Studies of electron—polyatomic-molecule collisions: Applications to e-CH_4

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We report the first application of the Schwinger multichannel formulation to low-energy electron collisions with a nonlinear polyatomic target. Integral and differential cross sections are obtained for e-CH_4 collisions from 3 to 20 eV at the static-plus-exchange interaction level. In these studies the exchange potential is directly evaluated and not approximated by local models. An interesting feature of the small-angle differential cross section is ascribed to polarization effects and not reproduced at the static-plus-exchange level. Our differential cross sections are found to be in reasonable agreement with existing measurements at 7.5 eV and higher energies.

I. INTRODUCTION

To date, most *ab initio* studies of electron-molecule collisions have concentrated on linear target molecules where single-center expansion techniques[1] are particularly well suited to exploit the cylindrical symmetry of such systems. However, a true multicenter method designed to be applicable to target molecules of arbitrary geometry would dramatically widen the range of interesting problems[2] amenable to theoretical treatments. Moreover, such a multicenter method can be readily applied to electron collisions with molecules adsorbed on surfaces[3] in which the surface effects are simulated by a small cluster of atoms.

The behavior of cross sections for low-energy electron-molecule collisions is governed by static, polarization, and exchange interactions.[1] Polarization effects are known to be important for low-energy electron collisions with molecules that do not possess a large permanent dipole moment. Recently there has been considerable progress in the development of accurate methods[4–9] for including the effects of polarization. In addition to the static and polarization interactions, a reliable treatment of low-energy electron-molecule scattering must incorporate the effects of antisymmetry on the total scattering wave function. This requirement gives rise to energy-dependent exchange terms in the scattering equations. The nonlocal character of these terms makes the numerical solution of the resulting equations arduous. These difficulties have justifiably stimulated attempts to model the effects of exchange by including approximate local terms[10–12] in the interaction potential. The traditional test for local models of exchange is to compare the static-model-exchange interaction cross sections with exact static-plus-exchange results. Such a comparison is even more important if, in addition, one is trying to assess the utility of an approximate treatment of polarization. So far, essentially exact treatments of the exchange terms have been restricted to linear systems.[13–17] Thus a set of accurate static-plus-exchange cross sections for polyatomic systems would be a useful and a logical first step for more complete studies including polarization effects.

Recently we have presented two different applications of the Schwinger multichannel theory[18,19] (SMC) to e-H_2 collisions. In one paper[20] we reported results for the inelastic process $X\,^1\Sigma_g^+ \rightarrow b\,^3\Sigma_u^+$ within the two-state approximation and in the other[9] we demonstrated the ability of the theory to account for polarization effects in an *ab initio* manner for elastic scattering. In this paper we report the preliminary application of the SMC theory to elastic e-CH_4 scattering in the static-plus-exchange approximation. Due to its presence in planetary atmospheres methane is an important system for study. As a result one needs cross-section data for modeling and understanding these planetary atmospheres. Theoretical[21–26] and experimental[27–29] e-CH_4 collision results are available for comparison. However, to our knowledge this is the first study of electron—polyatomic-molecule scattering at the static-plus-exchange level without the use of a local-exchange potential.

A brief review of our theoretical formulation is provided in Sec. II. In Sec. III we report differential cross sections for elastic e-CH_4 scattering at the static-plus-exchange level for selected energies in the (3—20)-eV range. These results are compared with available experimental data. We summarize our results and conclusions in Sec. IV.

II. THEORY

The details of the SMC formulation have been discussed previously[18,19] and hence we give only a brief review here. Our method begins with the projected Lippman-Schwinger equation

$$P\Psi_n^{(+)} = \frac{1}{\sqrt{N+1}} S_n + G_P^{(+)} V \Psi_n^{(+)} , \tag{2.1}$$

