RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 39, NUMBER 8 APRIL 15, 1989

Polarization effects in low-energy e-CH_4 collisions

M. A. P. Lima,* K. Watari,† and V. McKoy

A. A. Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

(Received 24 January 1989)

We have used the Schwinger multichannel formulation [Takatsuka and McKoy, Phys. Rev. A **24**, 2473 (1981)] to carry out *ab initio* studies of the effects of polarization on the cross sections for elastic scattering of electrons by the polyatomic molecule CH_4 for collision energies from 7.5 down to 0.02 eV. Although the closed-channel expansion through which polarization effects are included in this approach is not fully converged, the resulting cross sections do show a Ramsauer-Townsend minimum between 0.1 and 0.2 eV, about 0.3 eV below where it is seen experimentally. Our static-exchange cross sections show no Ramsauer-Townsend minimum. At the higher energy of 7.5 eV, where polarization effects are less significant, the calculated differential cross sections are in excellent agreement with the measured values. Differential cross sections are also shown at 3.0 eV.

Polarization effects are known to exert significant influence on the cross sections for elastic scattering of low-energy electrons by molecules.[1] In electron-methane scattering, for example, they can be expected to play an important role around the Ramsauer-Townsend minimum in the cross sections, a feature that has been extensively studied in both transmission[2-7] and swarm-type[8,9] experiments. Differential cross sections for these collisions have also been studied at low energies using crossed-beam techniques.[10-13] A comparison of these measured differential cross sections and those calculated in the static-exchange approximation, which neglects any effects due to polarization, also clearly reveals the influence of polarization on the scattering cross sections.

To date, most *ab initio* studies of the elastic cross sections for low-energy electron-polyatomic molecule collisions have been limited to calculations which used approximations to the exchange and polarization terms of the scattering potential. For example, elastic e-CH_4 scattering has been studied by Gianturco and Thompson[14] using a parameter-dependent polarization potential and orthogonalization to represent exchange and later by Jain and Thompson[15] with a Hara free-electron gas (plus orthorgonalization) approximation to exchange and a model parameter-free polarization potential. Jain[16] has also obtained e-CH_4 elastic cross sections for collision energies from 0.1 to 500 eV using a spherical model with local exchange and model polarization potentials. More recently, we have used the Schwinger multichannel method (SMC)[17] to determine the elastic-scattering cross sections for e-CH_4 at the static-exchange level for energies between 3 and 20 eV.[18] In the SMC method exchange is properly accounted for via antisymmetrization of the $(N+1)$-electron target wave function. A significant use of such static-exchange cross sections is that their comparison with the experimental data allows us to uniquely identify those features which are due to polarization.

In this Rapid Communication we present the results of calculations of the elastic e-CH_4 cross sections for collision energies from 7.5 to 0.02 eV in which polarization effects are included nonempirically. These studies, the first of their kind for a polyatomic target, are carried out in the fixed-nuclei approximation using the SMC method. In this approach polarization effects are accounted for by inclusion of energetically closed channels in a configuration-interaction-like expansion of the total scattering wave function in a basis of $(N+1)$-electron determinants. Although the closed-channel expansion used in these calculations is not fully converged, it is sufficient to show a Ramsauer-Townsend minimum, albeit at too low an energy, and to adequately represent the effects of polarization at higher energies where the magnitude of such effects decreases.

