Total Cross-Sections for Electron Scattering of C_3H_6 Isomers: A Modified Additivity Rule Approach

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A modified additivity rule approach has been presented. Total cross-sections (TCSs) for electron scattering of C_3H_6 isomers (C_3H_6 and c-C_3H_6) have been calculated at 10 – 300 eV employing the modified additivity rule. The approach for the TCSs of C_3H_6 isomeric molecules is simple, and it yields better accord with experiments in the present energy range.

Key words: Modified Additivity Rule; Cross-Sections; C_3H_6 Isomers.
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1. Introduction

Total cross-sections (TCSs) for electron scattering of molecules have important applications in plasma-assisted processing, gaseous laser, chemical etching, atmospheric science, semiconductor devices and military fields [1]. Therefore some procedures have been recently developed [2 – 4]. One such method develops from the consideration that, at high impact energy, the TCS of a molecule approaches the sum of the atomic TCSs of its constituents. This is the additivity rule (AR) [2]. The AR was employed to obtain the photo-ionization and electron impact ionization cross-sections as well as the molecular polarizability for a variety of molecules and is regarded as a successful concept. Raj [5] made the first application of the AR to obtain elastic cross-sections for electron scattering by a sample of four molecules, namely O_2, CO, CO_2 and CF_4, at 100 – 500 eV. Recently, the AR has been employed widely to calculate electron scattering cross-sections [6 – 8], and has been proved that it is proper for the calculation of the TCS of electron-molecules in the intermediate and high-energy range. However, the AR is not very successful at lower energies. This is obviously due to the fact that the AR neglects the interaction of constituent atoms in the formed molecule. Moreover the AR cannot discriminate between isomeric molecules.

Propene (C_3H_6) and cyclopropane (c-C_3H_6) are isomers between with the same number of constituent atoms but in considerably different geometrical arrangements. Propene is an open-chain hydrocarbon molecule, while its isomeric counterpart, cyclopropane, is a cyclic compound. Both molecules also exhibit the various forms of carbon bonds. It is obvious that isomers always show conspicuous difference in various physical and chemical properties. One would, therefore, expect that the difference in the target structure should reflect in the magnitude and the energy dependence of the electron scattering cross-sections for these molecules. To find differences in scattering processes of C_3H_6 isomers, comparative studies were carried out in some collision channels. A distinct difference was observed in the magnitude of total ionization cross-sections of propene and cyclopropane by Nishimura and Tawara [9]. The TCS results of Nishimura and Tawara [10], Makochekanwa et al. [11] and Floeder et al. [12] for C_3H_6 isomers differentiate more clearly. The disaccord in the magnitude of the TCS for this pair exceeds 20% near the maximum at around 10 eV. Experimental data of Makochekanwa et al. [11], Floeder et al. [12], Szmytkowski and Kwitnewski [13] have indicated that the TCS propene is generally higher by several percents than that cyclopropane, though the observed difference is within the limits of experimental error. The difference between TCSs of C_3H_6 isomers is not only quantitative but also qualitative. However, the AR cannot show these differences.

In this paper, we try to develop a different formulation of the additivity rule, which not only can discriminate between isomeric molecules, but is also proper for electron scattering at lower energies.

2. Theoretical Model

In the original additivity rule [5–7, 14] the implicit assumption is made that molecule orbits can be described by the sum of the valence orbits of all atoms present in the molecule. As a result, the TCS of electron-molecule scattering is written as the sum of the TCSs of atoms. Here we call it the AR, which is based on the optical theorem

$$\begin{aligned} Q_{\mathrm{AR}} &= \frac{4\pi}{k}\mathrm{Im} f_{\mathrm{M}}(\theta=0) \\ &= \frac{4\pi}{k}\mathrm{Im}\sum_{j=1}^{N} f_j(\theta=0) = \sum_{j=1}^{N} q_{\mathrm{T}}^{j}(E), \end{aligned} \tag{1}$$

where q_{T}^{j} and f_j are the TCS due to the j-th atom of the molecule and the complex scattering amplitude for constituent atoms of the molecule, respectively. Here it is obvious that no molecular geometry is involved in the AR. So, the molecular scattering problem is reduced to the atomic scattering problem that is easier to handle. Thus in the AR (1), one main effect is not considered: a closed-packed molecule is not fully transparent for low-energy electrons ($E < 100$ eV) and the inner atoms are shielded by the outer ones. The shielding effect, which leads to the smaller molecular scattering cross-sections than predicted by the AR, depends on the geometry of the molecule. In addition total cross-sections for electron scattering of isomeric molecules will be identical employing the AR. This is not in accordance with the experiments [10, 13]. At higher energies different inelastic channels are open, including multiple ionization and electronic excitations. Therefore, q_{T}^{j} can be described as a black sphere (i. e. perfectly absorbing). The atomic TCS q_{T}^{j} is given by a known quantity [15]

$$q_{\mathrm{T}}^{j} = 2\pi r_j^2, \tag{2}$$

where r_j is the black sphere radius.

