Electron collisions with boron trichloride (BCl₃) molecules

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Abstract: Absolute total cross section (TCS) for electron scattering by boron trichloride (BCl₃) molecules has been measured in a linear transmission method under single collision conditions. Measurements have been performed within electron energy range from 0.3 to 370 eV. The TCS energy function for BCl₃ is dominated with very pronounced enhancement peaked near 10 eV (61×10⁻²⁰ m² in the maximum). Low-energy slope of the enhancement is superimposed with two resonant-like structures located near 3.2 and 6.0 eV. On the descending high-energy side of the TCS curve only a weak shoulder between 30 and 60 eV is discernible. The present TCS is compared with the existing experimental and calculated cross sections for particular e⁻-BCl₃ scattering processes. Furthermore, the TCS for BCl₃ is also confronted with the TCS for BF₃ and the role of peripheral atoms in molecule is indicated and discussed.

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I. INTRODUCTION

Boron trichloride is extensively used in the industrial applications to materials processing (plasma-enhanced etching [1], deposition and/or doping of boron [2]) and in organic synthesis [3]. For thorough understanding, modeling and controlling undergo phenomena in plasma processing mixtures containing BCl₃, comprehensive sets of reliable cross sections and reaction rates for processes involving BCl₃ and its fragments in the ground and excited states are needed. Despite such importance of BCl₃ for present-day technologies, availability of basic data for electron-induced processes in this compound is still very poor. The deficiency of absolute experimental data on e⁻-BCl₃ scattering is mainly connected with physicochemical properties of BCl₃ gas. By the reason of its high reactivity and corrosiveness, scattering experiments with BCl₃—especially those with the use of crossed-beam techniques—are difficult to handle and the obtained results have serious uncertainties [4].

The early experimental studies of BCl₃ molecules involved electrons as projectile concerned electron diffraction [5]. Later, investigations focused mainly on the electron-induced formation of positive [6–11] and negative ions [8,10–15] using electron-beam and swarm techniques. Those experiments provided information on appearance potentials and/or gave only relative abundances of the observed ions. Absolute experimental cross-section data are fragmentary, and are available for the electron attachment to the BCl₃ molecule [12,15], partial and total electron-induced ionization [11], and for the emission from excited molecular fragments produced by electron impact [16–18]. Vibrational and dissociation (into neutral fragments) cross sections have been derived [19] from experimental electron drift velocities [20]. Furthermore, in the literature one can also find the threshold electron-impact excitation spectra [15] of BCl₃ molecules and the electron transmission spectra [21]. Most of the quantitative data on the electron-BCl₃ scattering have been derived from swarm experiments.

The lack of experimental data on elastic e⁻-BCl₃ scattering has been to some degree filled in with calculated elastic cross sections obtained using different theoretical formalisms [21–25]. Comparison shows that results of those calculations distinctly depend on the approach applied. Also available are calculations of the total cross section for the dissociation of BCl₃ by electron impact [22]. Further, model calculations are employed [26–28] to extend low-intermediate experimental ionization data [11] to higher energies.

Motivated by the scarcity of absolute e⁻-BCl₃ scattering data as a function of electron energy, we have performed an experiment in which the absolute total cross section (TCS) for the BCl₃ molecule has been determined over a wide energy range, from low to intermediates (0.3–370 eV). The TCS results provide some test of the reliability of theoretical models and computational procedures used in elastic calculations. They may also serve as an upper limit reference for future studies on e⁻-BCl₃ scattering. To get a better understanding of how peripheral atoms influence the electron scattering we have made a comparison of the present TCS data for BCl₃ with our recent measurements for BF₃ molecule. Some similarities and differences are point out.

II. EXPERIMENTAL PROCEDURE

The present total e⁻-BCl₃ scattering cross section has been measured using the electron transmission method [29] in a linear configuration. This method relates the TCS to the transparency of the gas target for a beam of electrons; higher transparency responds to lower TCS. The apparatus and measuring procedure used in the present experiment are essentially the same as described in detail elsewhere [30,31]. The electron beam is formed by an electron optics system which comprises an electron gun followed by an energy dispersing 127° cylindrical electrostatic monochromator, and a zoom lens system. Electrons of a given energy E, with an energy spread of 80–100 meV (full width at half maximum), are
injected into a scattering chamber. The electrons which pass the scattering volume are energy discriminated by a retarding-field element and eventually detected by a Faraday cup. When target molecules are admitted into the scattering cell, the transmitted electrons suffer scattering which reflects in the attenuation of a detected electron current.

