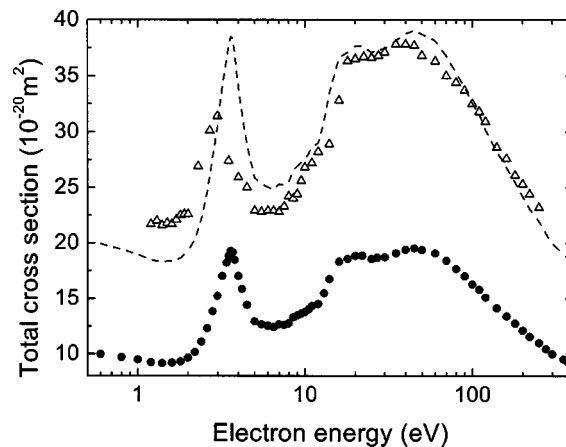


FIG. 2. Comparison of TCS for e^- - BF_3 scattering (closed circles) with the TCS for WF_6 (open triangles) from Ref. 38. For better illustration of shape similarities the TCS for BF_3 is also multiplied by the factor of 2 (dashed line).

5 eV). This discrepancy to the present resonance location is not surprising having neglected the long-range polarization contributions in the calculations. Accounting for deformation of molecular electron cloud by the projectile electron could lead to a substantial decrease in the resonance energy.³⁵ Comparison of calculations with experimental TCS suggests that the elastic channel at low energy may be predominating but, on the other hand, it also clearly indicates that the elastic results in the region of resonance are noticeably overestimated. That discrepancy could be lessened if vibrations of the nuclei were included in the calculations.³⁶

Near 6.5 eV the TCS curve exhibits a deep minimum ($12.4 \times 10^{-20} \text{ m}^2$). Over this energy a very broad enhancement dominates with two discernible humps. The first weak hump has maximum value of $18.8 \times 10^{-20} \text{ m}^2$ around 21 eV, while the second, much broader, is peaked near 45 eV with the value of $19.5 \times 10^{-20} \text{ m}^2$. Above 50 eV, the TCS for e^- - BF_3 scattering is monotonically decreasing function of energy. Due to lack of quantitative data for specific scattering channels allowed in the 20–100 eV energy region, it is yet not clear which particular processes are responsible for such broad intermediate-energy TCS enhancement. Partitioning of available experimental TCSs for other perfluorides into elastic and inelastic scattering channels suggests, however, that the intermediate TCS enhancement, common for all perfluorinated molecules studied so far, may be mainly due to elastic scattering.³⁷

In addition to the aforementioned structures, two weak TCS features are discernible: around 1.4 eV a weak Ramsauer-like minimum is located, while around 12 eV, on the left-hand side of the broad enhancement, some change of the slope is visible; the latter feature may be related to another resonant state created near 11.5 eV.^{11,14,17–22}

Looking for some regularities in TCS energy functions we compared the available TCSs for perfluorinated molecules and we have noticed that the TCS for BF_3 very closely resembles in shape the TCS energy function for another highly symmetric perfluoride WF_6 (Fig. 2).³⁸ Regarding the magnitude, the TCS values for WF_6 are nearly twice higher than these for BF_3 in the whole overlapping energy

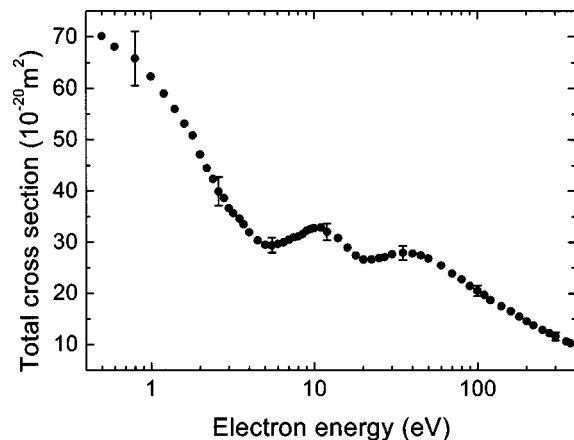


FIG. 3. Absolute TCS for electron scattering from PF_3 molecule. Error bars represent overall (systematic plus statistical) uncertainties.

range, 1–250 eV. Incidentally, this proportion is equal to the ratio of number of fluorine atoms in WF_6 and BF_3 molecules. For the explanation of this peculiar finding, the scattering calculations would be desirable.

