LETTERS TO THE EDITOR

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NOTES

Total electron scattering cross section for Cl_2

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Chlorine is used in a number of technologies such as rare-gas halide lasers and plasma processing. For this reason attempts have been made to model its behavior in gas discharges and plasma reactors. In these efforts, electron collision data are crucial and yet not sufficient.[1] A significant cross section for which measurements are needed over a wide range of energies is the total electron scattering cross section, $\sigma_{sc,t}(\varepsilon)$. At the time that we undertook to perform a measurement of $\sigma_{sc,t}(\varepsilon)$ for Cl_2 there were no measurements of $\sigma_{sc,t}(\varepsilon)$, except one unacceptably large cross section ($\sim 600\times 10^{-20}\,m^2$ near 8 eV) made in 1937.[2] As we were preparing our data for publication, a new measurement[3] of $\sigma_{sc,t}(\varepsilon)$ for Cl_2 was published for electron energies ranging from 20 meV to 9.5 eV.

In this note we report absolute measurements of $\sigma_{sc,t}(\varepsilon)$ for Cl_2 between 0.3 and 23 eV. The present measurements generally agree (within combined uncertainties) with the recent measurements of Gulley *et al.*,[3] thus confirming their measurements, and extend the range of electron energies to 23 eV. The present measurements are also compared with previously reported measurements[4] and calculations[5] of the total rotational excitation cross section, $\sigma_{rot,t}(\varepsilon)$, of Cl_2 to provide the first assessment of the contribution of vibrational excitation to $\sigma_{sc,t}(\varepsilon)$ for Cl_2.

Figure 1 shows the present measurements of $\sigma_{sc,t}(\varepsilon)$. The measurements were made using a total scattering apparatus described earlier.[6] The apparatus consists of an electron gun followed by a trochoidal monochrometer and a collision cell filled with the gas of interest. The cross section is determined by measuring the unscattered portion of the electron beam with and without the gas in the collision cell. The electron beam energy resolution was ~100 meV. The total estimated 1σ uncertainty for the cross-section measurements (±20%) is derived from the estimated uncertainties of the pressure measurement (±15%), the uncertainties in the effective length of the collision cell immersed in the magnetic field (<±10% above 1 eV),[6] and possible errors (±5%) caused by the finite acceptance angle of the detector (2°). Relative uncertainties, based upon the scatter in the measured signal, are ~2%.

The recently published total scattering cross sections[3] are also shown in Fig. 1 as small open circles (○). The two measurements of $\sigma_{sc,t}(\varepsilon)$ exhibit the same general shape, with our data falling below the previous data at all but the lowest energies. Agreement between the two measurements is within the combined uncertainties for energies above 0.5 eV. For comparison, previously measured[4] values of $\sigma_{rot,t}(\varepsilon)$ are also shown in Fig. 1, along with the calculated[5] values of $\sigma_{rot,t}(\varepsilon)$ and $\sigma_{rot,e}(\varepsilon)$, the cross section for rotational elastic scattering.[7] While our present measurements of $\sigma_{sc,t}(\varepsilon)$ are observed to fall below the measurements[4] of $\sigma_{rot,t}(\varepsilon)$ at

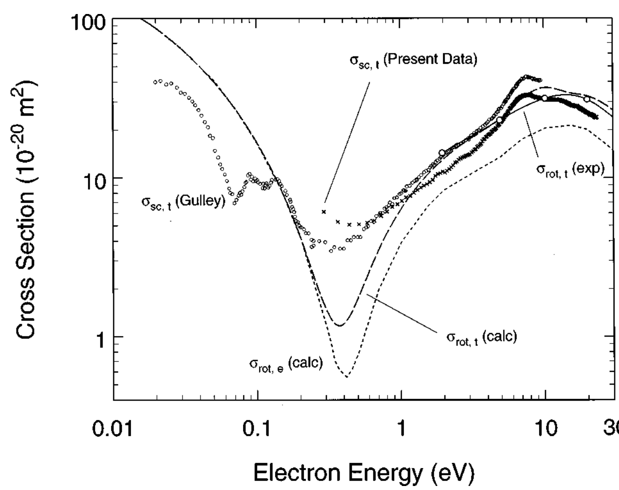

FIG. 1. Electron scattering cross sections for Cl_2: (×) present measurements of total electron scattering cross section, $\sigma_{sc,t}(\varepsilon)$; (○) previous measurements of $\sigma_{sc,t}(\varepsilon)$ by Gulley *et al.* (Ref. 3); (—○—) measurements of Gote and Ehrhardt (Ref. 4) of total rotational scattering cross section, $\sigma_{rot,t}(\varepsilon)$; (— —) calculation of Kutz and Meyer (Ref. 5) of the total rotational scattering cross section, $\sigma_{rot,t}(\varepsilon)$; (- - -) calculation of Kutz and Meyer (Ref. 5) of the total elastic rotational scattering cross section, $\sigma_{rot,e}(\varepsilon)$.

