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Electron-CH_4 scattering in the Ramsauer-Townsend minimum region (0.10—1.0 eV)

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We report *ab initio* calculations for the electron-CH_4 elastic scattering around the Ramsauer-Townsend (RT) minimum region (0.1—1.0 eV). A model potential approach, in the fixed-nuclei and one-center-expansion formalism, is employed in which the total optical potential is composed of three interaction terms: an accurate static potential of the Hartree-Fock level, an exchange interaction in the Hara free-electron-gas-exchange approximation (plus the orthogonalization), and a semiempirical polarization of the form $-(\alpha_0/2r^4)(1-e^{-r/r_c})^6$, where r_c is an adjustable parameter. The final results on the total and momentum-transfer cross sections compare reasonably well with experimental data. In particular, a shallow RT structure rather than a pronounced dip in the total cross section is reproduced, which is in good agreement with recent measurements. We also determine the scattering length to be $a=-3.4$ a.u. by extrapolating our very-low-energy eigenphases ($E \simeq 0.001$ eV) to the limit of zero energy: From a simple s-wave analysis, this value gives the RT minimum position around 0.4 eV, which is in close agreement with the correct value.

I. INTRODUCTION

Very recently, Ferch *et al.*[1] and Lohmann and Buckman[2] have measured total cross sections for electron-CH_4 scattering for a wide range of incident energy. In this paper we are concerned with very-low-energy scattering ($E<1$ eV). (Jones[3(a)] also measured similar cross sections from 1.3 eV up to few hundred eV while Sohn *et al.*[3(b)] obtained such data from their differential cross-section measurements in the range 0.1—1.8 eV. For earlier experimental studies on this system, see Table I of Ref. 4.) Data on the momentum-transfer cross sections have recently been reported by Hadded[5] in the range 0.01—10 eV. It is clear from these experimental data on the total and momentum-transfer cross sections that the maximum discrepancy between theory and experiment exists below the 1-eV energy region, where a well-known minimum occurs around 0.4—0.5 eV [Ramsauer-Townsend (RT) effect].

The agreement between various experiments, (Refs. 1—3) including that of a very old measurement by Ramsauer and Kollath,[6] is so good that it seems worthwhile to carry out a semiempirical study on this system in this low-energy range: the only exception to this agreement is the experimental data of Barbarito *et al.*[7] [and also from Ref. 3(b)]; their magnitude and the position for the RT minimum is in serious disagreement with all other experiments. However, as pointed out by Ferch *et al.*[1] and Lohmann and Buckman,[2] it seems that the results of Barbarito *et al.* are not correct below 1 eV. We therefore assume that the data of both the recent experiments[1,2] [and also of Ref. 3(a)] is reliable and accurate enough for the present purpose.

Theoretically, Gianturco and Thompson[8,9] (GT) made the first *ab initio* calculations on e-CH_4 elastic scattering. By using a parameter-dependent polarization potential of the form

$$V(r)=-(\alpha_0/2r^4)(1-e^{-r/r_c})^6 , \tag{1}$$

they tuned the position of the experimental value (approximately) of the RT minimum (with $r_c=0.89$ a.u.), but their cross sections were larger than the experimental data by about a factor of 3 at all energies below 1 eV. This disagreement is expected since their exchange interaction was included only through an orthogonalization technique: the tuned polarization potential [Eq. (1)], therefore, has to compensate for the weak exchange force, since in the orthogonalization procedure not all the continuum symmetry orbitals are available in the bound part of the target. Later, Jain and Thompson[10] tried to include exchange in a better (but approximate) way [through the Hara free-electron-gas-exchange (HFEGE) approximation plus orthogonalization] and introduced an approximate parameter-free polarization potential for general electron-molecule systems at low energy. Their results for e-CH_4 were in good agreement with experiment above the 1—2-eV region and reproduced the T_2 8—10-eV structure in the total cross-section curve; however, below 1 eV, their calculations are in serious disagreement with all the recent existing experimental cross sections except the one of Barbarito *et al.*[7] (and also Sohn *et al.*[3(b)]). In particular, the position of the RT minimum in the work of Jain and Thompson[10] was shifted to lower energy (around 0.2 eV) and the magnitude was much smaller. As we shall see later, this is due to the fact that the polarization potential of Jain and Thompson (to be called the JT potential) is too weak to let the minimum occur at the right place.

