INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS B: ATOMIC, MOLECULAR AND OPTICAL PHYSICS

J. Phys. B: At. Mol. Opt. Phys. **38** (2005) 2087–2095 doi:10.1088/0953-4075/38/13/003

Electron collisions with CS_2

M H F Bettega[1], M A P Lima[2] and L G Ferreira[2]

[1] Departamento de Física, Universidade Federal do Paraná, Caixa Postal 19044, 81531-990, Curitiba, Paraná, Brazil
[2] Instituto de Física 'Gleb Wataghin', Universidade Estadual de Campinas, Caixa Postal 6165, 13083-970, Campinas, São Paulo, Brazil

E-mail: bettega@fisica.ufpr.br

Received 14 February 2005, in final form 21 April 2005
Published 13 June 2005
Online at stacks.iop.org/JPhysB/38/2087

Abstract

We present elastic integral and differential cross sections for electron collisions with CS_2 molecules for energies up to 10 eV. To compute the cross sections we employed the Schwinger multichannel method implemented with pseudopotentials at the static-exchange plus polarization approximation. In particular, our integral cross section shows a sharp increase near zero energy, which is an indication of the existence of an s-wave virtual state, followed by a Ramsauer–Townsend minimum around 0.7 eV. Our results agree well with available experimental and theoretical results.

1. Introduction

CS_2 molecules, along its valence isoelectronics CO_2 and OCS, have important applications in lasers and in atmospheric science. Concerning collisions of electrons with CS_2 molecules, there are few theoretical and experimental studies available in the literature. Theoretical studies on electron collisions with CS_2 have focused mainly on the elastic scattering. Lynch *et al* [1] employed the continuum multiple-scattering model to calculate elastic cross sections for e^-–CS_2 collisions from 0 eV up to 100 eV. They reported the existence of a shape resonance belonging to the Π_u symmetry around 1.85 eV and a series of other resonances, belonging to different symmetries, for energies above 4 eV. Raj and Tomar [2] used the independent atom model to calculate cross sections for energies above 100 eV. Lee *et al* [3] calculated elastic differential, integral and grand total (elastic+inelastic) cross sections using the Schwinger iterative method combined with the distorted-wave approximation. They reported a Ramsauer–Townsend minimum around 0.2 eV and found no indication of the low-energy Π_u shape resonance reported by Lynch *et al*. Bettega *et al* [4] calculated elastic integral, differential and momentum transfer cross sections for energies from 5 eV up to 50 eV using the Schwinger multichannel method with pseudopotentials at the static-exchange (SE) approximation. Bettega [5] employed the Schwinger multichannel method and showed that

the Π_u shape resonance that appeared at the static-exchange cross section became a bound state when polarization effects were taken into account.

The experimental studies reported total, elastic and vibrationally inelastic cross sections. The total cross section for e^-–CS_2 collisions was measured by Szmytkowski [6]. This total cross section presented a minimum around 0.8 eV. Sohn *et al* [7] reported elastic, differential and vibrationally inelastic cross sections. They also found a minimum in the elastic cross section around 0.8 eV. They observed a steep increase of the differential cross sections towards threshold, and attributed this to the possible existence of a virtual state for the e^-–CS_2 system. The results of Szmytkowski and Sohn *et al* showed no indication of the Π_u shape resonance seen by Lynch *et al*. Sakamoto *et al* [8] measured elastic differential cross sections at selected energies. Recently, Jones *et al* [9] reported cross sections for electron collisions with CS_2 for energies below 0.2 eV. They reported some giant resonances superimposed on a sharp rise in the cross sections and attributed the sharp rise to a virtual state. They discussed the peaks that appeared in their cross sections according to the results obtained by calculations of Gutsev *et al* [10] on the electron affinities of CS_2. We can also quote the recent studies by Zubek and co-workers on electronic excitation and dissociation of CS_2 by electron impact [11].

In the present work, we report elastic integral and differential cross sections for e^-–CS_2 collision. We employed the Schwinger multichannel method with pseudopotentials at the static-exchange plus polarization (SEP) approximation. We have considered energies up to 10 eV. Our aim is to investigate the two features that appeared in our integral cross section. The sharp rise near zero energy is discussed in terms of an s-wave virtual state and the minimum around 0.7 eV is discussed in terms of a Ramsauer–Townsend minimum. The other valence isoelectronic triatomics to CS_2, namely, CO_2 and OCS, show a Π shape resonance (Π_u for CO_2). The existence of an s-wave virtual state for CO_2 and OCS has been discussed by several authors [7, 12–16].