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where $\Psi_n^{(+)}$ is the total $(N+1)$-particle wave function with plane-wave and outgoing-wave boundary conditions for the nth channel. The projection operator P defines the open-channel space in terms of the N-particle eigenfunctions of the target Hamiltonian H_N:

$$P=\sum_{m=1}^{N_0} |\Phi_m(1,2,\ldots,N)\rangle\langle\Phi_m(1,2,\ldots,N)| \quad (2.2)$$

and

$$H_N|\Phi_m\rangle=E_m|\Phi_m\rangle,\quad E-E_m>0\ , \quad (2.3)$$

where E is the total energy of the $(N+1)$-particle system. In Eq. (2.1), S_n is the free-particle solution of the unperturbed Hamiltonian $H_0=H_N+T_{N+1}$ and is given by

$$S_n=\Phi_n e^{i\mathbf{k}_n\cdot\mathbf{r}_{N+1}}\ . \quad (2.4)$$

The interaction between the incident electron and the target is

$$V=H_{N+1}-H_0 = \sum_{i=1}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_{N+1}|}-\sum_{\alpha}\frac{Z_\alpha}{|\mathbf{R}_\alpha-\mathbf{r}_{N+1}|}\ . \quad (2.5)$$

The outgoing-wave Green's function $G_P^{(+)}$, defined in the open-channel space, can be written as

$$G_P^{(+)}=\sum_{m=1}^{N_0}|\Phi_m\rangle g_m^{(+)}(\mathbf{r}_{N+1},\mathbf{r}'_{N+1})\langle\Phi_m| \quad (2.6)$$

with

$$g_m^{(+)}(\mathbf{r},\mathbf{r}')=-\frac{1}{2\pi}\frac{e^{ik_m|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\ . \quad (2.7)$$

To define a complete equation for $\Psi_n^{(+)}$ we must recover the unprojected component of Eq. (2.1). This is accomplished via the projected Schrödinger equation

$$[\hat{H}-a(P\hat{H}+\hat{H}P)]\Psi_n^{(+)}=a(VP-PV)\Psi_n^{(+)}\ , \quad (2.8)$$

where $\hat{H}=E-H_{N+1}$ and a is an arbitrary parameter. The above equation contains information about the closed channels without defining the closed-channel Green's function, which would require the inclusion of the target continuum states.[30] As shown by Takatsuka and McKoy,[18,19] a simple combination of Eqs. (2.1) and (2.8) together with $a=(N+1)/2$ defines a complete equation for $\Psi_n^{(+)}$, viz.

$$\left[\tfrac{1}{2}(PV+VP)-VG_P^{(+)}V+\frac{1}{N+1}\left[\hat{H}-\frac{N+1}{2}(P\hat{H}+\hat{H}P)\right]\right]\Psi_n^{(+)}=\frac{1}{\sqrt{N+1}}VS_n\ . \quad (2.9)$$

Based on Eq. (2.9), a variational functional for the fixed-nuclei scattering amplitude is

$$f^B(\mathbf{k}_m,\mathbf{k}_n)=-\frac{1}{2\pi}\frac{\langle S_m|V|\Psi_n^{(+)}\rangle\langle\Psi_m^{(-)}|V|S_n\rangle}{\langle\Psi_m^{(-)}|\{\frac{1}{2}(PV+VP)-VG_P^{(+)}V+[1/(N+1)][\hat{H}-\frac{1}{2}(N+1)(P\hat{H}+\hat{H}P)]\}|\Psi_n^{(+)}\rangle}\ , \quad (2.10)$$

where the superscript B on f^B indicates that this quantity is calculated in the body-fixed (molecular) reference frame.[1]

In our procedure $\Psi_n^{(+)}$ is expanded in a basis of $(N+1)$-particle Slater determinants that are constructed from an orthogonal set of molecular orbitals, additional basis functions, and plane-wave functions, if necessary. However, unlike the Feshbach partitioning technique,[31] we make no distinction among the open and closed configurations in $\Psi_n^{(+)}$. The molecular orbitals and additional basis functions used to construct the Slater determinants are further expanded in Cartesian Gaussian functions. With this choice of basis, all of the matrix elements appearing in Eq. (2.10), except those of $VG_P^{(+)}V$, can be evaluated analytically for molecules of arbitrary geometry. Furthermore, the $VG_P^{(+)}V$ matrix elements can be obtained in closed form if a large quadrature basis consisting of Cartesian Gaussian functions is inserted around $G_P^{(+)}$.[15,32,33] We have used this method in our two previous applications of the SMC theory to e-H_2 scattering.[9,20] In this study we use the same method to calculate the principal-value contribution of the $VG_P^{(+)}V$ matrix elements, but the residue is obtained via insertion of a complete set of plane waves around $G_P^{(+)}$. This procedure results in an S matrix that is very nearly unitary without resorting to an enormous quadrature basis. Details of this technique will be presented elsewhere.[34]

The present formulation allows us to calculate an analytical approximation to the body-frame fixed-nuclei[1,35] scattering amplitude for molecules of arbitrary geometry. As discussed in our previous paper,[20] we then expand $f^B(\mathbf{k}_m,\mathbf{k}_n)$ in a partial-wave series and make the requisite transformation into the laboratory frame. After accounting for the random orientation of the target, the differential cross section is obtained in the usual manner by performing the appropriate average over initial spin states and sum over final spin states.