There are several theoretical studies on the e-CH_4 total cross sections in the multiple-scattering (with $X\alpha$ potential) approach,[11,12] but they give very poor results at this low energy and therefore we would not include them in our comparison here. Jain, Gianturco, and Pantano[13] have used a parameter-free model potential approach for the same problem by including the correlation polarization potential as discussed and used earlier for atoms and diatomic molecules.[14] A more realistic elaborate calculation has recently been carried out by Lima *et al.*[15] for the e-CH$_4$ scattering at 3–20 eV in the Schwinger variational method; the exchange interaction is included exactly in their work.

We call the earlier model of Gianturco and Thompson[8] the static + tuned polarization + orthogonalization (STPO) model and the model of Jain and Thompson[10] the static + parameter-free polarization + orthogonalization and HFEGE potential for exchange (SPOH) model. In this paper we employ exactly the same semiempirical approach as used by Gianturco and Thompson with the only difference being in the exchange treatment, i.e., the STPO model along with the energy-dependent HFEGE potential (to be denoted as STPOH). It is clear from these calculations[8,10] and the experimental data of Refs. 1–3 that both the STPO and SPOH approaches are inadequate to reproduce the RT effect correctly.

This STPOH model has previously been used for e—diatomic-molecule scattering and was found to be quite successful among such model calculations.[16] In Sec. II we give a brief summary of our method and discuss the results in Sec. III. Atomic units are used throughout in this work unless otherwise specified.

II. THEORY

The final second-order coupled differential equations for the scattered electron function $F(r)$ is given by

$$\left[\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}+k^2\right]F^{p\mu}_{lh,l'h'}(r) =2\sum_{l'',h''} V^{p\mu}_{lh,l''h''}(r)F^{p\mu}_{l''h'',l'h'}(r)+\sum_i \lambda_i U^{p\mu}_{l_ih_i}(r)\ , \quad (2)$$

where k is the incident electron wave vector and the potential matrix $V^{p\mu}_{lh,l'h'}(r)$ couples various channels and consists of the static, polarization, and HFEGE potentials [the polarization potential is given by Eq. (1)]. The second term on the right-hand side of Eq. (2) represents the orthogonalization term with λ_i as the Lagrange multipliers and $U^{p\mu}_{lh}(r)$ the radial part of the bound orbital of symmetry $p\mu$. The explicit expressions for the static and the HFEGE potential can be found in Refs. 17 and 18, respectively. From standard techniques, the asymptotic solutions of Eq. (2) gives the desired K-matrix elements for a particular irreducible representation (IR) $p\mu$. From these K matrices, various cross sections can be evaluated easily.[10]

III. RESULTS AND DISCUSSIONS

A. Total and momentum-transfer cross sections

Most of the details of the present calculations are exactly the same as described in earlier papers.[8,10] The size of the target-wave-function basis set and various one-center expansions are exactly the same as in our previous works,[8,10] i.e., all expansions with terms only up to $l=7$. However, in this very-low-energy region, this size is sufficient for perfect convergence. We include only the dominant symmetries A_1, T_2, E, and T_1 in the evaluation of final cross sections: however, at this low energy, only the A_1 and the T_2 (starting with $l=0$ and 1, respectively) contribute more than 90% to the total cross section (see Table I). The A_2 symmetry (starting with $l=6$) is neglected altogether. In Table II, we have shown partial cross sections into individual dominant channels $(lh,l'h')$ for A_1, T_2, and E symmetries: the T_1 symmetry is very small throughout. As expected, at the lower bound of the present energy region only the s wave (in A_1 symmetry) dominates.