Considering the above factors, we present a modified additivity rule (MAR):

$$Q_{\mathrm{MAR}} = g Q_{\mathrm{AR}}. \tag{3}$$

We assume that

$$\begin{aligned} g = {} & \frac{r_0}{r_1+r_2} h(r_1+r_2-r_0) \\ & + \frac{k^2}{k^2+CZ} h(r_0-r_1-r_2), \end{aligned} \tag{4}$$

where r_1 and r_2 are the black sphere radii of carbon and hydrogen atoms, respectively; $k^2 = 2E$ and E is the incident electron energy, in units of eV; Z is the number of electrons in the molecule; $r_0 = \sqrt{\alpha/d}$, where α is the molecular polarizability and d the sum of the bond lengths of the shortest C-H chain in the molecule; $h(x)$ is the Heaviside function. We let $C = 1$ in units of eV considering the reasonable dimensional relation. The coefficient g will approach unity at higher energies, so in this range the present method merges with the simple AR method. That is to say, the higher the energy, the smaller the shielding effect on the TCSs should be. Note also that, as the atomic cross-sections q_{T}^{j} depend on energy, also the coefficient g is energy-dependent. The Q_{AR} can be obtained by the AR (1). The q_{T}^{j} of (2) for the j-th atom is obtained by the method of partial waves:

$$q_{\mathrm{T}}^{j} = \frac{\pi}{k^2}\sum_{l=0}^{l_{\max}}(2l+1)\left[|1-s_l^j|^2 + (1-|s_l^j|^2)\right], \tag{5}$$

where s_l^j is the l-th complex scattering matrix element of the j-th atom, which is related to the partial wave phase shift as $s_l^j = \exp(2\mathrm{i}\delta_{lj})$. To obtain s_l^j we solve the radial equation

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} + k^2 - 2V_{\mathrm{opt}} - \frac{l(l+1)}{r^2}\right) u_l(r) = 0, \tag{6}$$

under the boundary condition

$$u_l(kr) \sim kr[j_l(kr) - \mathrm{i}n_l(kr)] + s_l kr[j_l(kr) + \mathrm{i}n_l(kr)], \tag{7}$$

where j_l and n_l are spherical Bessel and Neumann functions separately. V_{opt} is the complex optical potential

$$V_{\mathrm{opt}} = V_{\mathrm{s}}(r) + V_{\mathrm{e}}(r) + V_{\mathrm{p}}(r) + \mathrm{i}V_a(r). \tag{8}$$

It incorporates all the important physical effects. Presently the static potential $V_{\mathrm{s}}(r)$ for electron-atom systems is calculated by using the atomic charge density, determined from the well-known Hartree-Fock atomic wave functions [16]. The exchange potential $V_{\mathrm{e}}(r)$ provides a semi-classical energy-dependent

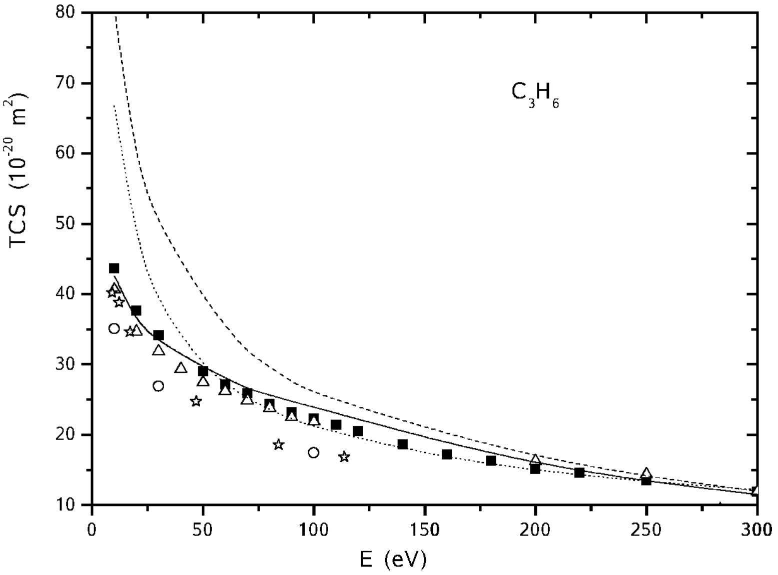

Fig. 1. Total cross-sections of C_3H_6. MAR results (solid line); AR results (dashed line) [14]; calculations of Nishimura and Tawara [10] (dotted line). Experimental data: (■), [13]; (○), [12]; (☆), [11]; (△), [10].