III. PROCEDURES AND RESULTS

As a first application of our formulation to polyatomic systems we have calculated differential and integral cross sections for elastic collisions between CH_4 and 3—20-eV electrons. This polyatomic system provides a convenient test for our procedures because it has five centers and possesses no permanent dipole or quadrupole moment. There have been several static—model-exchange—polarization (SMEP) studies[21–26] of this system, and mea-

TABLE I. Cartesian Gaussian basis set. Cartesian Gaussian functions are defined by

$$X_{lmn}^{(\alpha)} = N_{lmn}(x-A_x)^l(y-A_y)^m(z-A_z)^n e^{-\alpha|\mathbf{r}-\mathbf{A}|^2},$$

where **A** is the position of the Gaussian center. The basis set is used for the ground state of CH_4, in the expansion of the scattering functions and for insertion around $VG_P^{(+)}V$.

Atom[a] and type	Exponents (α)
C, 12s	4233, 634.9, 146.1, 42.5, 14.19, 5.148, 1.967, 0.4962, 0.1533, 0.0496, 0.02, 0.01
C, 8p	18.16, 3.986, 1.143, 0.3594, 0.1146, 0.046, 0.018, 0.0072
C, 4d	2.4, 0.6, 0.15, 0.0375
H, 7s	19.240 56, 7.45, 2.899 152, 0.653 410 1, 0.177 576 5, 0.071, 0.025

[a]At the equilibrium internuclear distance of $R_{\text{C-H}} = 2.05a_0$.

sured cross sections are available.[27–29]

Our calculations are performed within the framework of the fixed-nuclei approximation. Here, the nuclei are held at their equilibrium values and the dependence of the scattering amplitude on internuclear separation is neglected. The rotational levels are treated as degenerate and the physical cross sections are obtained by averaging the fixed-nuclei results over all molecular orientations. Unless otherwise stated, atomic units are used throughout.

For the ground state of CH_4 we used a self-consistent-field (SCF) wave function obtained with a [12s 8p 4d] uncontracted Cartesian Gaussian basis on the carbon and a [7s] basis on each hydrogen. The Gaussian exponents shown in Table I are from the [9s 5p] basis given by Huzinaga[36] together with an additional set of d functions and diffuse s- and p-type functions. A set of CH_4 virtual orbitals calculated with the same SCF basis and Schmidt-orthogonalized to the occupied orbitals $1a_1$, $2a_1$, $1t_{2x}$, $1t_{2y}$, and $1t_{2z}$ were used to expand the scattering functions and to satisfy the closure relation of the insertion technique. The use of totally uncontracted Gaussian functions permits greater flexibility in the scattering and insertion basis set. With this basis we obtain a SCF energy of $-40.2029E_h$ at a carbon-hydrogen nuclear distance of $2.050a_0$ to be compared with $-40.2124E_h$ obtained by Meyer[37] at the same geometry.

Our calculations in the body frame include contributions from the $^2A_1$, $^2T_2$, and ^2E symmetries in $\Psi_1^{(\pm)}$. Indeed, all 83 available virtual (scattering) orbitals from the molecular SCF calculation, $21a_1$, $18t_{2x}$, $18t_{2y}$, $18t_{2z}$, and $8e$, were used in the expansion of $\Psi_1^{(\pm)}$, i.e., $\Psi_1^{(\pm)}$ is constructed from linear combinations of $(N+1)$-particle Slater determinants