In Fig. 1 we have plotted the spherical part of the static, HFEGE (at 0.4 eV), the JT parameter-free polarization, and the *semiempirical* polarization [Eq. (1) with $r_c=1.175$ (present) and 0.89 a.u. (Ref. 8)] potentials. It is clear from this figure that the JT potential is quite weak, consequently giving the RT minimum at a lower energy. Obviously, the GT potential is too strong. In Fig. 2 we compare partial cross sections for the A_1 and T_2 symmetries at a few r_c values; the T_2 symmetry is not sensitive qualitatively to the value of r_c. The A_1 symmetry, which is responsible for the RT effect, dominates at all energies except around the RT minimum. The partial cross sections in the STPO and SPOH models (Fig. 2) differ with the present calculations significantly.

Our final total cross sections (σ_t) in the present

TABLE I. e-CH$_4$ partial total cross sections (10^{-16} cm^2) with $r_c=1.175$ a.u.

Energy (eV)	A_1	T_2	E	T_1
0.1	3.96	0.192	0.008	0.001
0.2	1.19	0.283	0.014	0.002
0.3	0.134	0.321	0.022	0.003
0.4	0.025	0.334	0.03	0.004
0.5	0.029	0.329	0.038	0.005
0.6	0.160	0.315	0.046	0.006
0.8	0.570	0.282	0.064	0.0082
1.0	1.03	0.253	0.08	0.011

TABLE II. Partial cross sections in the dominant individual channels $\sigma^{p\mu}_{lh,l'h'}$ of e^--CH$_4$ scattering (other symmetries contribute very little to the total cross sections). All cross sections are in atomic units and multiplied by a factor of $100/k^2$.

Energy (eV)	$\sigma^{A_1}_{01,01}$	$\sigma^{T_2}_{11,11}$	$\sigma^{T_2}_{21,21}$	$\sigma^{E}_{21,21}$
0.1	3.292	0.154	0.006	0.006
0.2	1.987	0.445	0.024	0.023
0.3	0.727	0.739	0.056	0.053
0.4	0.070	0.990	0.104	0.097
0.5	0.098	1.180	0.170	0.154
0.6	0.765	1.280	0.254	0.225
0.8	3.750	1.310	0.490	0.415
1.0	8.507	1.150	0.830	0.666

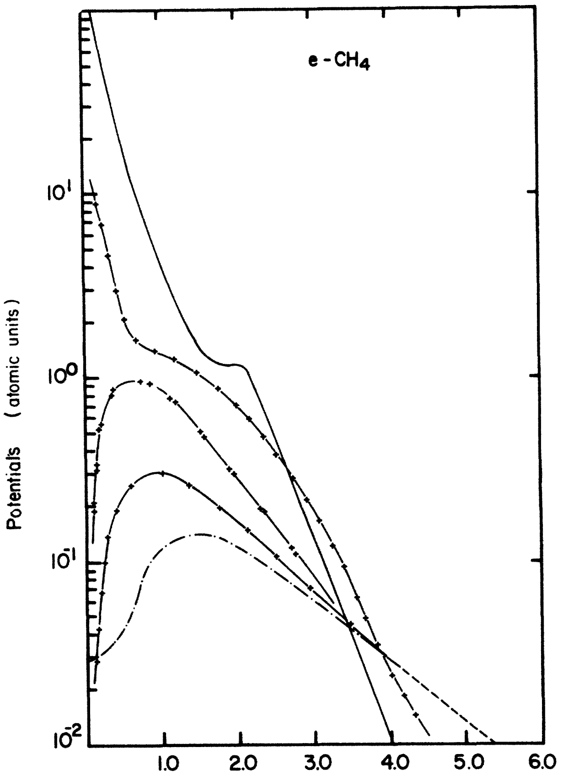

FIG. 1. Spherical part ($l=0, h=1$) of various e-CH$_4$ potentials: ——, static interaction; —+—+— (upper curve). HFEGE potential at 0.4 eV: —·—·—, JT polarization potential; —++—++—, GT polarization potentials with $r_c=0.88$ a.u.; —+—+— (lower curve), GT polarization potential with $r_c=1.175$ a.u.