The quantities taken in the present experiment are: \( I(p, E) \) and \( I(p=0, E) \)—the intensities of the transmitted currents of electrons of given energy \( E \) in the presence and absence of the target gas in the scattering cell, respectively, \( p \)—the pressure of the investigated target gas in the scattering cell, \( T_s \)—the temperature of the scattering cell, and \( T_m \)—the temperature of the mks manometer head (322 K). To determine the TCS value, \( Q(E) \), we used the Bouguer-de Beer-Lambert (BBL) attenuation formula:

\[
I(p, E) = I(p = 0, E) \exp \left( -\frac{p l}{kT_s} Q(E) \right)
\]

where \( l \) is the effective path length of electrons in the target volume, \( T_s = \sqrt{T_w T_e} \) is the effective temperature of the target gas when the thermal transpiration effect [32] is accounted for, and \( k \) is the Boltzmann constant. As all required quantities are directly measured or evaluated, the resulting TCS values are absolute. The energy scale of the incident electrons was defined by the voltage applied to a lens element and the energy calibration against the well-known standard—the 2.3-eV resonant oscillatory structure in \( \text{N}_2 \). The uncertainty of the energy scale is about 0.1 eV; half of this value is related to the shift in the contact potentials observed in the course of experiment.

Before the TCS measurements commenced, the electron optics and gas supplying system were carefully processed to remove traces of moisture from surfaces what reduces high hydrolycity of \( \text{BCl}_3 \) molecule leading to possible presence of \( \text{HCl} \) in the sample. Because the TCS for \( \text{HCl} \) is relatively high at low energies and tends to increase towards zero energy (from \( 26 \times 10^{-20} \text{ m}^2 \) at 2 eV to \( 43 \times 10^{-20} \text{ m}^2 \) around 0.8 eV [34]), the presence of \( \text{HCl} \) may distinctly enlarge the measured TCS at the lowest energies used. On the other hand, above 2 eV, where TCS for \( \text{BCl}_3 \) becomes to be higher than that for \( \text{HCl} \), the presence of \( \text{HCl} \) can lower the measured TCS for \( \text{BCl}_3 \). We believe, however, that this factor does not exceed the statistical scatter of results because the measured TCS was independent of whether the sample gas was injected into scattering volume directly from the cylinder or from the auxiliary storage-gas reservoir. A commercially supplied sample of \( \text{BCl}_3 \) from Aldrich with a stated purity of 99.9% was used without further purification and no analysis of the gas in the scattering cell was made. The other effect which contributes to the TCS uncertainty is related to the influence of the \( \text{BCl}_3 \) molecules on the electron optics elements which, in consequence, shifts the energy scale in the course of the experiment. This effect leads to broadening and flattening of sharp features in the TCS energy function; resulting uncertainties in the present experiment may be especially troublesome below 6 eV where they amount to 2–4 %.

The overall systematic uncertainty in the measured TCS is estimated as a quadrature sum of all possible systematic errors encountered in the measurements of individual quantities used for the derivation of the TCS. Below 4 eV it is about 5–6 %, decreasing gradually to 3% between 5 and 150 eV, and increasing again to 4% at the highest applied energies.

III. RESULTS AND DISCUSSION

A. Boron trichloride, \( \text{BCl}_3 \)

Figure 1 shows the variation of our absolute total electron-scattering cross section for the \( \text{BCl}_3 \) molecule with
an incident electron energy. Results have been obtained in
the linear electron transmission experiment over the energy
range from 0.3 to 370 eV. In Table I the numerical TCS
values from the present experiment are listed.

The most striking feature of the measured TCS in the
investigated energy range is a broad, very distinct enhance-
ment with the maximum (61×10^{-20} m^2) located near 10 eV.
On the low-energy slope of the enhancement two weak fea-
tures are superimposed: the first peak is more pronounced,
and spans between 2.6 and 3.5 eV with the maximum (40
×10^{-20} m^2) at 3.2 eV, while the second one, less marked,
peaks around 6 eV (57×10^{-20} m^2). Beyond 10 eV the TCS
energy function decreases with the energy increase. Up to 30
eV the TCS decreases quite steeply. From 30 eV the slope of
the TCS curve distinctly changes and a weak shoulder is
discernible between 30 and 60 eV. Above 60 eV the decline
increases again and the behavior of the TCS energy function
can be described with the regression formula \( Q(E) \sim E^{-a} \),
where \( a=0.45\pm0.1 \). Such an energy dependence means that
the intermediate-energy TCS is nearly proportional to the
time the incoming electron needs to pass the distance equal
to dimension of the target molecule. At the highest energy
used, 370 eV, the TCS falls to nearly 16×10^{-20} m^2, the
value which rather accidentally coincides with the low-
energy TCS around the minimum visible close to 1 eV.

