

Total electron scattering cross sections for NO, CO, NO₂, N₂O, CO₂ and NH₃ ($E_i \geq 50$ eV)

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Abstract. Various total cross sections for electron scattering on the heteronuclear molecules NO, CO, NO₂, N₂O, CO₂ and NH₃ are calculated at energies from 50 eV onwards. The approximate additivity rule used earlier has been modified by separating e[−]–molecule interactions into short-range and long-range parts. The resulting modified additivity rule for e[−]–molecule cross sections is simple but more effective and it yields better accord with experiments, especially above 100 eV incident energy.

1. Introduction

Scattering of fast electrons by simple, light molecules offers a relatively simpler theoretical picture. Recently, several theoretical calculations (Joshipura and Patel 1994—to be referred to as paper I, Jiang *et al* 1995 and references therein) have been carried out on total (elastic + inelastic) cross sections for molecules like O₂, N₂, CO, NO as well as CO₂, NO₂ etc, together with those of F and Cl atoms, at intermediate to high electron energies E_i . Quite a few experimental measurements (e.g. Zecca *et al* 1992, 1995, Szmytkowski *et al* 1987, 1991, 1992, Kwan *et al* 1983 etc) have also been carried out on the total cross sections of well known and some of the exotic molecules, at energies in the intermediate and high range. For light diatomic and triatomic molecules, the calculations based on the additivity rule (e.g. paper I) along with the optical model calculations for the respective atoms in the targets have yielded reasonable agreement with experimental data at $E_i > 100$ eV or so. The said theoretical approach employs the high-energy impulse approximation (Massey *et al* 1969, Bransden 1983) which assumes $kR \gg 1$, with k as the incident momentum (in au) and R as a typical internuclear distance in the target molecule. This approach to electron–molecule scattering ignores atomic bonding in molecules, multiple scattering within the target and also anisotropic interactions. Attempts should be made to bring in more realistic features here. The importance of various molecules—both well known and exotic, in natural and man-made systems needs no emphasis. The theory may also help where experiments are difficult.

The present work on e[−]–molecule scattering is, therefore, an improvement over the aforementioned additivity rule. Our modification is tested against the measured data for NO, CO, NO₂, CO₂ and NH₃. The conclusions drawn are favourable.

2. Theoretical models and calculations

In the high-energy impulse approximation, the e^- -molecule scattering amplitude f_M is a superposition over the atomic scattering amplitudes $f_i(\theta; k)$ i.e. (paper I),

$$f_M(\mathbf{q}; \mathbf{R}) = \sum_{i=1}^n f_i(\theta; k) \exp(i\mathbf{q} \cdot \mathbf{R}_i) \quad (1)$$

where \mathbf{q} is the elastic momentum transfer (in au), n is the number of constituent atoms in the target, θ is the angle of scattering and \mathbf{R}_i is the position of the i th scattering centre (atom) from the molecular centre of mass. The optical theorem applied to (1) yields the total e^- -molecule cross section $Q_T(M)$ as follows:

$$Q_T(M) = \frac{4\pi}{k} \text{Im } f_M(\theta = 0, k) = \frac{4\pi}{k} \sum_{i=1}^n \text{Im } f_i(\theta = 0; k) \quad (2)$$

or

$$Q_T(M) = \sum_{i=1}^n Q_T^{(i)}(A) \quad (3)$$

where $Q_T^{(i)}$ is the total (elastic + inelastic) cross section for the i th atom. Thus in the high-energy additivity rule, equation (3), the total e^- -molecule cross section is an incoherent addition of the corresponding e^- -atom cross sections in the molecule. This is a generalization of the approximate additivity rule for total molecular ionization cross section $\sigma_I(M)$ given by Younger and Mark (1985). Accordingly at a certain high energy,

$$\sigma_I(M) = \sum_{\alpha=1}^n \sigma_I(\alpha) \quad (4)$$

with the right-hand side indicating a simple sum over total e^- -atom ionization cross section $\sigma_I(\alpha)$.