In these calculations we used a $(12s\,8p\,4d)$ and a $(7s)$ uncontracted Cartesian Gaussian basis centered on the carbon and hydrogens, respectively. The exponents of these basis functions, which were also used in earlier static-exchange studies of e-CH_4 collisions, are given in Ref. 18. This basis was used for both the SCF wave function of CH_4 and to obtain a set of natural orbitals for the negative ion CH_4^- which are orthogonalized to the target orbitals $1a_1$, $2a_1$, $3a_1$, $1b_1$, and $1b_2$ (in C_{2v} symmetry) and used to expand the scattering functions and to construct the closed channel space. In the SMC method,[17] as in the original Schwinger variational principle,[19] the trial-scattering wave function need not satisfy any specific boundary conditions and hence could be expanded in L^2 functions such as Cartsian Gaussians. For the negative-ion natural orbitals we used a $^2A_1$ (T_d) state which is the symmetry in which the Ramsauer minimum occurs. The effectiveness of such negative ion natural orbitals to describe polarization effects has been discussed previously.[20] Our calculation of the body-frame amplitudes includes contributions in the C_{2v} group from 350 configurations of $^2A_1$ symmetry, 150 of $^2A_2$, 200 of $^2B_1$, and 200 of $^2B_2$ in the expansion of the total-scattering wave function, i.e., $\Psi = \sum_i a_i \chi_i$, where χ_i is a $(N+1)$-electron Slater determinant. In the static-exchange approximation, the elec-

TABLE I. Configurations for closed-channel expansion of the scattering wave function for basis I, in C_{2v} notation and relative to the static-exchange configurations $1a_1^2 2a_1^2 3a_1^2 1b_1^2 1b_2^2 ka_1$ ($^2A_1$), $1a_1^2 2a_1^2 3a_1^2 1b_1^2 1b_2^2 ka_2$ ($^2A_2$), $1a_1^2 2a_1^2 3a_1^2 1b_1^2 1b_2^2 kb_1$ ($^2B_1$), and $1a_1^2 2a_1^2 3a_1^2 1b_1^2 1b_2^2 kb_2$ ($^2B_2$).

$^2A_1$	$^2A_2$	$^2B_1$	$^2B_2$
$[3a_1 \rightarrow na_1]ka_1$	$[3a_1 \rightarrow nb_1]kb_2$	$[3a_1 \rightarrow na_1]kb_1$	$[3a_1 \rightarrow na_1]kb_2$
$[1b_1 \rightarrow nb_1]ka_1$	$[1b_1 \rightarrow nb_2]ka_1$	$[1b_1 \rightarrow nb_1]kb_1$	$[1b_1 \rightarrow nb_1]kb_2$
$[1b_2 \rightarrow nb_2]ka_1$	$[1b_2 \rightarrow nb_1]ka_1$	$[1b_2 \rightarrow nb_2]kb_1$	$[1b_2 \rightarrow nb_2]kb_2$

tron configurations of these determinants are as follows in C_{2v} symmetry:

$$1a_1^2 2a_1^2 3a_1^2 1b_1^2 1b_2^2 ka_1\ (^2A_1)\,,$$

$$1a_1^2 2a_1^2 3a_1^2 1b_1^2 1b_2^2 ka_2\ (^2A_2)\,,$$

$$1a_1^2 2a_1^2 3a_1^2 1b_1^2 1b_2^2 kb_1\ (^2B_1)\,,$$

and

$$1a_1^3 2a_1^2 3a_1^2 1b_1^2 1b_2^2 kb_2\ (^2B_2)\,.$$

The configurations of the determinants used in the closed-channel space are given in Table I in the notation $[\phi_h \rightarrow \phi_p]\phi_s$ where ϕ_h, ϕ_p, and ϕ_s represent a hole, particle, and scattering orbital, respectively.

Figure 1 shows our calculated elastic integral cross sections in the static-exchange (SE) and static-exchange-plus-polarization (SEP) approximations for e-CH$_4$ collisions along with the experimental data of Refs. 4, 5, and 12 and the theoretical results of Jain obtained using a local exchange and model polarization potential.[16] The significant feature of these results is that our cross sections with target polarization do show a Ramsauer-Townsend minimum in distinct contrast to the static-exchange results where no indication of such a minimum is seen. Comparison with the experimental data shows that the calculated minimum occurs at too low an energy and is too deep and steep. These differences are due to the lack of convergence of our closed-channel expansion through which polarization effects are included. For example, the position of the calculated minimum reflects this lack of convergence in $^2A_1$ (T_d) symmetry. As the minimum moves to higher energy the contributions to the cross sections from other symmetries will increase and hence should change the shape around the minimum. We also include in Fig. 1 static-"exchange" cross sections obtained by Gianturco, Jain, and Pantano[21] using two different approximations to exchange based on the free-electron-gas model. With one of these approximations [the orthogonalized asymptotically adjusted (OAA) results of Fig. 4 in Ref. 21] the static-model-exchange cross sections show a Ramsauer minimum in strong contrast to our static-exchange results which are essentially flat in this energy range. The other static-model-exchange result of Ref. 21 shown in our Fig. 1 [the orthogonalized Hara (OH) model] are closer to our static-exchange cross sections below 1 eV. It is important to note, however, that at energies above 1 eV this same model potential yields cross sections which are very different from our static-exchange results and those obtained with the OAA model.[21]