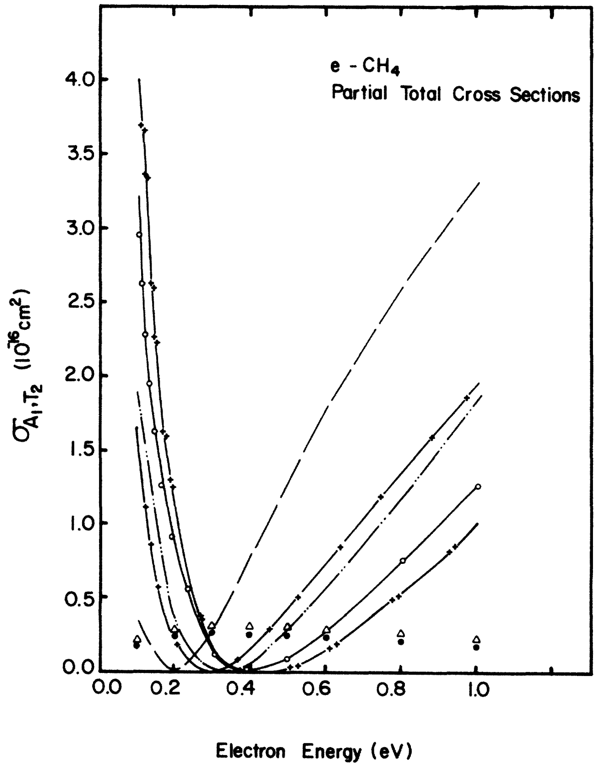

FIG. 2. Partial total cross sections ($\sigma^{p\mu}$) for A_1 and T_2 symmetries. A_1 symmetry (present): —+—+—, $r_c=1.241$; —·—·—, $r_c=1.191$; —++—++—, $r_c=1.175$. T_2 symmetry (present): ●, $r_c=1.241$; △, $r_c=1.191$. A_1 symmetry (Ref. 8), —··—··—; A_1 symmetry (Ref. 10), — — —.

STPOH approximation along with the STPO and SPOH calculations and recent experimental points are depicted in Fig. 3. The STPOH model gives a shallow RT structure (out of several r_c values, the $r_c=1.175$ a.u. value seems to be a most successful one) and agrees well with the experimental shape (and magnitude) as compared to earlier calculations. The RT structure in the STOH model is a well-pronounced dip, while the STPO curve is too high.

For the momentum-transfer (σ_m) cross sections, we plot our results in Fig. 4 along with other theoretical and swarm data. The RT minimum is quite pronounced here, which is mainly due to the fact that in these cross sections the forward scattering does not contribute and, as shown in Fig. 5, the RT minimum occurs only at middle and higher angles ($\theta > 45°$). The position of the RT minimum in the σ_m cross sections is generally lower than the total cross-section one, due to still very small contributions from the p-wave phase shifts; however, in the present case the σ_m RT location is almost the same as the σ_t position (thus, the higher partial waves are negligible in the present case).

It is to be noted here that a correlation polarization potential[14] along with the HFEGE potential (and its asymptotic version)[16] totally fails in this energy region.[13] It may