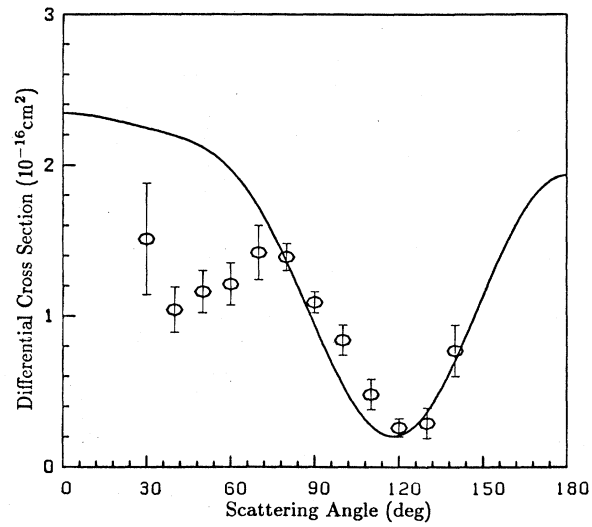

FIG. 2. DCS for e-CH_4 scattering at 5 eV: present SE results (solid line), measured values of Ref. 28 (○).

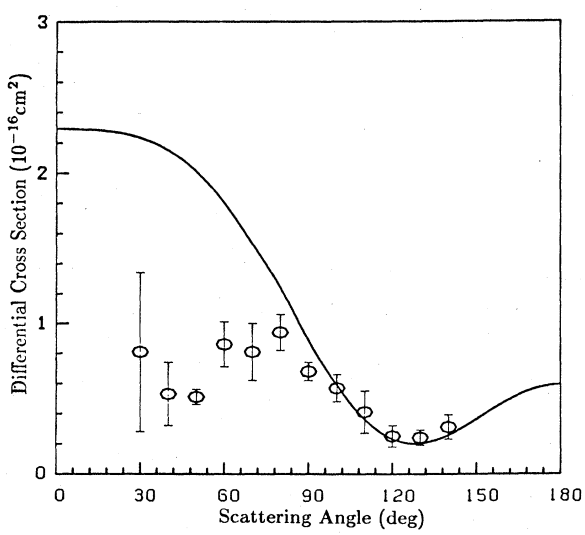

FIG. 1. Differential cross sections (DCS) for e-CH_4 scattering at 3 eV: present static-plus-exchange (SE) results (solid line), measured values of Ref. 28 (○).

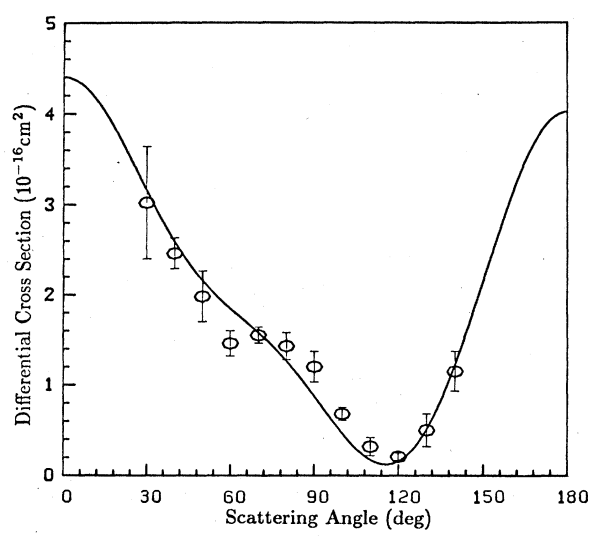

FIG. 3. DCS for e-CH_4 scattering at 7.5 eV: present SE results (solid line), measured values of Ref. 28 (○).

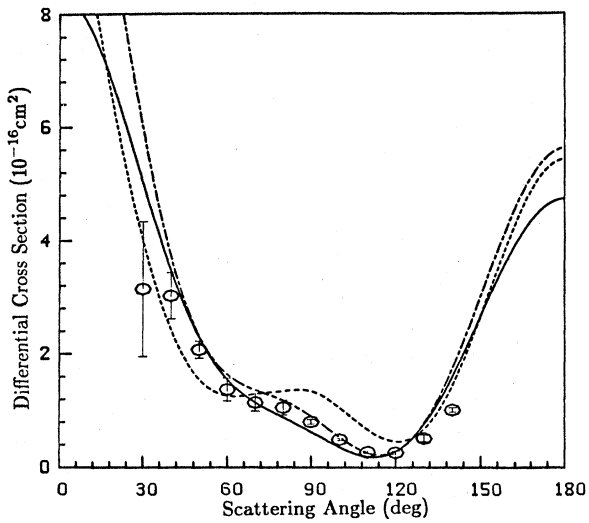

FIG. 4. DCS for e-CH_4 scattering at 10 eV: present SE results (solid line), static—model-exchange—polarization (SMEP) results of Ref. 24 using an adiabatic polarization potential (dashed line), SMEP results of Ref. 24 using a local-kinetic energy semiclassical potential (long-short dashed line), measured values of Ref. 28 (○).