To further explore this Ramsauer-Townsend minimum we have also carried out calculations expanding the scattering wave function only in terms of $^2A_1$ configurations which give a nonzero contribution to K^{00}_{00}, the s-wave element of the K matrix. The Ramsauer minimum occurs in this s-wave scattering amplitude and use of 350 such $^2A_1$ configurations, the maximum allowable in the present computer programs, allows us to look at the position of the minimum more closely. The resulting closed-channel configurations are given in Table II. Note that the choice of $^2A_1$ configurations in the basis shown in Table I, with which scattering cross sections are actually obtained, is made so as to be consistent, e.g., t_{2x}, t_{2y}, and t_{2z} should be equivalent, with those of the other symmetries ($^2A_2$, $^2B_1$, $^2B_2$). The values of K^{00}_{00} using this basis are shown in Table III along with the static-exchange values and those obtained with basis I of Table I. The static-exchange values show no change in sign and hence no Ramsauer minimum. On the other hand, with polarization K^{00}_{00} changes sign around 0.1 eV with basis I and at slightly higher energy with basis II which includes a large number of closed-channel $^2A_1$ configurations with nonzero s-wave contributions.

To assess the effects of polarization at higher collision energies where their influence should not be as pronounced as around the Ramsauer minimum, Figs. 2 and 3 show calculated differential cross sections in both the

TABLE II. Configurations for closed-channel expansion of the $^2A_1$ scattering wave function for basis II. Notation used here is the same as that for Table I. These configurations give nonzero contributions to the pure s-wave element of the K matrix K^{00}_{00}.

$^2A_1$	$^2A_1$	$^2A_1$	$^2A_1$
$[3a_1 \rightarrow na_1]ka_1$	$[1b_1 \rightarrow nb_1]ka_1$	$[1b_2 \rightarrow nb_2]ka_1$	$[2a_1 \rightarrow na_1]ka_1$
$[3a_1 \rightarrow nb_1]kb_1$	$[1b_1 \rightarrow nb_2]ka_2$	$[1b_2 \rightarrow nb_1]ka_2$	$[2a_1 \rightarrow nb_1]kb_1$
$[3a_1 \rightarrow nb_2]kb_2$			$[2a_1 \rightarrow nb_2]kb_2$

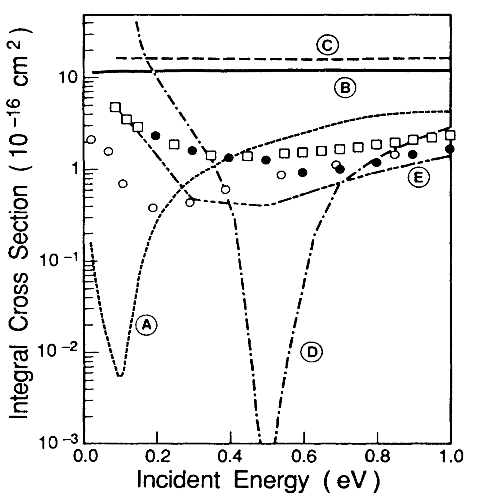

FIG. 1. Integral cross sections for c-CH_4 collisions below 1 eV: curve A, present static-exchange-polarization results; curve B, present static-exchange results; curves C and D, static-exchange results OH and OAA, respectively, of Ref. 21; curve E, local exchange-model polarization results of Ref. 16. ○, □, and ● represent the experimental results of Refs. 4, 5, and 12, respectively.