Now to evaluate $Q_T^{(i)}$ of (3) for the i th atom, a complex (spherical) optical potential $V^{\text{opt}}(r, k)$ is constructed, to account for the static, exchange, polarization and absorption interactions. The model potentials for these interactions can be written down in terms of basic atomic properties like electron-charge density, ionization energy, mean excitation energy (Δ), dipole polarizability (α_d) etc, as discussed in paper I (see also Joshipura and Patel 1993). The static-exchange potentials are determined through the charge density derived from the atomic wavefunctions (Clementi and Roetti 1974). The polarization potential is adopted to have a well known dynamical form:

$$V_{\text{dp}}(r, k) = -\frac{\alpha_d \cdot r^2}{2(r^2 + r_c^2)^3} \quad (5)$$

with

$$r_c = \frac{3k}{8\Delta}$$

which works well at high energies. Typically below 100 eV or so, this must be replaced by an energy-independent correlation-polarization potential V_{cp} (paper I, Jiang *et al* 1995). Further, the imaginary part V_{abs} of V^{opt} is chosen following Staszewska *et al* (1983). The details of obtaining the (atomic) total elastic cross section $Q_{\text{el}}(E_i)$ and the total inelastic cross section $Q_{\text{inel}}(E_i)$ in the partial-wave method are given in our earlier papers. Thus, for a particular atom,

$$Q_T^{(i)} = Q_{\text{el}} + Q_{\text{inel}} \quad (6)$$

Going back to (3), we obtain the molecular total (elastic + inelastic) cross section $Q_T^S(M)$ which includes only spherical interactions.

Now, the additivity rule (3) lacks any dependence on the molecular property, except for the separated-atom limit of the molecule. In particular the long-range polarization effect is considered inadequately, as the 'atomic' polarizabilities are employed here, *vide* equations (2) and (5). The said effect contributes significantly in the forward direction which is of our present interest, cf equation (2). Let us, therefore, separate out the total spherical e^- -molecule interaction V into short-range (V_S) and long-range (V_L) parts, i.e.

$$V = V_S + V_L. \quad (7)$$

Thus the T -matrix element and the molecular scattering amplitude are also split up into short-range (SR) and long-range—mainly polarization—contributions (Hayashi and Kuchitsu 1976). We restrict the impulse approximation to the SR-part only and write the total molecular amplitude as the sum of two terms, namely

$$f_M(\theta = 0; k) = \sum_{i=1}^n f_i^{SR}(\theta = 0; k) + f_M^{pol}(\theta = 0; k) \quad (8)$$

where on the right-hand side, the first term shows the superposition of the e^- -atom scattering amplitudes f_i^{SR} obtained in short-range potentials. The second term is the molecular polarization amplitude f_M^{pol} calculated through the potential of (5). But now here, r is the radial distance of the electron from the molecular centre of mass. Further, we now employ the molecular average spherical dipole polarizability α_0 in (5). We emphasize its significance by noting that, for a CO molecule, for example, $\alpha_0 = 13.17$ au while the polarizabilities (α_d) of the free atoms C and O are 14.17 and 5.2 in au, respectively.

The e^- -molecule total cross section is obtained in this modification by applying the optical theorem to (8). This introduces the modified additivity rule

$$Q_T^S(M) = \sum_{i=1}^n Q_i^{SR}(A) + Q_{pol}(M) \quad (9)$$

wherein the first term is a simple sum of relevant e^- -atom cross sections Q_i^{SR} in short-range potentials only and the second term is the contribution from the molecular polarization potential. In the absence of information on Δ for some of our target molecules we have used the corresponding ionization energies. Besides, at lower energies (< 100 V) r_c of (5) is replaced by half of a typical bond length of the target.

This approach of adding short-range and long-range interactions incoherently, *vide* equation (9), is similar to that of Mu Tao and Frietas (1983) who calculated e^- -molecule elastic differential cross sections. Presently, for a given target, we evaluated the first term of (9) by defining a complex short-range potential for e^- -atom scattering. This has the real part in the form of (static + exchange) potentials and the imaginary part again as given by Staszewska *et al* (1983). In the present work the required cross sections Q_i^{SR} for C, N and O atoms are determined through the partial-wave decomposition scheme. The second term of (9) is calculated similarly at a direct molecular level.