As no total \( e^-\text{-BCl}_3 \) cross section is available in the litera-
ture to compare with the present results, in Fig. 2 we have
shown our TCS together with experimental cross sections for
particular electron-induced processes leading to vibrational
excitation [19], dissociation [19], and to ionization [11] of
\text{BCl}_3 molecule. Calculated cross sections for elastic scatter-
ing [21–24], dissociation [22], and for ionization [27] are
also presented. Figure 2 clearly shows that explicit explana-
tion of the TCS behavior below 1 eV, based on those data, is
a rather difficult task. The magnitude of the summed cross
section for electron impact excitation of \text{BCl}_3 vibrational lev-
els (\( n=1+2, 3, \) and 4) [19] may suggest that the vibrational
excitation contributes essentially to TCS below 1 eV; note

\begin{table}[h]
\centering
\caption{Absolute electron-scattering total cross sections for
\text{BCl}_3 molecules in 10^{-20} m^2.}
\begin{tabular}{cccccc}
\hline
\( E \) (eV) & TCS & \( E \) (eV) & TCS & \( E \) (eV) & TCS \\
\hline
0.3 & 18.1 & 4.5 & 45.6 & 35 & 41.0 \\
0.4 & 17.8 & 5.0 & 50.4 & 40 & 39.7 \\
0.6 & 16.9 & 5.5 & 53.3 & 45 & 39.1 \\
0.8 & 15.3 & 6.0 & 57.2 & 50 & 38.6 \\
1.0 & 15.5 & 6.5 & 57.0 & 60 & 36.9 \\
1.2 & 15.3 & 7.0 & 56.3 & 70 & 34.8 \\
1.4 & 16.0 & 7.5 & 57.2 & 80 & 33.0 \\
1.6 & 17.2 & 8.0 & 58.4 & 90 & 31.9 \\
1.8 & 20.0 & 8.5 & 59.7 & 100 & 30.2 \\
2.0 & 22.4 & 9.0 & 60.5 & 110 & 29.2 \\
2.2 & 25.2 & 9.5 & 61.1 & 120 & 27.8 \\
2.4 & 26.4 & 10 & 61.4 & 140 & 26.2 \\
2.6 & 30.0 & 11 & 59.8 & 160 & 24.2 \\
2.8 & 33.2 & 12 & 58.4 & 180 & 22.8 \\
3.0 & 36.4 & 14 & 54.7 & 200 & 21.5 \\
3.1 & 38.5 & 16 & 52.5 & 220 & 20.2 \\
3.2 & 39.9 & 18 & 51.2 & 250 & 19.0 \\
3.3 & 39.3 & 20 & 48.6 & 275 & 18.0 \\
3.4 & 37.3 & 22 & 47.2 & 300 & 17.4 \\
3.5 & 36.7 & 25 & 44.6 & 350 & 16.2 \\
3.7 & 38.2 & 27 & 43.0 & 370 & 15.6 \\
4.0 & 40.1 & 30 & 42.1 & & \\
\hline
\end{tabular}
\end{table}
also that the shape of this “total” vibrational cross section is below 1 eV very similar to the TCS curve. Critical analysis of the procedure used in the determination of that cross section indicate, however, that the magnitude of the vibrational data might be distinctly overestimated (see Ref. [4]). On the other hand, the integral cross sections calculated by different groups differ to such an extent that no definite conclusions could be drawn onto the role of elastic scattering at very low energies. While elastic calculations of McKoy et al. [22] monotonously decrease below 1 eV in reasonable accord with the present TCS, the results of Tossell et al. [21] and Isaacs et al. [23] below 1 eV rapidly increase as the energy approaches zero. Dissociative electron attachment, which seems to be a leading scattering channel at near-zero energies [15], between 0.3 and 1 eV contributes a little to electron scattering [12].

Calculations [21–24] clearly show that the increase of the TCS beyond the 1-eV minimum (16 × 10^{-20} m^2) must be essentially associated with elastic processes. Along with the pronounced broad background related to direct scattering, the calculations also revealed some distinct resonant structures located below 10 eV. These structures were attributed to formation of temporary negative-ion states when the impinging electron attaches to the target molecule. The resonant peaks in calculated cross sections are placed, however, at energies that differ from those visible in the present experimental TCS, and the difference depends on the potential used in calculations. In the experiment, the resonant structures were noticed near 2.5 and 8 eV by Stockdale et al. [13] in the threshold electron impact excitation spectrum and at 2.86, 5.16, 7.57, and 9.05 eV by Tossell et al. [21] in their derivative transmission spectra. The location of the 2.86-eV feature corresponds to our 3.2-eV TCS maximum, while the 5.2- and 7.6-eV features are situated within the region of our 6.0-eV structure. It is worth noting that the structures located between 5 and 8 eV and 10 eV were also observed in TCSs for other perchlorinated molecules (CCl4, SiCl4, and GeCl4) [30] and therefore we believe the 6.0- and 10-eV features visible in the TCS for BCl3 are characteristic for targets with peripheral chlorine atoms. Integral cross sections calculated in static-exchange approximation for metal trichlorides (BCl3, AlCl3, and GaCl3) clearly display the presence of resonant structure at around 8 eV [25]; it could be shifted towards lower energy by about 1–2 eV, in better agreement with our TCS, if more realistic potential is used. A similar shift in the energy of the maximum was also observed in the calculated cross section for the BF3 molecule [25].