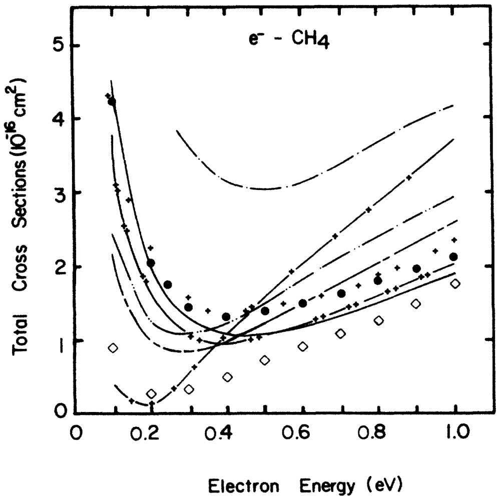

FIG. 3. Total cross sections for e-CH$_4$ elastic scattering (rotationally summed). Present calculations: ——, $r_c=1.175$; —++—++—, $r_c=1.191$; — — —, $r_c=1.241$. Other calculations: —·—·—, Gianturco and Thompson (Ref. 8) with $r_c=0.84$; —··—··—, Gianturco and Thompson (Ref. 8) with $r_c=0.88$; —+—+—, Jain and Thompson (Ref. 10). Experimental data: ●, Lohmann and Buckman (Ref. 2); +, Ferch *et al.* (Ref. 1); ◇, Barbarito *et al.* (Ref. 7).

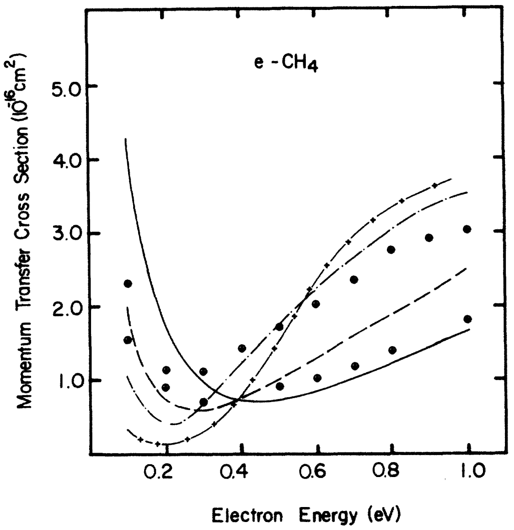

FIG. 4. Momentum transfer cross sections for e-CH$_4$ elastic scattering (rotationally summed). Present calculations: ——, $r_c=1.175$; — — —, $r_c=1.241$. Other calculations: —+—+—, Jain and Thompson (Ref. 10); —·—·—, Gianturco and Thompson (Ref. 8). Experimental data: ●, Ref. 5; ⊕, Ref. 23.

be a better approach to include the exchange effects exactly[15,19] along with an approximate charge-distortion potential. This should be relatively easy rather than incorporating polarization effects rigorously. The separable form of the nonlocal exchange kernel[20] has been found quite successful in linear molecular cases.[21]

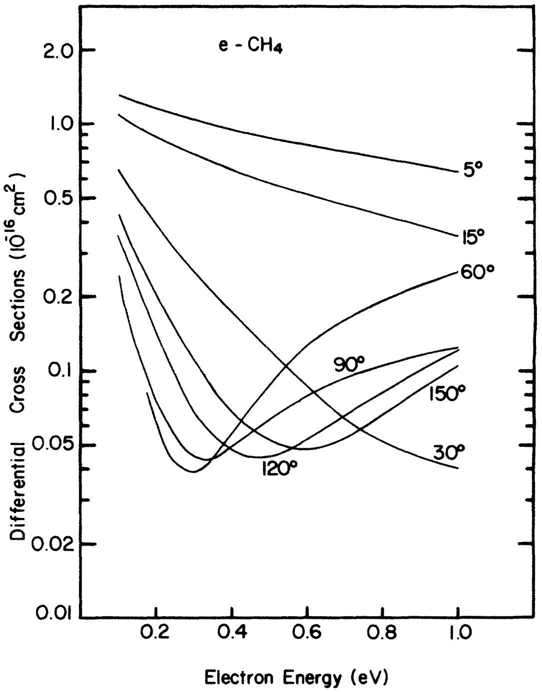

FIG. 5. Differential cross sections for the e-CH$_4$ elastic scattering (rotationally summed) as a function of energy at 5°, 15°, 30°, 60°, 90°, 120°, and 150° angles (present results with $r_c=1.175$ a.u.).