$$^2A_1:\ 1a_1^2 2a_1^2 1t_{2x}^2 1t_{2y}^2 1t_{2z}^2 ka_1\ ,$$

$$^2T_{2x}:\ 1a_1^2 2a_1^2 1t_{2x}^2 1t_{2y}^2 1t_{2z}^2 kt_{2x}\ ,$$

$$^2T_{2y}:\ 1a_1^2 2a_1^2 1t_{2x}^2 1t_{2y}^2 1t_{2z}^2 kt_{2y}\ ,$$

$$^2T_{2z}:\ 1a_1^2 2a_1^2 1t_{2x}^2 1t_{2y}^2 1t_{2z}^2 kt_{2z}\ ,$$

$$^2E:\ 1a_1^2 2a_1^2 1t_{2x}^2 1t_{2y}^2 1t_{2z}^2 ke$$

with ka_1, kt_2, and ke being continuum functions represented by the virtual orbitals. We have shown in an earlier paper[19] that this type of expansion reduces the SMC expression for the scattering amplitude to the static-plus-exchange level of approximation. Finally, for the partial-wave expansion of the scattering amplitude, we include values of $l \leq 5$.

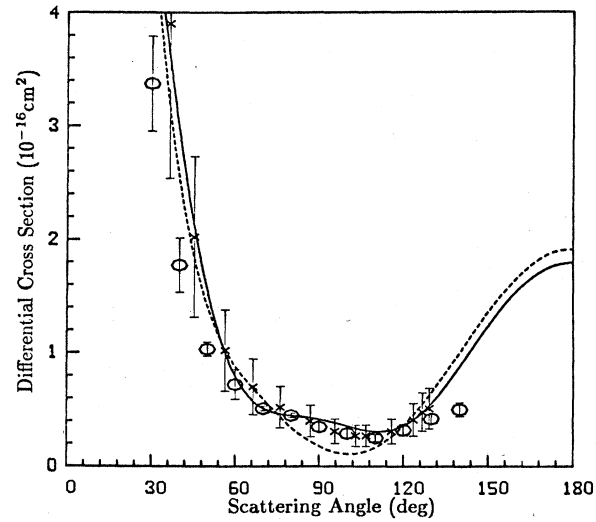

FIG. 6. DCS for e-CH_4 scattering at 20 eV: present SE results (solid line), theoretical results of Ref. 25, measured values of Ref. 28 (○), measured values of Ref. 29 (×).

In Figs. 1—6 we present the calculated differential cross sections for incident energies of 3, 5, 7.5, 10, 15, and 20 eV, respectively. Also shown at each energy are the experimental results of Tanaka *et al.*[28] At 10 eV the theoretical results of Abusalbi *et al.*[24] obtained using two different SMEP potentials, are also included. At 20 eV the experimental data of Vušković *et al.*[29] and the calculations of Jain[25] are presented along with our results and the measurements of Tanaka *et al.*[28]

The differential cross section in this range of energies are characterized by forward peaking, a minimum around

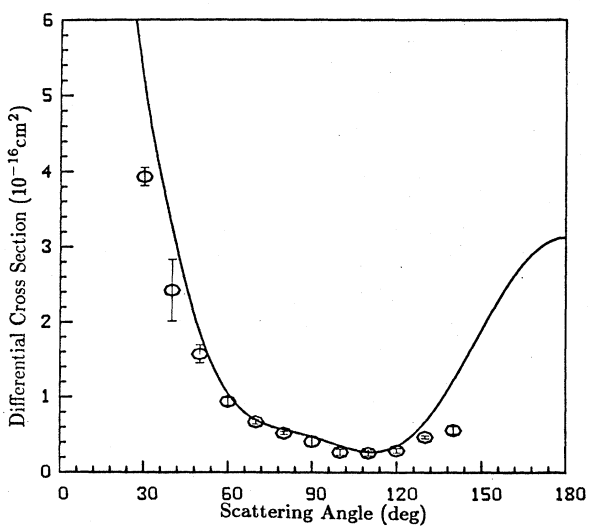

FIG. 5. DCS for e-CH_4 scattering at 15 eV: present SE results (solid line), measured values of Ref. 28 (○).