B. Phosphorus trifluoride, PF_3

The absolute total cross section for PF_3 measured in the electron energy range from 0.5 to 370 eV is displayed in Fig. 3. No quantitative experimental or theoretical e^- - PF_3 cross sections are yet available for comparison.

The most striking feature of the measured e^- - PF_3 total cross section is its high magnitude at the lowest energies used. Below 5 eV, as the collision energy becomes smaller, the cross section steeply increases, it shows a very weak structure around 3.2 eV, and at 0.5 eV it reaches a value of $70 \times 10^{-20} \text{ m}^2$. Such significant increase of low-energy TCS towards zero energy is rather common for highly polar molecules (e.g., H_2O) and is explained through long-range direct contribution.³⁹ In the case of PF_3 the long-range interaction can hardly be the only reason for the low-energy TCS behavior because the PF_3 molecule has rather low permanent electric dipole moment (Table I). Low-energy TCS dependence for PF_3 cannot be also simply related to the presence of three fluorine atoms. TCSs measured for series of polar molecules containing three fluorine atoms [CF_3H and CF_3X ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)]⁴⁰ demonstrate markedly different low-energy dependence and magnitude than those for PF_3 : (i) the increase of TCS as the electron energy approaches 0 eV for trifluoromethane and trifluorohalomethanes is much steeper and it starts at much lower energy than for PF_3 and, (ii) the TCSs for substituted methane derivatives are distinctly lower be-

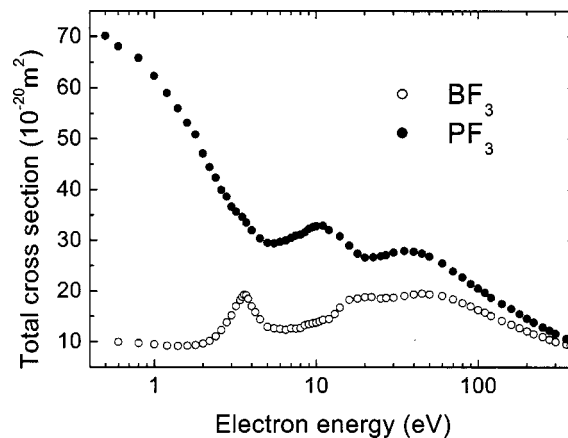


FIG. 4. Comparison of electron impact TCSs for BF_3 and PF_3 .

tween 0.5 and 2 eV. On the other hand, very similar trend of the low-energy TCS curve—like that for PF_3 —was noticed also for nonpolar perfluoride GeF_4 .⁴¹ Strong increase of cross section, however at near-zero energy, was observed for another nonpolar perfluorinated molecule SF_6 , and was explained in terms of metastable parent negative-ion formation.¹ Concluding, the origin of the low-energy e^- - PF_3 TCS behavior still requires further intense investigations. The same is called for GeF_4 .

Close to 5.5 eV, the TCS exhibits local minimum followed with marked enhancement centered near 10–11 eV with the peak value of about $33 \times 10^{-20} \text{ m}^2$. Experiments on the electron attachment to PF_3 molecule^{17,27,28,30} show that between 10 and 13 eV various negative fragments are produced with PF_2^- , PF^- , and F_2^- as dominant ions and most likely indicate that the 10–11 eV feature is a manifestation of the resonant state created in this energy range. Beyond the minimum at 21 eV, a very broad hump centered near 35 eV is visible. Above 40 eV the TCS monotonically decreases with the energy increase and falls down to $10.3 \times 10^{-20} \text{ m}^2$ at 370 eV.

In Fig. 4 the total cross section energy dependence for PF_3 is compared to that for BF_3 . Some differences and similarities in the shape and magnitude of both measured in this work TCSs molecules are worth specification. The most spectacular TCS features appear at low impact energies as given below:

(i) Below 25 eV the TCSs curves for PF_3 and BF_3 look antipathetic to each other—while at given energy range the PF_3 curve increases that for BF_3 decreases and vice versa. That behavior is difficult to explain through direct comparison of parameters describing electron-molecule interaction (Table I). The charge distribution of the target molecule (permanent electric dipole moment), deformation of the molecular charge by the approaching electron (electric polarizability), number of valence electrons, and simply the molecular geometry (the BF_3 is in its electronic ground state a planar and symmetric while PF_3 is a trigonal pyramid) or the target size are not enough to estimate the behavior of the low-energy TCS curve. The observed differences are rather attributed to more subtle structural properties that can be singled out in the sophisticated theoretical studies.