static-exchange and static-exchange-polarization approximations at 3.0 and 7.5 eV, respectively, along with experimental data taken from Refs. 11, 12, and 22. Comparison of these results at 3 eV illustrates the importance of polarization effects below 90° at this lower energy. Although our present closed-channel expansion does lead to substantial change in these cross sections at lower angles, it is not large enough to show the minimum seen experimentally around 30° to 40°. At angles beyond 90°, the cross sections are quite well described at the static-exchange level. At 7.5 eV, the static-exchange results reproduce the general shape and magnitude of the differential cross sections. However, when polarization effects are included, the agreement between the calculated and measured cross sections is excellent.

As a preliminary test of the convergence of our results we have carried out calculations in which the scattering basis used above was augmented with diffuse s- and p-type Gaussian functions on the carbon and hydrogen atoms, respectively. These additional functions led to no significant changes in the cross sections. Further studies of these cross sections including a larger number of configurations and a direct numerical quadrature of the second-Born-like matrix elements,[23] i.e., $\langle \Psi | VGV | \Psi \rangle$ arising in our theory are under way.

In summary, we have presented the first results of entirely *ab initio* studies of the cross sections for the collisions of low-energy electrons by the nonlinear polyatomic molecule CH_4. These calculations show explicitly that

TABLE III. The pure s-wave element of the K matrix for e-CH_4 collisions.

Energy (eV)	SE[a]	SEP[b] (Table I)	SEP[c] (Table II)
0.02	−0.069	+0.008	+0.014
0.1	−0.159	−0.003	+0.007
0.2	−0.218	−0.033	−0.022
0.5	−0.331	−0.136	−0.125

[a] Static-exchange result.

[b] SEP with polarization using the closed-channel expansion of Table I.

[c] SEP with polarization using the closed-channel expansion of Table II.

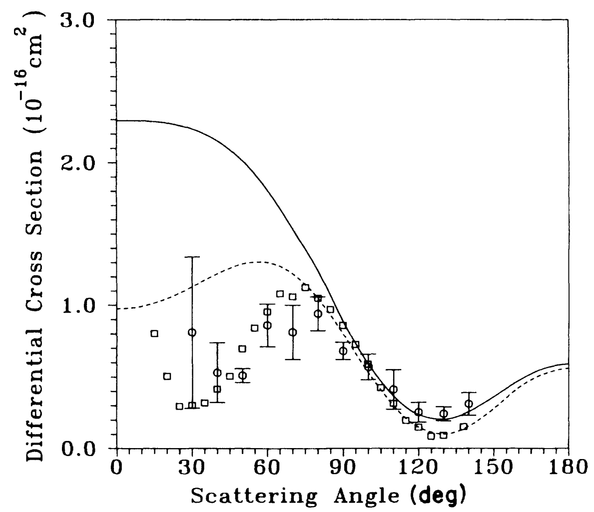

FIG. 2. Differential cross sections for e-CH_4 collisions at 3.0 eV: the dashed line and the solid line, present static-exchange-polarization and static-exchange results, respectively; ○ and □ represent the experimental data of Refs. 11 and 12, respectively.

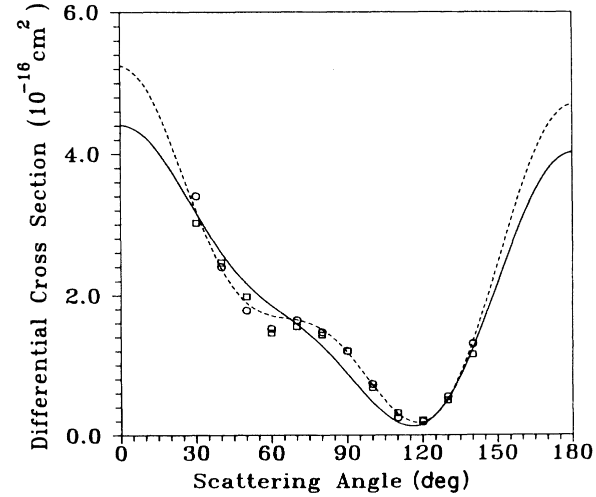

FIG. 3. Differential cross sections for e-CH_4 collisions at 7.5 eV: dashed line and solid line, present static-exchange-polarization and static-exchange results, respectively; □ and ○ represent the experimental data of Refs. 11 and 22, respectively.

the Ramsauer-Townsend minimum in these cross sections arises from polarization effects and are not present in the static-exchange approximation.