In what follows, we present a brief description of the Schwinger multichannel method and some computational details of our calculations, with particular attention to the inclusion of polarization effects. We finally report our main results and a discussion with a brief summary of our findings.

2. Theory

The Schwinger multichannel method [17–19] has been described in detail in several publications. Here we will describe only the relevant points concerning the present work.

In the SMC method, the scattering amplitude is given by

$$f(\vec{k}_f, \vec{k}_i) = -\frac{1}{2\pi} \sum_{m,n} \langle S_{\vec{k}_f} | V | \chi_m \rangle (d^{-1})_{mn} \langle \chi_n | V | S_{\vec{k}_i} \rangle, \tag{1}$$

where

$$d_{mn} = \langle \chi_m | A^{(+)} | \chi_n \rangle \tag{2}$$

and

$$A^{(+)} = \frac{\hat{H}}{N+1} - \frac{(\hat{H}P + P\hat{H})}{2} + \frac{(VP + PV)}{2} - VG_P^{(+)}V. \tag{3}$$

In the above equations, $|S_{\vec{k}_{i,f}}\rangle$ is a solution of the unperturbed Hamiltonian H_0 and is a product of a target state and a plane wave, V is the interaction potential between the incident electron and the electrons and nuclei of the target, $|\chi_m\rangle$ is a set of $(N+1)$-electron Slater determinants (configuration state functions—CSFs) used in the expansion of the trial scattering

Table 1. Cartesian Gaussian functions used for C and S.

	C	S
Type	Exponent	Exponent
s	12.494 080	7.382 257
s	2.470 291	2.063 167
s	0.614 027	0.878 009
s	0.184 029	0.245 161
s	0.036 799	0.061 630
s	0.013 682	0.015 560
p	5.228 869	7.203 417
p	1.592 058	3.134 723
p	0.568 612	0.529 380
p	0.210 326	0.154 155
p	0.072 250	0.035 523
d	0.831 084	1.689 035
d	0.229 204	0.476 317
d	0.075 095	0.151 558

wavefunction, $\hat{H} = E - H$ is the total energy of the collision minus the full Hamiltonian of the system, with $H = H_0 + V$, P is a projection operator onto the open-channel space defined by the target eigenfunctions, and $G_P^{(+)}$ is the free-particle Green's function projected on the P-space. The direct configuration space is constructed as follows,

$$\{\chi_i\} = \{\mathcal{A}(\Phi_1 \otimes \varphi_i)\} \tag{4}$$

where Φ_1 is the single-configuration N-electron Hartree–Fock wavefunction which describes the ground state of the molecular target, φ_i is a one-electron function represented by an unoccupied (virtual) orbital, and $\mathcal{A}$ is the antisymmetryzer. To take polarization into account, the configuration space is enlarged by including new CSFs given by

$$\{\chi_{ju}\} = \{\mathcal{A}(\Phi_j \otimes \varphi_u)\} \qquad j \geqslant 2 \tag{5}$$

where Φ_j are virtual (energetically closed-channel) states of the target which are obtained from the ground state by performing single excitations of the type $[\varphi_h \rightarrow \varphi_p]$, where φ_h is an occupied (hole) orbital and φ_p is an unoccupied (particle) orbital. φ_u is a one-electron function to be defined later.

3. Computational details

The ground state of the molecule was described by a single-configuration wavefunction (Hartree–Fock level) at the experimental geometry [20]. The atomic cores were replaced by the pseudopotentials of [21]. The basis functions used in the description of the target ground state and in the description of the scattering wavefunction, presented in table 1, are those of [4, 5] and were obtained as described in [22]. We have not included in our calculations the symmetrical combination of d functions ($[(x^2 + y^2 + z^2)\exp(-\alpha r^2)]$), which is in fact an s-type function, in order to avoid linear dependence in the basis set.

