Cross sections for positron collisions with small molecules

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Outline:

✓ Motivation.

✓ Schwinger multichannel (SMC) method.

✓ Applications:

HCOOH, CH₂O, CH₄, C₂H₄, C₂H₆, isomers of C₃H₆, N₂O, C₃H₄.

✓ Conclusions.

✓ Acknowledgements.
Motivation

What are we missing?


Positron scattering on molecular hydrogen: Analysis of experimental and theoretical uncertainties

Kamil Fedus,¹,* Jan Franz,²,† and Grzegorz P. Karwasz¹,‡

FIG. 1. (Color online) Total cross sections for positron scattering from the ground state of H₂. Present DFT results are compared with the calculations of Mukherjee et al. [17], Zhang et al. [18], Zammit et al. [19], and experiments of Karwasz et al. published in 2006 [4] and the same set presently reanalyzed (Karwasz et al.*), Zecca et al. [5] and Machacek et al. [6] (directly measured and corrected).
The Schwinger multichannel (SMC) method:


- Extension of the Schwinger variational principle for the scattering amplitude for applications to low-energy positron-molecule collisions;

- Capable of addressing important aspects of these collisions as:
  - effects arising from the polarization of the target by the incident positron (*ab initio*);
  - electronic excitation (multichannel coupling).

- Does not take the positronium formation channel into account.

- Uses $L^2$ functions (Cartesian Gaussian functions) in the expansion of the scattering wave function (the Green’s function accounts for the scattering boundary condition).
**Applications: HCOOH**

**PHYSICAL REVIEW A 78, 042707 (2008)**

**Positron scattering from formic acid**

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**FIG. 2.** (Color online) The present experimental total cross sections ($10^{-16}$ cm$^2$) for positron scattering from formic acid. The lines are the least-squares fits to the two subsets of points on the right and left, where the division is chosen to give the largest ratio of the slope on the left to the slope on the right, subject to the condition that each subset contains at least 10 points. The lines intersect at 4.3 eV.

$$E_P = 4.6 \pm 0.2 \text{ eV}$$
$$\mu_{\text{calc}} = 1.71 \text{D}$$
$$\mu_{\text{expt}} = 1.41 \text{D}$$

**FIG. 3.** (Color online) The present experimental (●) total cross sections and theoretical elastic cross sections (both in $10^{-16}$ cm$^2$) for positron scattering from formic acid. The static level (---), static plus Born dipole correction (——), static plus polarization (——), and static plus polarization plus Born dipole correction (———) results are shown.
Applications: CH$_2$O

An experimental and theoretical investigation into positron and electron scattering from formaldehyde

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**Figure 2.** Present experimental (●) TCSs and theoretical elastic ICSs at the SMC-S + Born (— — —) and SMC-SP + Born (− − −) levels for positron-CH$_2$O scattering. The positronium formation threshold and the first ionization potential are indicated by arrows labelled ‘Ps’ and ‘IP’. Also plotted are our electron scattering TCSs within the IAM-SCAR + dipole (—) formalism.

$E_{Ps} = 4.07$ eV

$\mu_{calc} = 2.85$D

$\mu_{expt} = 2.43$D
Applications: hydrocarbons (nonpolar)

✓ Potential scattering/partial wave method:

\[
\sigma_{tot}(k) = \sum_{\ell=0}^{\infty} \sigma_{\ell}(k); \quad \sigma_{\ell}(k) = \frac{4\pi}{k^2} (2\ell + 1) \sin^2 \delta_{\ell}(k)
\]

\[
\alpha = -\lim_{k \to 0} \frac{\tan \delta_0(k)}{k}
\]

✓ Virtual state

\[
\delta_0 \xrightarrow[k \to 0]{} \pi/2;
\]

\[
\alpha \xrightarrow[k \to 0]{} -\infty
\]

\[
\sigma_{tot} \xrightarrow[k \to 0]{} \infty
\]

Potential: \( V_{\text{static}} + V_{\text{polarization}} \)

✓ Common features: Ramsauer-Townsend minimum and virtual state (s-wave).
✓ RT mimimum: potential changes from attractive to repulsive (the s-wave eigenphase changes sign).
Applications: CH$_4$

Angelic discrimination (energy dependent): distinguish between scattered from unscattered positrons

\[ E_{Ps} = 5.81 \text{eV} \quad \alpha = -7.40a_0 \]

RT minimum at 2.2 eV
Applications: $\text{C}_2\text{H}_4$

 PHYSICAL REVIEW A 86, 022709 (2012)

 Positron collisions with ethene

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![Graph 1]

FIG. 3. (Color online) (Top panel) Cross sections for positron collisions with ethene. Circles (black), present TCS; solid line (gray), present elastic ICS; dotted line (green), results from [11]; triangles (blue), results from [8]; squares (red), results from [9]; dot-dashed line (magenta), ICS from [10]; dashed line (orange), ICS from [12]. (Lower panel) Same as top panel, in a smaller scale, except that here we have also, at 0.1, 0.5, 1, 5, and 10 eV, included the present TCSs corrected for the forward angle scattering effect (using our theoretical differential cross sections), open circles (black). See text for discussion.