TABLE I. Molecular electric dipole moments μ , electric dipole polarizabilities α , and the gas-kinetic cross sections σ .

Molecule	μ (Debye) ^a	α (10^{-30} m^3)	σ (10^{-20} m^2) ^b
BF_3	0	3.31 ^a	9.66
PF_3	1.03	4.43 ^c	10.9

^aReference 45.

^bEstimated from van der Waals constant b (Ref. 45).

^cReference 46.

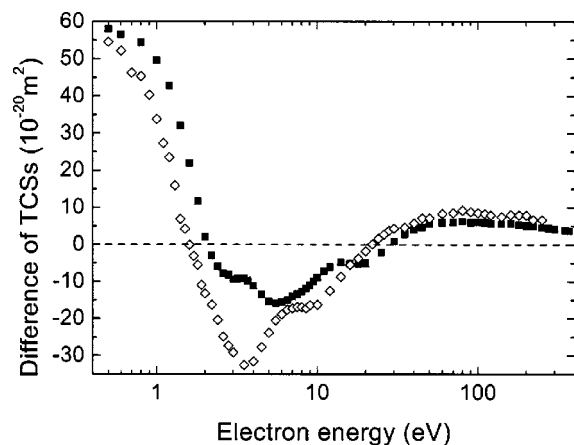


FIG. 5. Illustration of perfluorination effect. The filled squares represent the difference of TCS for PF_3 and TCS for PH_3 (from Ref. 43). For comparison, the difference (open diamonds) of TCSs for GeF_4 (Ref. 41) and GeH_4 (Ref. 44) is also included.

(ii) From ionization threshold towards higher energies, the differences in the shape and magnitude of TCSs remarkably decrease. The magnitude of TCS becomes nearly proportional to geometrical size of target molecule. Above 50 eV the energy dependences can be described with the function $Q(E) \sim E^{-0.5}$; such an energy dependence means that the cross section at given energy is proportional to the time the electron needs for traversing the geometrical size of molecule. Calculations with the use of the additivity rule⁴² suggest that at higher energies the TCS for molecule is less sensitive to geometrical arrangement of constituent atoms and reflects rather their individual size. Therefore the observed difference in TCSs for both trifluorides at intermediate energies seems to be mainly related to difference in size of phosphorus and boron atoms. In the range 300–370 eV, the ratio of TCSs for PF_3 and BF_3 is nearly 1.1, the value being equal to the ratio of gas-kinetic cross sections for these molecules (see Table I).

To demonstrate how the substitution of fluorine atoms for hydrogen influences the electron scattering, we present in Fig. 5 the difference of the experimental TCS for e^- - PF_3 scattering and the respective data for e^- - PH_3 .⁴³ It is evident that the perfluorination changes substantially the magnitude and shape of TCS over the entire energy range studied. Regarding the influence of perfluorination on the magnitude of TCS, three distinct energy regions can be discerned: (i) below 1.7 eV the TCS for e^- - PF_3 scattering is considerably higher than that for PH_3 , (ii) between 2 and 25 eV the TCS for PF_3 is distinctly lower than TCS for PH_3 , while (iii) over that energy, at intermediates, the ordering of compared TCSs changes again—the electron scattering from PF_3 becomes more effective. Similar behavior of TCSs for another pair of molecules, GeF_4 and GeH_4 , is also shown in Fig. 5 for comparison. Up to date studies suggest that such relation of TCSs is typical for all pairs of perhydrides and their perfluorinated counterparts, although at the lowest energies the differences are usually an order of magnitude lower than those presented in Fig. 5.

IV. CONCLUDING REMARKS

We have measured the absolute total electron-scattering cross sections for BF_3 and for PF_3 molecules in a transmission experiment from low to intermediate energies. The TCS for BF_3 shows two pronounced enhancements: the resonant-like narrow peak centered near 3.6 eV and a very broad hump superimposed with two weak features located around 21 and 45 eV. The low-energy TCS for e^- - PF_3 scattering has entirely different low-energy dependence: below 5 eV it increases steeply towards lowest applied energies, while near 11 eV the weak resonant enhancement is visible. With respect to the shape, above 20 eV, both TCSs resemble each other as well as the TCS curves for other perfluorides: they all have a very broad enhancement centered around 40 eV with some additive weak features. Comprehensive understanding of the observed TCS behavior needs further detailed experiments as well as theoretical studies. A comparison of the TCSs for PF_3 and for PH_3 reveals distinct perfluorination effect over entire impact energy range studied.

ACKNOWLEDGMENTS

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