The molecular polarizability was calculated using the sum-over-states method [23]. Our calculated value is 11.84×10^{-24} cm^3, which is larger than the experimental values of 8.74×10^{-24} cm^3 and 8.88×10^{-24} cm^3 [20].

To take polarization effects into account, we considered the resonant and the non-resonant symmetries separately. To construct the Φ_j states of equation (5) for the non-resonant symmetries we considered only single excitations from the hole orbitals to a small set of particle orbitals represented by 'polarized' orbitals [24, 26] given by

$$\varphi_{h\mu} = \sum_{k \in \text{virtuals}} \varphi_k \frac{\langle \varphi_k | r_\mu | \varphi_h \rangle}{E_k - E_h} \tag{6}$$

where φ_h is an occupied orbital and the summation runs over the Hartree–Fock virtual orbitals. There are three polarized orbitals in equation (6) for each occupied orbital φ_h, corresponding to each component $r_\mu (\mu = 1, 2, 3)$ of the dipole moment operator $\vec{r}$. Therefore the N-electron wavefunctions Φ_j are determinants obtained by making single excitations of the type $[\varphi_h \rightarrow \varphi_p]$ where h runs over the occupied orbitals and p runs over the polarized orbitals.

In the case of non-resonant symmetries, the scattering orbitals φ_u of equation (5) are represented by an orthonormal set of orbitals $\{\varphi_{h\mu}, \varphi_k\}$, which is constructed from the polarized orbitals $(h\mu)$ and the virtual (k) orbitals. The configurations χ_{ju} defined in equation (5) can then be represented by $[\varphi_h \rightarrow \varphi_p]\varphi_u$.

In the case of the resonant symmetry $^2\Pi_u$, the procedure described above has to be modified because the first-order perturbation assumed in equation (6) is not strong enough. In this case, we follow the work of Winstead and McKoy and used the modified virtual orbital φ_l^{mod} as the first unoccupied $2\pi_u$ spin-orbital of a Fock operator of a reduced configuration. The reduced configuration is obtained from the ground state configuration depleted of its four topmost spin-orbitals $1\pi_g$ [25, 26]. The Fock operator corresponds to a total charge of +4 and the reduced configuration maintains the symmetry $^1\Sigma_g$ of the ground state. Then the scattering orbital φ_u in equation (5) is set equal to the modified virtual orbital φ_l^{mod} of the reduced configuration (which belongs to the Π_u symmetry). The N-electron wavefunction, which has $^1\Sigma_g$ symmetry, is a one-particle excitation $[\varphi_h \rightarrow \varphi_p]$ from a hole orbital to the set of particle orbitals $\{\varphi_l^{\text{mod}}, \varphi_k\}$, where l corresponds to the $2\pi_u$ modified virtual and k runs over the virtual orbitals. As discussed above, the configurations χ_{ju} can also be represented by $[\varphi_h \rightarrow \varphi_p]\varphi_u$.

CS_2 belongs to the $D_{\infty h}$ group, but for symmetry reasons part of our calculations were performed within the D_{2h} group. Through a partial wave analysis we obtained the cross sections according to the $D_{\infty h}$ group. Polarization effects were included in the following symmetries of the D_{2h} group: A_g, with 2307 CSFs; B_{1u}, with 2300 CSFs; B_{2g}, with 2134 CSFs; B_{3g}, with 2134 CSFs. The A_g symmetry of the D_{2h} group includes the Σ_g symmetry and one component of the Δ_g symmetry of the $D_{\infty h}$ group. The B_{1u} symmetry of the D_{2h} group includes the Σ_u symmetry and one component of the Δ_u symmetry of the $D_{\infty h}$ group. The B_{2g} and B_{3g} symmetries of the D_{2h} group correspond to the twofold degenerated Π_g symmetry of the $D_{\infty h}$ group. The other components of the Δ_g (with 6 CSFs) and Δ_u (with 3 CSFs) symmetries were computed at the SE approximation. For the Π_u symmetry the calculations included only 264 CSFs. The entire calculation employed 8881 CSFs.