Let us now devote attention to non-spherical potentials which are excluded in formulating equations (3) and (9). Although the e^- -molecule interactions are, in general, anisotropic the non-spherical part of the potential yields cross sections that are dominant only at low energies. Molecules possessing a permanent dipole moment D ($= 0.574$ au, for NH_3) exhibit a long-range dipole potential $-D \cdot \hat{r}/r^2$, at large r . The corresponding Born cross

section for the rotational excitation $J \rightarrow J' = J + 1$, is given by (Collins and Norcross 1978)

$$Q_{JJ'}(D, E_i) = \frac{8\pi D^2}{3k^2} \frac{J'}{2J+1} \ln \left(\frac{k+k'}{k-k'} \right) \quad (10)$$

with k and k' as the initial and the final momenta of the scattering electron. The rotational excitation cross section $Q_{01}(D, E_i)$ with $J = 0$ and $J' = 1$, calculated in this way for NH_3 (Jain 1988) is about 17% of the measured cross sections at 100 eV. Thus with $E_i > 50$ eV, it is sufficient and meaningful to add the dipole contribution $Q_{01}(D, E_i)$ to (9), for polar molecules having low to moderate values of D . We therefore extend the modified additivity rule to such cases and define the grand total cross section as

$$Q_{\text{tot}}(E_i) = Q_{\text{T}}^{\text{S}}(E_i) + Q_{01}(D, E_i). \quad (11)$$

We have demonstrated earlier (Joshipura *et al* 1994) that such an incoherent addition of spherical and non-spherical effects (*vide* equation (11)) brings about a better accord with measurements for the electron impact total cross sections of H_2O ($D = 0.728$ au). Amongst the targets considered in the present work, the second term of (11) is significant for NH_3 only.

Finally, the total cross section $Q_{\text{tot}}(E_i)$ of (11) does not cover vibrational excitation and dissociative ionization which are not so significant in the present range of energies (roughly 50 eV onwards).

3. Results, discussion and conclusions

We have obtained the electron-impact total (elastic + inelastic) cross sections $Q_{\text{T}}^{\text{S}}(E_i)$ for heteronuclear molecules NO, CO, NO_2 , CO_2 , N_2O and NH_3 at $E_i \geq 50$ eV. Our results in the approximate additivity rule (AR) (3) and the modified additivity rule (MAR) (9) have been compared here and examined within the background of various experimental measurements. We find a good general accord between these two approaches and the experiments in the limit of high energy ($\gtrsim 1000$ eV). Both of our theories exceed experimental values below about 200 eV, but the MAR approach fares better in general.

Figures 1 and 2 exhibit the total cross sections Q_{T}^{S} for e^- -NO and e^- -CO scattering, respectively, along with the measured data by various groups. The previous results of paper I overestimate these data by about 15% at 100 eV. The present MAR results reduce this difference and bring the overestimation below 10%. For diatomic molecules NO and CO the difference between the AR and the MAR approaches persists up to about 400 eV. The polarization effect dwindles as E_i increases, making the second term in (9) less and less significant.

The lower curves in figures 1 and 2 exhibit the molecular inelastic cross sections Q_{inel} as sums of the respective quantities of the constituent atoms, similar to (4). The curves rise from the ionization threshold upwards and reach a maximum around 50 eV, decreasing slowly beyond this and indicating the Bethe-Born behaviour (see Inokuti 1971).

Figures 3 and 4 correspond to e^- - NO_2 and e^- - CO_2 scattering. The limit of validity of both the AR and the MAR is pushed up to higher energies for triatomic and larger molecules. Comparisons with the measured values from various investigators mentioned in figures 3 and 4 shows that at 300 eV, our AR and MAR results overestimate the results by 10% or less. The present modification over paper I, *vide* equation (9) is more effective here too. Zecca *et al* (1995) have noted that our earlier results on total (elastic + inelastic) cross sections showed a correct trend in the variation of the cross sections with the number of electrons in the molecules studied in paper I. At 50 eV the present overestimation for NO_2