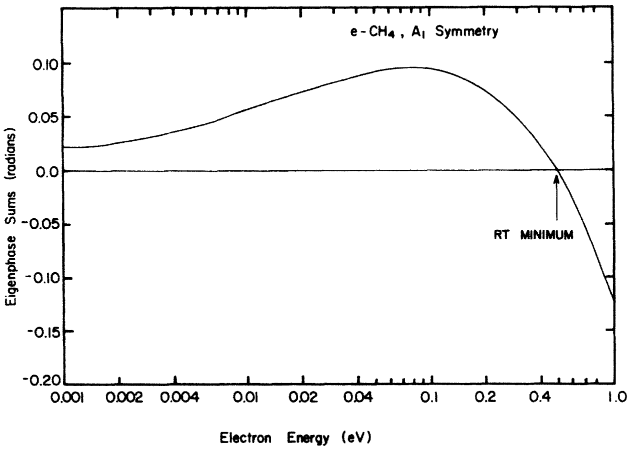

FIG. 6. Eigenphase sum for the e-CH$_4$ A_1 scattering with $r_c=1.175$ a.u.

B. Scattering length

In order to extract information on the scattering length in e-CH$_4$ scattering, we extended our calculations to further lower energies up to 0.001 eV. The full curve of the A_1 symmetry eigenphase sums is shown in Fig. 6 in the energy range 0.001–1 eV. Clearly, the eigenphase sum changes sign around 0.48 eV (location of the RT minimum). At very low energy ($E \leq 0.1$ eV) the A_1 eigenphase sum of Fig. 6 contains only the s-wave ($l=0$) part (other partial waves are almost zero). We extrapolate this curve (Fig. 6), by a four-parameter fitting procedure,

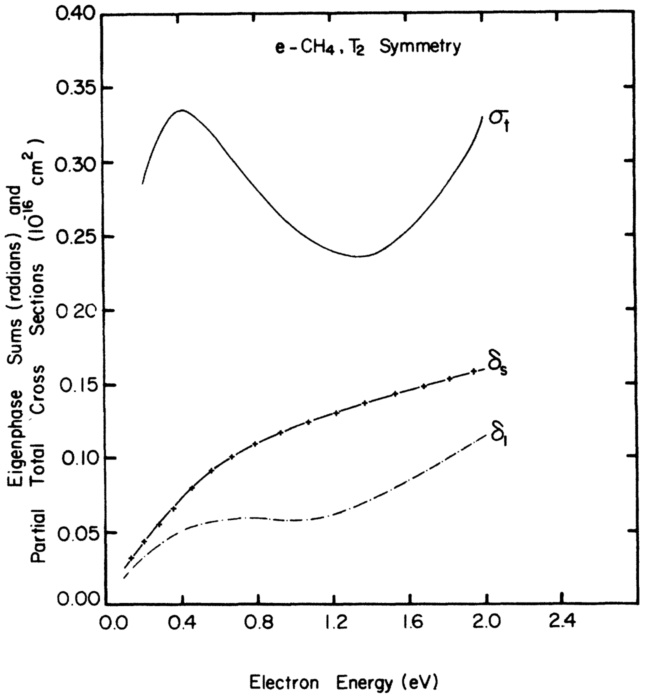

FIG. 7. Eigenphase sum (δ_s), eigenphase shift in the p wave (δ_1) and the partial total cross sections (σ_t) in the T_2 symmetry of e-CH$_4$ scattering. Notice that the structure in the σ_t curve is not visible in Fig. 2.

up to the zero-energy limit of the relation

$$\lim_{k\to 0} k \cot\delta_0^{A_1}(k) = -\frac{1}{a_0} , \tag{3}$$

where a_0 is the s-wave scattering length and $\delta_0^{A_1}$ is the phase shift in the A_1 symmetry. We obtain $a_0=-3.41$ a.u. at $k=0.0003$ ($\delta_0=0.00102$ rad). Notice that this value is quite close to the scattering length of Kr whose polarizability is 16.6 a.u. By extrapolating their experimental data (up to 0.5 eV) up to the zero-energy limit, Ferch *et al.*[1] obtained a_0 to be -2.475 a.u. This large discrepancy may be due to the limitation of the present model as well as in the extrapolation in both the cases.