4. Results and discussion

Figure 1 shows a comparison between our calculated cross sections at SE and SEP approximations with the available experimental and theoretical results. As already shown by Bettega [5], the shape resonance that appears in the Π_u symmetry at the SE approximation becomes a bound state when polarization is included. Except for the results of Lynch *et al*, which show the shape resonance, references [3, 6, 7, 9, 10] do not report a shape resonance in this symmetry. Our SEP results agree well with the experimental elastic cross section of

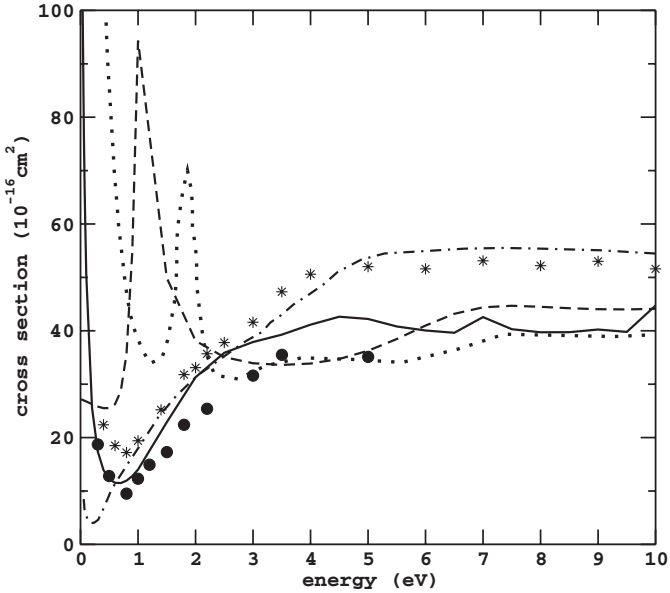

Figure 1. Integral cross section for CS_2. Solid line, present results at the SEP approximation; dashed line, present results at the SE approximation; dotted line, results of [1]; dotted-dashed line; results of [3]; circles, experimental results of [7]; stars, the total cross section of [6].

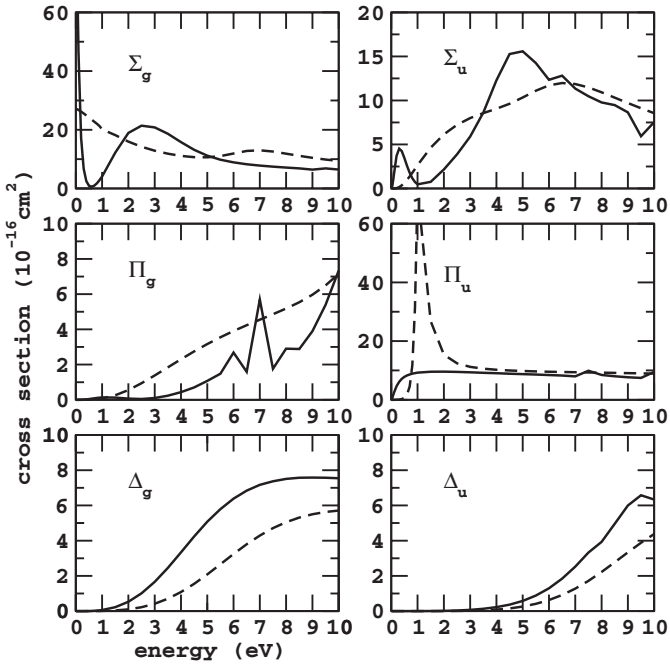

Figure 2. Symmetry decomposition of the integral cross section for CS_2. Solid line, present results at the SEP approximation; dashed line, present results at the SE approximation.

Sohn *et al*, and also with the total cross section of Szmytkowski [6]. The calculated elastic cross section of Lee *et al* lies above ours for energies above 3 eV. In figure 2 we show the