$E_{Ps} = 3.70 \text{eV} \quad \alpha = -47.76 a_0$
Applications: $C_2H_4$

**FIG. 4.** (Color online) (Upper panel) Elastic ICS for the $A_x$ symmetry. Solid line (blue), present results; dot-dashed line (green), results from [10]. (Lower panel) $s$-wave eigenphase corresponding to the present calculations. See text for discussion.
Applications: $\text{C}_2\text{H}_6$

Cross sections for positron scattering from ethane

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Fig. 3. (Color online) The present measured TCS (●) and calculated elastic ICS (—) for positron collisions with ethane are compared with the previous TCS measurements from Sueoka and Mori [5] and Floeder et al. [4] and with the earlier ICS computation by Occhigrossi and Gianturco [6]. The present experimental TCS corrected for the forward angle scattering effect (see text) is also shown at selected energies (○). See also the legend in the figure.

$E_{\text{Ps}} = 4.72\text{eV} \quad \alpha = -13.83a_0$
Applications: isomers of $\text{C}_3\text{H}_6$

Positron collisions with $\text{C}_3\text{H}_6$ isomers

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**Figure 2.** Integral cross sections for the $\text{C}_3\text{H}_6$ isomers in the static plus polarization (SP) approximation with and without the Born closure for propene. The experimental TCSs are from [6].

$E_{PS} = 3.06\text{eV}$

$E_{PS} = 2.93\text{eV}$  

$\alpha = -22.60a_0$
Applications: N₂O


Elastic scattering of low-energy electrons by N₂O*

S.M.S. da Costa and M.H.F. Bettega

Electron scattering from N₂O: absolute elastic scattering and vibrational excitation

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Abstract. We report absolute measurements, using the relative flow technique, of low-to-middle energy (1.5–100 eV) differential cross sections (DCSs) for elastic electron scattering and vibrational excitation of nitrous oxide. These results, which have been undertaken independently in our two laboratories on different experimental apparatus, are compared in detail with each other and with previous experimental results and theoretical calculations. For elastic scattering the level of agreement between the DCSs from the two laboratories is generally very good. However, the agreement with recent theoretical calculations is rather poor, particularly at energies below 10 eV. For vibrational excitation DCS results have been measured at 2.4 and 8 eV—energies corresponding to the positions of two broad 2Π and 1Σ shape resonances respectively.

at forward angles has become considerably deeper and moved to a smaller angle (18°). The good agreement between the two experimental DCSs is again observed at this energy, as is the failure of the theoretical calculation, in this case that of da Costa and Bettega (1998), to correctly predict the forward-angle behaviour of the DCS. At energies less than about 10 eV this calculation, which omits the effects of polarization, is generally too large in magnitude.

12°. The theoretical calculation of da Costa and Bettega shows the same general shape as the experimental DCS at larger angles but predicts the second minimum at a slightly larger angle than either experiment. It once again fails to predict the structure in the DCS at forward angles.
Applications: N$_2$O

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Low-energy electron scattering by N$_2$O

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We present elastic integral, differential, and momentum-transfer cross sections for electron collisions with N$_2$O. We show that, with a slight modification of a method of incorporating polarization effects proposed recently by us [Winstead, McKoy, and Bettega, Phys. Rev. A 72, 042721 (2005)] along with a flexible one-particle basis set, we can reproduce features in the experimental data that were not reproduced by earlier calculations. We also find evidence of a Ramsauer-Townsend minimum, which our calculation places at about 0.2 eV.

FIG. 2. (Color online) Differential cross sections for N$_2$O at 1.5, 2, 2.5, 3, 3.5, and 4 eV. Solid line (blue), our results with 44 extra centers; circles (green) experimental data from Ref. [12] obtained at Sophia University; squares (red), experimental data from Ref. [12] obtained at the Australian National University.

FIG. 3. (Color online) As in Fig. 2 at 5, 6, 7, 7.5, 8, and 10 eV and with the following additional results: diamonds (yellow), experimental data from Ref. [4]; triangles (orange), experimental data from Ref. [5]; crosses (light blue), experimental data from Ref. [6]; dashed line (brown), calculations from Ref. [9].
Applications: N₂O

Positron and electron collisions with nitrous oxide: Measured and calculated cross sections

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FIG. 4. (Color online) The present experimental TCS for positron scattering from nitrous oxide is compared to the TCS calculated with our IAM-SCAR method and the elastic ICSs computed with our SMC approach, without and with Born dipole closure. Shown are our SMC + Born elastic ICSs obtained by integrating the elastic DCSs from θ_min = 0° and θ_min = 1° (see text). Also plotted are the present experimental TCSs corrected for the forward scattering effect at selected energies (again, see text). The current results are also compared against the TCSs measured by Kwan et al. [13] and calculated by Baluja and Jain [15], as well as the theoretical elastic ICSs of Arretche et al. [16]. The threshold energies for Ps formation in its ground and first excited states, and the first ionization in N₂O, are indicated by the vertical black arrows denoted by “Ps”, “Ps⁺”, and “IP”, respectively.