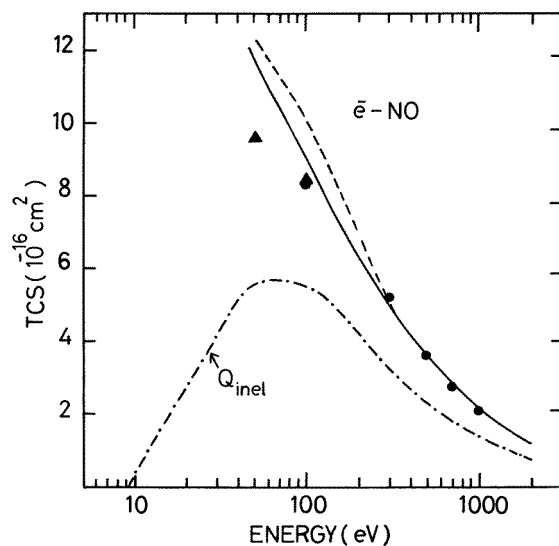


Figure 1. Total cross sections of e^- -NO scattering. --- AR, equation (3); — MAR, equation (9); — · — Q_{inel} by AR, similar to equation (4). Experimental data: \blacktriangle , Szmytkowski *et al* (1991); \bullet , Dalba *et al* (1980).

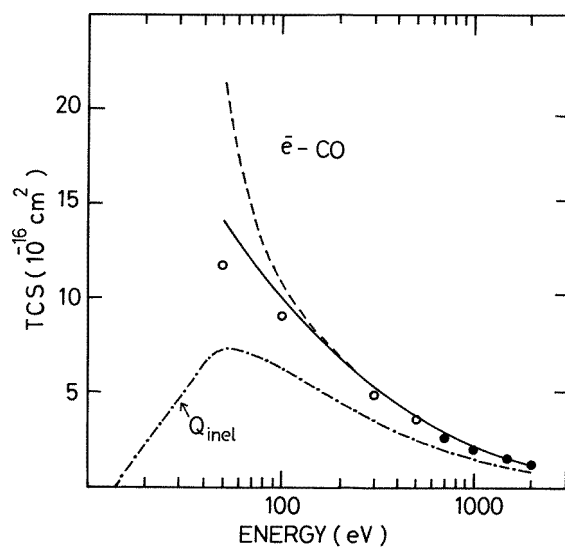


Figure 2. Same as in figure 1, but for e^- -CO scattering. Experimental data: \circ , Kwan *et al* (1983); \bullet , Garcia *et al* (1990).

and CO_2 is quite large ($\gtrsim 20\%$). On the other hand, the new results in the MAR calculation tend to merge with the earlier results (paper I) above 600 eV.

Our theoretical total cross sections for e^- - N_2O scattering are given in table 1. At 100 eV the experimental total elastic cross section of Marinkovic *et al* (1986) for N_2O is slightly more than half of our Q_{T}^{S} value. No other data are known to be available for the N_2O molecule.

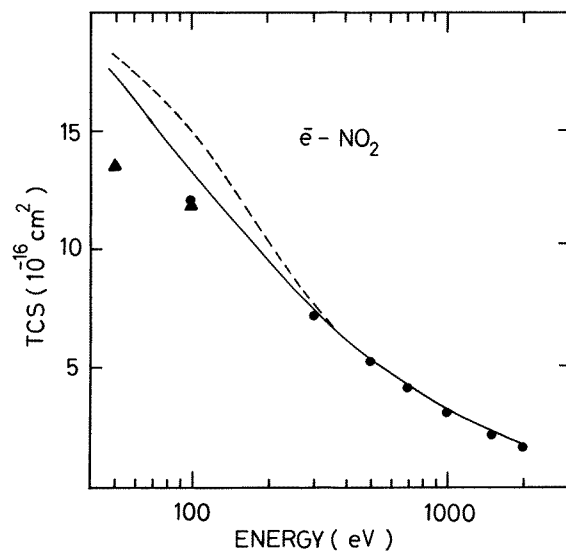


Figure 3. Total (elastic+inelastic) cross sections of e^- - NO_2 scattering. --- AR, equation (3); — MAR, equation (9). Experimental data: ▲, Szmytkowski *et al* (1992); ●, Zecca *et al* (1995).