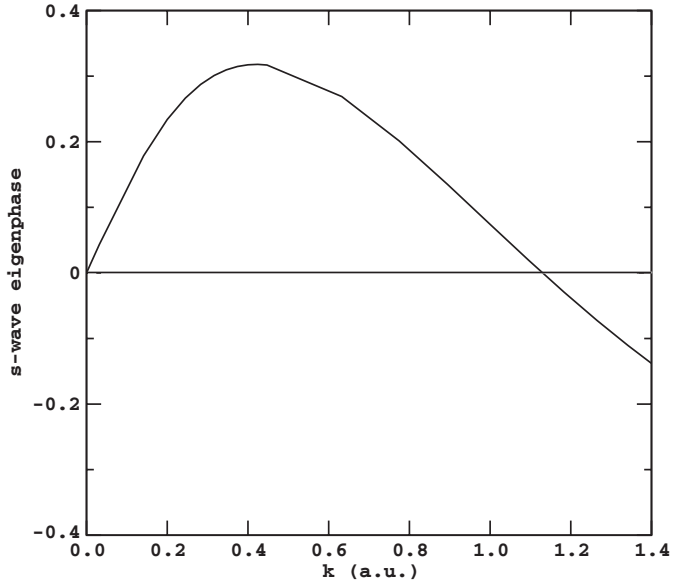

Figure 3. The s-wave eigenphase.

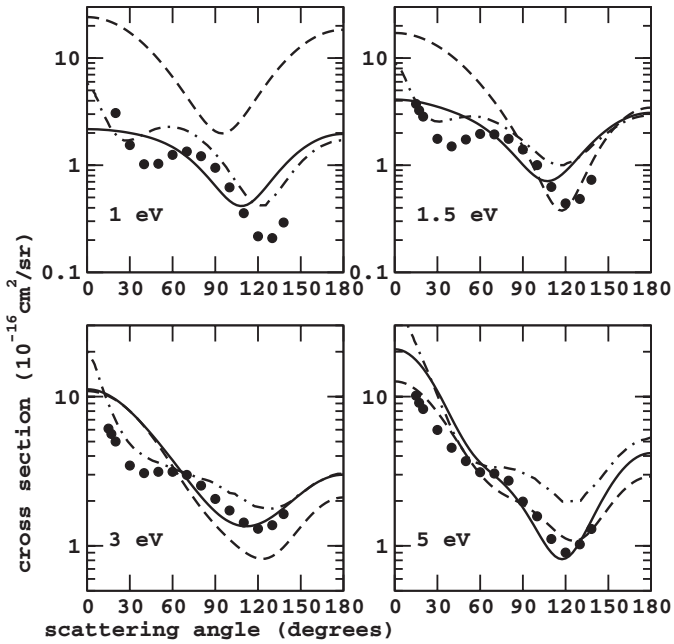

Figure 4. Differential cross sections at 1, 1.5, 3, and 5 eV for CS_2. Solid line, present results at the SEP approximation; dashed line, present results at the SE approximation; dotted-dashed line; results of [3]; circles, experimental results of [7].

symmetry decomposition of our integral cross section. The inclusion of polarization effects changes substantially the cross sections of the Σ_g and Π_u symmetries. The structure seen in the cross section of the Π_g symmetry around 7 eV may be due to a closed channel that should

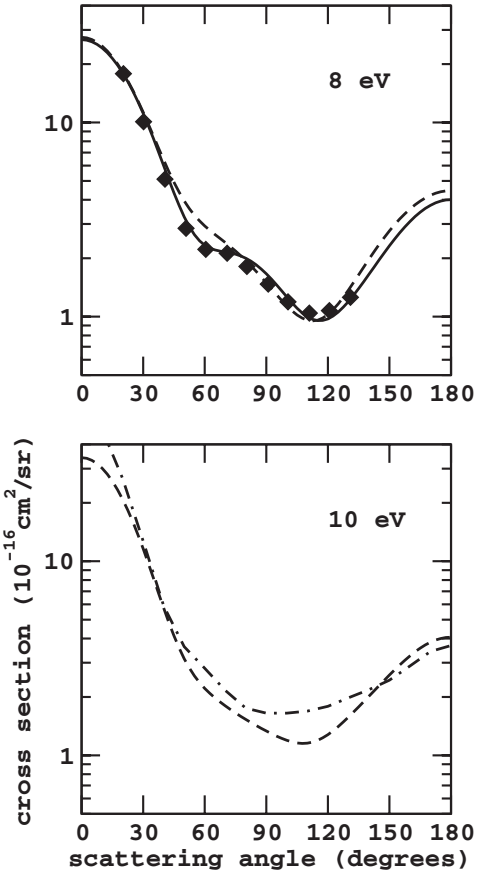

Figure 5. As in figure 4 at 8 and 10 eV, except that the diamonds are results from [8].

be open since its threshold, obtained through an improved virtual orbital calculation, is around 7.3 eV.