It is interesting to see that the scattering length can be used to determine approximately the position of the RT minimum. When only the polarization potential ($-\alpha_0/2r^4$) dominates at large distances, which is the case in the present e-CH_4 scattering, we can have, approximately,[22]

$$\tan\delta_0(k) = |a_0| k - \frac{\pi\alpha_0}{3} k^2 \tag{4}$$

(this relation is exact in the limit $k\to 0$). In case of the RT effect, $\delta_0(k)$ vanishes when $k=3|a_0|/\pi\alpha_0$ provided that the higher partial waves can be neglected; we get $k=0.019$, i.e., the RT minimum around 0.4 eV, which is in good agreement with the present value.

There is an analog of the RT effect in the p wave also (such an effect has been seen in the case of rare gases except for the helium gas[22]), which occurs at somewhat higher energy. From Fig. 7 we observe that the T_2 symmetry (which starts with $l=1$) partial eigenphase δ_1 curve has a structure around 1.1 eV (while the total eigenphase sum δ_s does not reveal such a minimum). This behavior is more pronounced in the partial total cross section (amplified curve) in Fig. 7. We can calculate a similar quantity a_1 (scattering length) for the p wave. One can now find that[22]

$$a_1 = \frac{\pi}{15}\alpha_0 k^{-1} ;$$

$a_1=12.98$, using the minimum occurring at 1.1 eV.

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

[2] B. Lohmann and S. J. Buckmann, J. Phys. B (to be published); see also *Book of Abstracts of the Fourteenth International Conference on the Physics of Electronic and Atomic Collisions, Palo Alto, 1985,* edited by M. J. Coggiola, D. L. Huestis, and R. P. Saxon (ICPEAC, Palo Alto, 1985), p. 106.

[3] (a) R. K. Jones, J. Chem. Phys. **82**, 5424 (1985); (b) W. Sohn, K. Jung, and H. Ehrhardt, J. Phys. B **16**, 891 (1983).

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

[5] G. N. Hadded, Aust. J. Phys. **38**, 677 (1986).

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

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

[8] F. A. Gianturco and D. G. Thompson, J. Phys. B **9**, L383 (1976); **13**, 613 (1980).

[9] P. G. Burke and N. Chandra, J. Phys. B **5**, 1696 (1972).

[10] A. Jain and D. G. Thompson, J. Phys. B **15**, L631 (1982); **16**, 3077 (1983); a computer code is available to evaluate various cross sections, see A. Jain and D. G. Thompson, Comput. Phys. Commun. **32**, 367 (1984).

[11] Z. Varga, I. Gyemant, and M. G. Benedict, Acta Phys. Chem. **25**, 85 (1979).

[12] J. A. Tossell and J. W. Davenport, J. Chem. Phys. **80**, 813 (1984).

[13] A. Jain, F. A. Gianturco, and L. Pantano, J. Phys. B (to be published).

[14] J. O. O'Connel and N. F. Lane, Phys. Rev. A **27**, 1893 (1983); N. T. Padial and D. W. Norcross, Phys. Rev. A **29**, 1590 (1984).

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

[16] M. A. Morrison and L. A. Collins, Phys. Rev. A **17**, 918 (1978).

[17] F. A. Gianturco and D. G. Thompson, Chem. Phys. **17**, 111 (1976).

[18] S. S. Salvini and D. G. Thompson, J. Phys. B **14**, 3797 (1981).

[19] F. A. Gianturco and A. Jain, Phys. Rep. (to be published).

[20] B. I. Schneider and L. A. Collins, Phys. Rev. A **24**, 1264 (1981); T. N. Rescigno and A. E. Orel, *ibid.* **24**, 1267 (1981).

[21] A. Jain and D. W. Norcross, Phys. Rev. A **32**, 134 (1985).

[22] T. F. O'Malley, Phys. Rev. **130**, 1020 (1963); **134**, 1188 (1964).

[23] C. W. Dunkan and I. C. Walker, J. Chem. Soc. Faraday Trans. II **68**, 1514 (1972).