FIG. 5. (Color online) The present measured and calculated positron cross sections (see Fig. 4) are compared to the corresponding electron-impact results for nitrous oxide. Shown is the present electron TCS computed with our IAM-SCAR method, as well as the earlier electron TCSs measured by Szmytkowski et al. [63] and calculated by Vinodkumar and Barot [17].
Applications: $\text{C}_3\text{H}_4$

12 extra centers

16 extra centers

24 extra centers
Applications: C$_3$H$_4$

\[ \alpha = -127a_0, -637a_0 \]

➢ Alessandra Barbosa’s poster!
Conclusions:

- RT minimum and virtual state are common features among the (nonpolar) hydrocarbons.

- Discrepancies between the elastic integral cross sections and the experimental total cross sections at low energies (below the positronium formation threshold).

- Discrepancies between experimental data from different groups (angular discrimination). The same for theory.

- What are we missing?
  - single-particle basis set (extra centers)
  - poor description of the polarization effects
  - $f$, $g$ etc type functions
  - double virtual excitations (polarization)

- More experiments and calculations!
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The SMC method:

- The collision Hamiltonian: $H = (H_N + T_{N+1}) + V = H_0 + V$

- We know how to solve the target (Hartree-Fock): $H_N \Phi_\ell = E_\ell \Phi_\ell$

- The Lippmann-Schwinger equation:

$$A^{(\pm)} \Psi^{(\pm)}_m = V S_m; \quad S_m = \Phi_m \exp(i \vec{k}_m \cdot \vec{r}_{N+1})$$

- The $A^{(+)}$ operator:

$$A^{(+)} = Q \hat{H} Q + PV P - V G_P^{(+)} V$$

$$\hat{H} = E - H; \quad P = \sum_{\ell \in \text{open}} |\Phi_\ell\rangle \langle \Phi_\ell|; \quad Q = 1 - P$$

- $G_P^{(+)}$ is the free-particle Green’s function projected on the $P$-space.

- Variational stability: $A^{(+)^\dagger} = A^{(-)}$
The SMC method:

- The functional

\[
[f(\vec{k}_{out}, \vec{k}_{in})] = -\frac{1}{2\pi} \left[ \langle S_{\vec{k}_{out}} | V | \Psi^{(+)}_{\vec{k}_{in}} \rangle + \langle \Psi^{(-)}_{\vec{k}_{out}} | V | S_{\vec{k}_{in}} \rangle - \langle \Psi^{(-)}_{\vec{k}_{out}} | A^{(+)} | \Psi^{(+)}_{\vec{k}_{in}} \rangle \right]
\]

- The scattering wave function is expanded in a basis of (N+1)-particle Slater determinants \{ |\chi_m\rangle \}

\[
|\Psi^{(\pm)}_k\rangle = \sum_m a^{(\pm)}(\vec{k}) |\chi_m\rangle
\]

\{ a^{(\pm)}(\vec{k}) \} are then variationally determined.

- The “working” expression for the scattering amplitude (in the body-frame) is

\[
f(\vec{k}_{out}, \vec{k}_{in}) = -\frac{1}{2\pi} \sum_{m,n} \langle S_{\vec{k}_{out}} | V | \chi_m \rangle (d^{-1})_{mn} \langle \chi_n | V | S_{\vec{k}_{in}} \rangle
\]

where

\[
d_{mn} = \langle \chi_m | A^{(+)} | \chi_n \rangle
The SMC method:

- Configuration state functions (CSFs):

\[ |\chi_\mu\rangle = [|\Phi_1\rangle \otimes |\varphi_\mu\rangle] \text{ – direct space (static approximation)}; \]

\[ |\chi_{\sigma\lambda}\rangle = [|\Phi_{\sigma}\rangle \otimes |\varphi_{\lambda}\rangle] (\sigma > 1) \text{ – polarization (plus the direct space – static plus polarization approximation)}. \]

\[ |\Phi_1\rangle = \text{target ground state (RHF)}; \]

\[ |\varphi_\mu\rangle = \text{scattering orbital}; \]

\[ |\Phi_\sigma\rangle = \text{[hole \rightarrow particle] virtual single excitation}. \]

- Single-particle basis \(\rightarrow\) Cartesian Gaussian functions!

- Fixed-nuclei approximation.