This work was supported by National Science Foundation Grant No. PHY-8604242, the Innovative Science and Technology Program of the Strategic Defense Initiative Office under Contract No. DAAL03-86-K-0140 of the Army Research Office, and NASA-Ames Cooperative Agreement NCC 2-319. We also acknowledge use of the computer resources of the NASA-Ames Research Center. M.A.P.L. and K.W. acknowledge support from Conselho Nacional de Desenvolvimento Científico e Technológico (Brazil).

---

[*] Permanent address: Instituto de Estudos Avançados, Centro Técnico Aeroespacial, Caixa Postal 6044, 12231 São José dos Campos, São Paulo, Brazil.

[†] On leave from: Instituto de Física, Universidade de São Paulo, Caixa Postal 20516, 01498 São Paulo, São Paulo, Brazil.

[1] See, for example, N. F. Lane, Rev. Mod. Phys. **52**, 29 (1980), and references therein.

[2] E. Brüche, Ann. Phys. (Leipzig) **83**, 1065 (1927); **4**, 387 (1930).

[3] C. Ramsauer and R. Kollath, Ann. Phys. (Leipzig) **4**, 91 (1930).

[4] E. Barbarito, M. Basta, M. Calicchio, and G. Tessari, J. Chem. Phys. **71**, 54 (1979).

[5] J. Ferch, B. Granitza, and W. Raith, J. Phys. B **18**, L445 (1985).

[6] R. K. Jones, J. Chem. Phys. **82**, 5424 (1985).

[7] B. Lohmann and S. Buckman, J. Phys. B **19**, 2565 (1986).

[8] T. L. Cottrell and I. C. Walker, Trans. Faraday Soc. **63**, 549 (1967).

[9] C. W. Duncan and I. C. Walker, J. Chem. Soc. Faraday Trans. 2 **68**, 1514 (1972).

[10] K. Rohr, J. Phys. B **31**, 4897 (1980).

[11] H. Tanaka, T. Okada, L. Boesten, T. Suzuki, T. Yamamoto, and M. Kubo, J. Phys. B **15**, 3305 (1982).

[12] W. Sohn, K.-H. Kochem, K.-M. Scheuerlein, K. Jung, and H. Ehrhardt, J. Phys. B **19**, 3625 (1986).

[13] R. Müller, K. Jung, K.-H. Kochem, W. Sohn, and H. Ehrhardt, J. Phys. B **18**, 3971 (1985).

[14] F. A. Gianturco and D. G. Thompson, J. Phys. B **9**, L383 (1976).

[15] A. Jain and D. G. Thompson, J. Phys. B **15**, L631 (1982).

[16] A. Jain, Phys. Rev. A **34**, 3707 (1986).

[17] K. Takatsuka and V. McKoy, Phys. Rev. A **24**, 2473 (1981); **30**, 1734 (1984).

[18] M. A. P. Lima, T. L. Gibson, W. M. Huo, and V. McKoy, Phys. Rev. A **32**, 2696 (1985).

[19] B. A. Lippmann and J. Schwinger, Phys. Rev. **78**, 135 (1950).

[20] W. M. Huo, T. L. Gibson, M. A. P. Lima, and V. McKoy, Phys. Rev. A **36**, 1632 (1987).

[21] F. A. Gianturco, A. Jain, and L. C. Pantano, J. Phys. B **20**, 571 (1987).

[22] P. J. Curry, W. R. Newell, and A. C. H. Smith, J. Phys. B **18**, 2303 (1985).

[23] M. A. P. Lima, L. M. Brescansin, A. J. R. Silva, C. Winstead, and V. McKoy (unpublished).