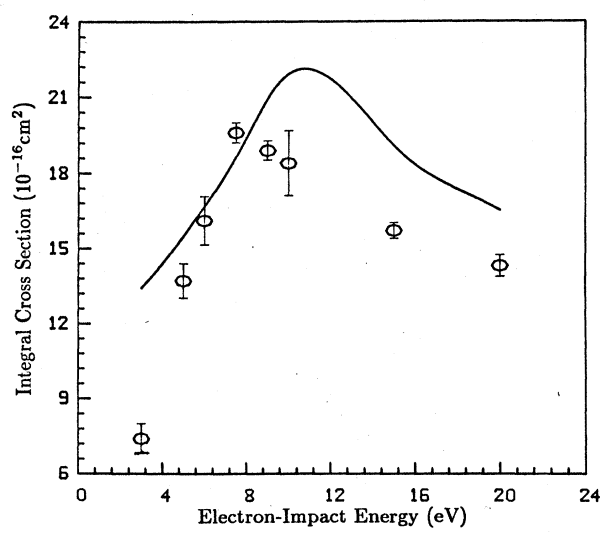

FIG. 7. Elastic cross section for e-CH_4 scattering: present SE results (solid line), measured values of Ref. 28 (○).

120°, and a backward peak. The minimum is rather sharp at low energies and becomes broader with increasing energy. In addition experiment shows a secondary minimum occurring near 45° at 3 eV. As the incident energy is increased to 7.5 eV the minimum moves to 60°, and becomes a much less pronounced shoulderlike structure. The present calculations reproduce both the forward and backward peaks as well as the primary minimum near 120°. However, at low energies the calculated forward peak is much stronger than experiment. The secondary minimum is also missing, indicating that this feature is most likely due to polarization effects and cannot be reproduced at the present level of approximation.

The sensitivity of the low-energy differential cross section to the particular way in which polarization effects are modeled has been demonstrated by Gianturco *et al.*[21,22] They used a semiempirical polarization potential[8,21] with the correct asymptotic form but with a short-range cutoff parameter r_0 chosen by calibration to experimental data. These studies showed that even small changes in the cutoff parameter substantially affect the differential cross sections. Moreover, when the cutoff parameter is increased from 0.84 to 0.92, which makes the inner region of the potential look more like the static-plus-exchange potential, the shoulder at low energy becomes less pronounced, indirectly supporting our conjecture that the secondary minimum is a polarization effect. The secondary minimum is also reproduced by the model polarization potential studies of Abusalbi *et al.*,[24] at 10 eV. However, at this energy the polarization effect is relatively small so that the difference between their "best" polarization curve and our static-plus-exchange curve is rather small.

In Fig. 7 our integral cross sections are presented along with the measurements of Tanaka *et al.* Compared with experiment, the maximum of our total cross section is shifted to higher energies by about 2.5 eV. Above this maximum the qualitative agreement between the calculated and measured cross sections is reasonable. However, some of the discrepancy in the integral cross sections can arise from uncertainties in extrapolating the measured differential cross sections to small ($<30°$) and large ($>140°$) angles. Future polarization studies will determine whether the inclusion of these effects are sufficient to bring these results into better agreement.

IV. CONCLUSIONS

In this paper we have reported the first application of the Schwinger multichannel formulation to low-energy electron impact collisions with a nonlinear polyatomic target. Integral and differential cross sections at the static-plus-exchange level of approximation have been obtained for e-CH_4 collisions from 3 to 20 eV. A very interesting feature of the small-angle differential cross sections is ascribed to polarization effects. Our differential cross sections were found to be in very reasonable agreement with existing measurements at 7.5 eV and above. A more complete study including polarization effects via the inclusion of closed channels in the expansion of the wave function is underway. Our implementation of the SMC formulation has been designed for its general applicability to target molecules of arbitrary geometry. The present study helps to demonstrate the utility of this approach and represents considerable progress toward obtaining accurate *ab initio* cross sections for a variety of polyatomic targets.

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