form of Jiang et al. [17]. Zhang et al. [18] give a smooth form at all r for the polarization potential $V_p(r)$, which has a correct asymptotic form at large r's and approaches the free-electron-gas correlation potential in the near-target region. This potential model has been proved fairly successful to the TCS for electron-atom scattering [18]. The imaginary part of the optical potential $V_a(r)$ is the absorption potential, which represents approximately the combined effect of all inelastic channels. Here we employ a semi-empirical absorption potential as discussed by Staszewska et al. [19]. The absorption potential is a function of the atomic charge density, incident electron energy and the mean excitation energy Δ of the target. It is written as [19]

$$\begin{aligned} V_a(r) = &-\rho(r)(T_L/2)^{\frac{1}{2}}(8\pi/5k^2k_f^3) \\ &\cdot h(k^2-k_f^2-2\Delta)(A+B+C), \end{aligned} \tag{9}$$

where

$$T_L = k^2 - V_s - V_e - V_p,$$
$$A = 5k_f^3/2\Delta,$$
$$B = -k_f^3(5k^2-3k_f^3)/(k^2-k_f^2)^2,$$
$$C = 2h(2k_f^3+2\Delta-k^2)(2k_f^2+2\Delta-k^2)^{\frac{5}{2}}/(k^2-k_f^2)^2.$$

Here k^2 and k_f are the energy of an incident electron and the Fermi momentum, respectively. $h(x)$ is the Heaviside function. The limit l_{max} of (5) is taken to be 30.

3. Results and Discussion

In this paper, employing the MAR along with the optical potential model, we have obtained the TCS for e-C_3H_6 isomers scattering at 10 – 300 eV. Nishimura and Tawara [10] calculated the TCSs of C_3H_6 isomers by a semi-empirical formula. Jiang et al. [17] calculated the TCS of e-C_3H_6 scattering employing the AR, and these results have been compared here and examined within the background of available experimental data. We find a good general accord between these approaches in the energy range ($\geq$ 200 eV). The MAR gives better agreement against the measured data than the AR in the present energy range. This is because the MAR considers the shielding effect. TCSs of e-propene (C_3H_6) and e-cyclopropane (c-C_3H_6) employing the MAR are also compared. They are shown in Figures 1 – 3.

For the C_3H_6 molecule, the four group measurements are shown in Figure 1. The present MAR and AR results are in good agreement with experiments at energies above 200 eV. But at lower energies, the results of the MAR are better than that of the AR. The AR results are about 16 – 36% higher than the measurement of Szmytkowski and Kwitnewski [13] at $E \leq$ 200 eV, while our MAR results are only about 0.5 – 7.4% higher than the measurement of Szmytkowski and Kwitnewski between 30 eV and 200 eV. Our MAR results are a little lower than the experiment of Szmytkowski and Kwitnewski [13], while a lit-

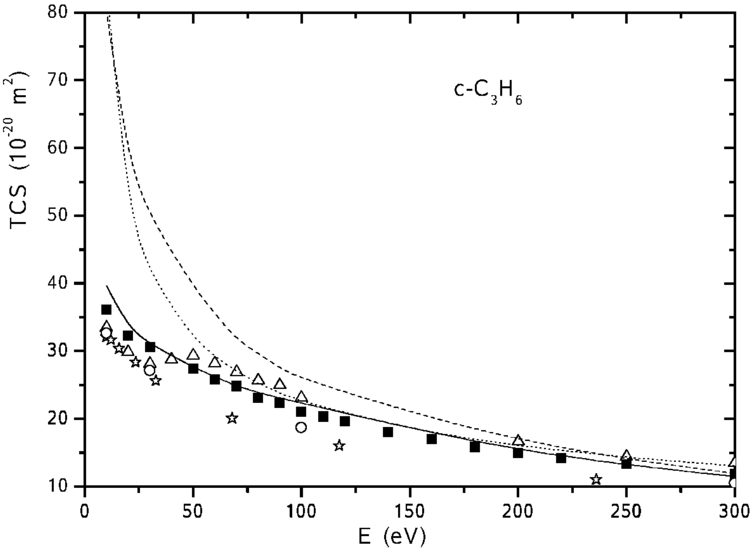

Fig. 2. Same as in Fig. 1 but for the c-C_3H_6 case.