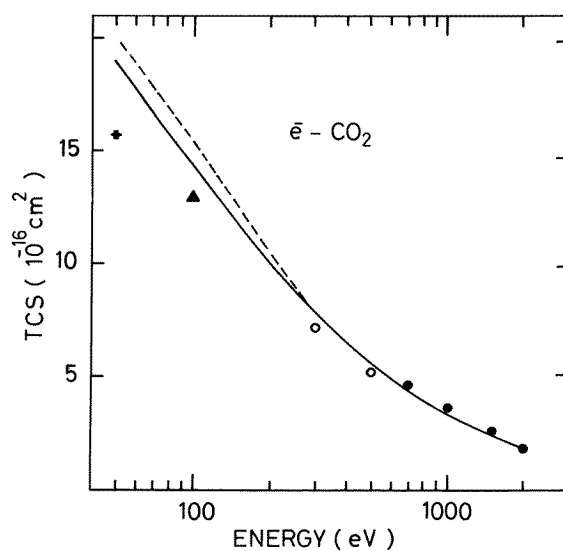


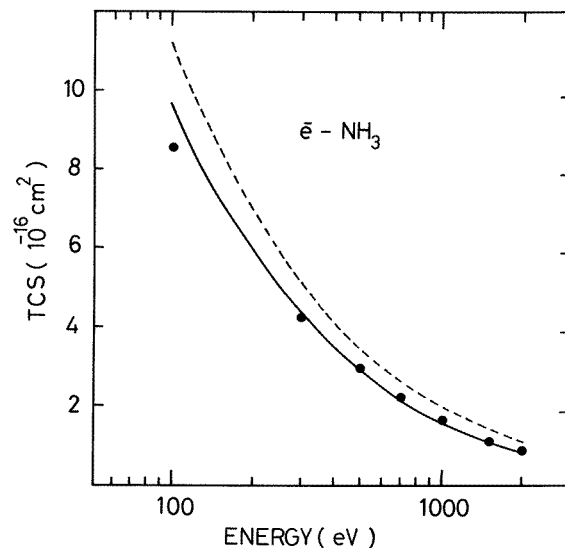
Figure 4. Same as in figure 5, but for e^- - CO_2 scattering. Experimental data: +, Hoffman *et al* (1982); ▲, Szmytkowski *et al* (1992); ○, Kwan *et al* (1983); ●, Szmytkowski *et al* (1987).

Now consider the e^- - NH_3 scattering represented in figure 5. A simple addition of atomic cross sections to yield the molecular cross section (3) overestimates the measured data of Zecca *et al* (1992) in this case even up to 2000 eV. We have used the Born-dipole rotational excitation cross sections Q_{01} along with the present MAR results to obtain $Q_{\text{tot}}(E_i)$, *vide* equation (11). With this our results show a good accord with experiments at and above 300 eV (figure 5). Our theory succeeds here owing to the presence of three light

Table 1. Total cross section Q_T^S (in 10^{-16} cm^2) for electron scattering by N_2O .

E_i (eV)	Present	Paper I
50	17.74	18.73
100	13.53	15.2 (7.9) ^a
300	7.34	7.64
500	5.25	5.23
700	4.09	4.09

^aTotal elastic cross section, Marinkovic *et al* (1986).

**Figure 5.** Total cross section Q_{tot} (equation (11)) for $e^- - \text{NH}_3$ scattering. --- AR; — MAR; ●, measurements by Zecca *et al* (1992).

scatterers (H atoms) in NH_3 .

Thus we conclude that the modified additivity rule given here offers a better approximation to the e^- -molecule total (elastic + inelastic) scattering at $E_i \gtrsim 100$ eV. It is easy to use if the molecular polarizabilities are known. For polyatomic and/or heavy molecules the rule becomes valid at higher energies, depending on the target. Even then the rule can explain qualitatively the correlation between molecular polarizability and the total cross sections. Such a correlation is indicated in the recent measurements of Szmytkowski and Krzysztofowicz (1995) on molecular targets CH_3X , with $\text{X} = \text{F}, \text{OH}, \text{NH}_2$ and CH_3 .

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