Beyond the main TCS maximum at 10 eV the role of elastic scattering still remains essential, although above the threshold the contribution of electron-induced ionization processes constantly increases. The weak shoulder spanning between 30 and 60 eV may just reflect the significant increase of ionization efficiency with the maximum around 60–70 eV.

### B. Comparison of TCSs for BCl3 and BF3

To examine how external atoms in a molecule affect the electron-scattering cross sections we compared the present TCS for e^-–BCl3 scattering with our measurements for BF3 (Fig. 3) [35].

The neutral boron halides BCl3 and BF3 are “closed shell” planar and symmetric (D_{3h}) molecules (see Fig. 4), both are nonpolar. Therefore one would expect some similarities in the shape of their electron impact cross sections. Earlier results [30], however, indicate the lack of any similarities in the shape of TCSs for the other perfluorinated targets and their perchlorinated counterparts. From Fig. 3 it is clearly evident that the substitution of chlorine atoms for fluorine in the target molecule changes drastically the magnitude and shape of the TCS over the whole energy range studied. According to the shape of TCSs for BCl3 and BF3, the only similarities worth attention are visible below 3 and 4 eV. Especially interesting is that both compared TCSs have their resonant maximum located around similar energy: close to 3.6 eV for BF3 and near 3.2 eV for BCl3. Such similarity may suggest that both resonances are mostly associated with the central boron atom.

Regarding the magnitude, over the entire energy range investigated the TCS for BCl3 is significantly higher than

<table>
<thead>
<tr>
<th>Molecule</th>
<th>IP (eV)</th>
<th>B–X (Å)</th>
<th>σ (10^{-20} m^2)</th>
<th>α (10^{-30} m^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCl3</td>
<td>11.60</td>
<td>1.742</td>
<td>16.6</td>
<td>9.38</td>
</tr>
<tr>
<td>BF3</td>
<td>15.56</td>
<td>1.313</td>
<td>9.66</td>
<td>3.31</td>
</tr>
</tbody>
</table>

**TABLE II.** Molecular ionization potentials IP, bond lengths B–X (X=Cl, F), the gas-kinetic cross sections σ, and electric dipole polarizabilities α; data are from Ref. [36].
that for BF$_3$. This difference only in part may be explained in terms of the larger geometrical size of a chlorine containing molecule. That is, in the vicinity of 1 eV and around 300 eV where the ratio of TCSs for BCl$_3$ and BF$_3$ is about 1.7 and equals the proportion of their geometrical dimensions as well as their gas-kinetic cross sections (see Table II).

In the remaining energy range, differences significantly exceed those resulting from the molecular geometry and become particularly striking between 4 and 60 eV where TCSs for BF$_3$ and BCl$_3$ behave quite differently. One of the reasons for such great difference is that the TCS for BF$_3$ has the minimum in the energy range where the TCS for BCl$_3$ has its maximum. Such behavior is characteristic for all perfluorides studied so far; the TCS for perfluorinated targets has the minimum located between 6 and 20 eV (cf. Refs. [35,37]) and around 10 eV is even smaller than that for perhydrides—molecules of smaller size. On the other hand, the prominent magnitude of TCS for BCl$_3$ around 10 eV must be related to distinctly higher electric polarizability of the molecule (Table II). Due to lack of static dipole field, the long-range polarization potential becomes the important component of electron-molecule interaction. The same holds also for other molecules with peripheral chlorine atoms.

IV. SUMMARY

We presented the absolute total electron-scattering cross section for BCl$_3$ molecule measured in a linear transmission experiment from 0.3 to 370 eV. The TCS energy dependence for BCl$_3$ shows one very distinct enhancement peaked near 10 eV. This enhancement is superimposed with resonant features located at 3.2, 6, and 10 eV. The 6- and 10-eV structures seem to be characteristic for perchlorinated targets. On the high-energy slope of the TCS curve a broad shoulder spans between 30 and 60 eV. From the comparison of the TCS data with available experimental and theoretical results for particular electron impact processes it is clear that the current level of understanding $e^-$-BCl$_3$ scattering is still not satisfactory and to explain all observed features of TCS for BCl$_3$ and quantify the scattering process more detailed experimental studies, especially those with the use of high-resolution crossed-beam techniques in various scattering channels, are required. A comparison of the TCS for BCl$_3$ with that for BF$_3$ indicates an essential role of the external atoms in the electron-scattering process.

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