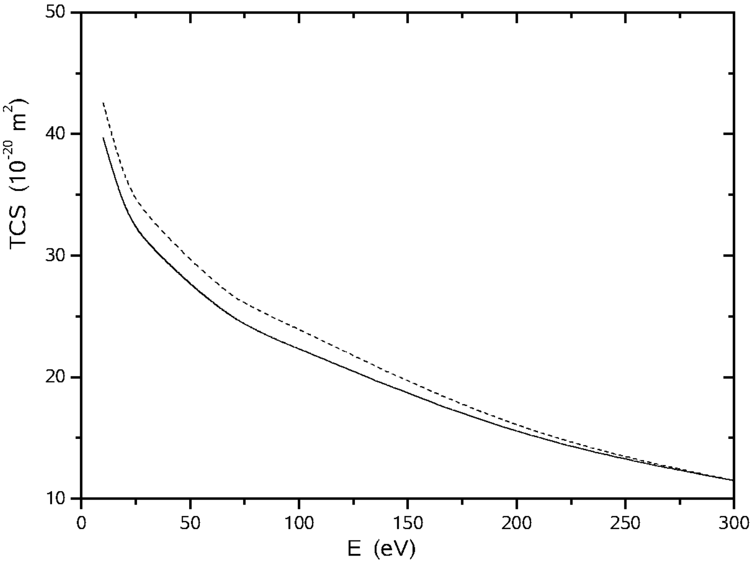

Fig. 3. Comparison of C_3H_6 (dashed line) and c-C_3H_6 (solid line) by MAR.

tle higher than the measurements of Nishimura and Tawara [10] at $E \leq 30$ eV and much higher than the experimental data of Makochekanwa et al. [11] and Floeder et al. [12] between 30 eV and 100 eV. The calculations of Nishimura and Tawara, which are generally lower than the present results, agree with the measurements of Szmytkowski and Kwitnewski above 50 eV. The discrepancy has two reasons. Firstly, the linear C_3H_6 is not so compact as the c-C_3H_6, which results in a larger electron spatial distribution of C_3H_6 compared with c-C_3H_6. This larger spatial distribution for C_3H_6 would lead to a larger TCS. Secondly, we should also notice that large differences lie between the experimental measurements shown in Figure 1.

Figure 2 shows that the results of the MAR, which are lower than the AR results, and the calculations of Nishimura and Tawara [10] at $E \leq 100$ eV merge well with calculations of Nishimura and Tawara and the various experimental data at $E > 100$ eV. At $E \geq 50$ eV our MAR results are a little higher than the measurements of Szmytkowski and Kwitnewski [13], while a little lower than the measurements of Nishimura and Tawara. Figures 1 and 2 show that the results of the MAR approach agree excellently with the experiments.

Figure 3 shows that the results of the MAR for C_3H_6 and c-C_3H_6 are obviously different at $E \leq 250$ eV. The TCS of C_3H_6 is generally higher than that of c-C_3H_6, which is accordant with the experiment [13]. We may expect from the larger geometrical size of the C_3H_6 molecule that C_3H_6 should have a higher cross-section. From 10 eV to 100 eV, the difference between calculated TCSs for both isomers is nearly constant. Above 150 eV, the difference between calculated TCSs is negligible, while in the experiments above 50 eV the difference is negligible. The interference effect originating from each constituent group in a molecule is not considered in the present calculations, which may be important below 150 eV.

4. Conclusions

The modified additivity rule (MAR) has been introduced with the aim of generating reliable TCSs for electron scattering of C_3H_6 isomeric molecules in low and intermediate energy regions. Considering the geometric shielding effects, the MAR, depending on the molecular property, is simple but effective for the TCSs on electron scattering of C_3H_6 isomers. Despite the present mathematical calculation not being exact, the present results provide a good qualitative comparison and will be useful in the experimental research. So, it is successful that the MAR and the optical model of related atoms are used to calculate qualitatively the TCS for e-C_3H_6 isomers scattering in the low and intermediate energy range. The MAR gives an interesting attempt for TCS of electron scattering of isomeric molecules and is worth for further research. At the same time, we also notice larger differences that lie among the experimental data. Since the contribution from the interference occurring between the scattering amplitudes originating from the different constituent atoms of the molecule is not included in the MAR, the results of TCS using the MAR show a small discrepancy compared with the experimental data in the present energy range.

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