some energies (a physical impossibility), these data are not inconsistent with each other within the combined estimated uncertainties of the two measurements. The lower values of our measurements of $\sigma_{sc,t}(\varepsilon)$, compared to the other data in Fig. 1, may result in part from the fact that electrons scattered forward into small angles ($\leqslant 2°$) with little energy loss are detected as ''unscattered'' in our measurements due to the presence of the magnetic field. This may be a significant factor in the present experiment, as previous measurements[4] have shown that forward electron scattering is appreciable at all energies for Cl_2.

As can be seen in Fig. 1, the $\sigma_{sc,t}(\varepsilon)$ data exhibit peaks (or bumps) that can be attributed to resonance-enhanced electron scattering. The peaks at low energies observed by Gulley *et al.* and the bump in our data near 2.5 eV correspond to the negative ion states identified by electron attachment studies[1,8–10] near 0.3 and 2.5 eV. The large peak in the $\sigma_{sc,t}(\varepsilon)$ data near 8 eV corresponds to the negative ion state[1,8–10] at 5.5 eV overlapping with the lowest electron-excited Feshbach resonance of Cl_2 at 7.50 eV, identified by an electron transmission study.[11] The minimum near 0.4 eV is a distinctive feature common to all the cross sections in Fig. 1.

The comparable magnitude of the measured values of $\sigma_{sc,t}(\varepsilon)$ and $\sigma_{rot,t}(\varepsilon)$ implies a significant role for rotational scattering over most of this electron energy range; however, the fact that $\sigma_{sc,t}(\varepsilon)$ exceeds $\sigma_{rot,t}(\varepsilon)$ in certain energy ranges indicates that there exists a vibrational excitation contribution to the total scattering cross section. Chlorine is a homopolar molecule, and measurements on other homopolar molecules, such as N_2, O_2, and H_2, have shown that direct vibrational excitation is much smaller than indirect (or resonance enhanced) vibrational excitation.[12,13] Thus, the contribution to $\sigma_{sc,t}(\varepsilon)$ from direct vibrational excitation should be small, so the large magnitude of $\sigma_{sc,t}(\varepsilon)$ compared to $\sigma_{rot,t}(\varepsilon)$ for electron energies below 1 eV implies the presence of significant indirect vibrational excitation, most probably via scattering through the low-lying ($\sim$0.03 eV) negative ion state of Cl_2. The vibrational excitation energy of Cl_2 is only 0.07 eV,[14] and the spacing of the peaks and inflections in the data of Gulley *et al.*[3] at 0.089, 0.14, and 0.2 eV are not inconsistent with expected excitations of progressively higher vibrational levels with decreasing probability. Similarly, the higher values of $\sigma_{sc,t}(\varepsilon)$ around 8 eV suggest a contribution from indirect vibrational scattering via the negative ion states of Cl_2 in this energy range. In this energy range, electronic excitation is also possible, but calculations by Rescigno[15] indicate that the cross section for this processes would be only about 1×10^{-20} m^2 at 8 eV. The degree to which the total scattering cross section exceeds the rotational excitation cross section in this region suggests that the magnitude of the vibrational excitation cross section could be 10×10^{-20} m^2 or larger. This is significantly higher than the values attributed to vibrational excitation cross sections derived by Boltzmann-based models.[16] Some vibrational excitation would also be expected at energies near the negative ion state at 2.5 eV. This conclusion is contrary to the general statement of Gulley *et al.*[3] that there is relatively little contribution to $\sigma_{sc,t}(\varepsilon)$ from inelastic events in the energy range between 200 meV and 9.5 eV. In fact, rotational and vibrational excitation appear to account for the majority of $\sigma_{sc,t}(\varepsilon)$ in this energy range.

In conclusion, the data in Fig. 1 indicate that: (i) The scattering cross sections exhibit a minimum around 0.4 eV, (ii) the largest contribution to the total scattering cross section of Cl_2 comes from rotational scattering, except for electron energies near the minimum, (iii) the total cross section has a significant contribution from indirect vibrational excitation at energies near the minimum, presumably via the lowest negative ion state of Cl_2, and (iv) in the energy range around 8 eV there is a significant contribution to $\sigma_{sc,t}(\varepsilon)$ from indirect vibrational scattering, in addition to the large rotational inelastic scattering (rainbow scattering).[4,5]

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