Our SEP cross section shows two main features that are not seen in the SE cross section: a sharp increase near zero energy and a Ramsauer–Townsend minimum around 0.7 eV. This sharp increase is characteristic of a virtual state. This state is neither a true bound state nor a resonance: it is related to a zero of the s-wave Jost function on the negative imaginary k-axis [27]. We estimated the scattering length, α, using our calculated s-wave eigenphase, $\delta_0(k)$, shown in figure 3, by extrapolating our data according to the definition [28]

$$\alpha = -\lim_{k\to 0} \frac{\tan \delta_0(k)}{k}.$$

Our calculated scattering length is negative, $-7.15\,a_0$, which is in accordance with the existence of an s-wave virtual state [27]. Our results are in agreement with the results of Sohn *et al* and Jones *et al* who also discussed the existence of a virtual state for CS_2. In particular, Jones *et al* also reported a minus sign to the s-wave scattering length looking at the ratio σ_B/σ_T, where σ_B is the backward scattering cross section and σ_T is the total integral scattering cross section. On the other hand, our cross section does not show the giant resonances seen by Jones *et al* and is smaller than theirs. This is not surprising, since these authors attribute the giant resonances to vibronic processes that our fixed nuclei calculation cannot describe.

Our calculated s-wave eigenphase crosses the zero at $E \sim 0.7$ eV ($k \sim 1.2$ au). This behaviour indicates the existence of a Ramsauer–Townsend minimum at 0.7 eV, which is in agreement with the observations of Lee *et al*, although the authors found the minimum at 0.2 eV. Our minimum position of 0.7 eV agrees with the results of Sohn *et al* and Szmytkowsi [6] of 0.8 eV for the minimum position.

Figures 4 and 5 show our SEP and SE differential cross sections (DCSs) at 1, 1.5, 3, 5, 8 and 10 eV. At 10 eV we show our results at the SE approximation only. We also present the DCSs of Lee *et al*, Sohn *et al* and Sakamoto *et al*. There is good agreement between our SEP and the experiment at 5 and 8 eV. At 5 eV our results agree better with the experiment than the results of Lee *et al*. At 8 eV our SEP results agree very well with the experiment; very small deviations are seen between our SE and SEP calculations at this energy. At 10 eV there is qualitative agreement between our results and the results of Lee *et al*.

The calculations of Lee *et al* seem to overestimate the DCSs at low scattering angles. This could explain why the elastic cross section of Lee *et al* lies above of the other theoretical elastic cross sections and the cross section of Sohn *et al* for energies up to 5 eV and then above the total cross section for energies greater than 5 eV.

5. Summary and conclusions

We presented elastic cross sections for e^-–CS_2 collisions for energies up to 10 eV. Polarization effects were taken into account in our calculations. We found good agreement between our results and other results available. In particular, our calculated integral cross section showed a sharp rise near zero energy, which indicates the presence of an s-wave virtual state, and a Ramsauer–Townsend minimum around 0.7 eV.

Acknowledgments

MHFB, MAPL and LGF acknowledge support from Brazilian agency Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq). MHFB acknowledges support from the Paraná state agency Fundação Araucária and from FINEP (under project CT-Infra 1). MHFB also acknowledges Professor Carlos M de Carvalho for computational support at Departamento de Física–UFPR. These calculations were made at CENAPAD–SP, at DF–UFPR, at Centro de Computaç ao Científica e Software Livre (C^3 SL) at DINF-UFPR and at the UFPR computer facilities.

References

[1] Lynch M G, Dill D, Siegel J and Dehmer J L 1979 *J. Chem. Phys.* **71** 4249
[2] Raj D and Tomar S 1977 *J. Phys. B: At. Mol. Phys.* **30** 1989
[3] Lee M T, Michelin S E, Kroin T and Veitenheimer E 1999 *J. Phys. B: At. Mol. Opt. Phys.* **32** 3043
[4] Bettega M H F, Natalense A P P, Lima M A P and Ferreira L G 2000 *Braz. J. Phys.* **30** 189
[5] Bettega M H F 2000 *Aust. J. Phys.* **53** 785
[6] Szmytkowski C 1987 *J. Phys. B: At. Mol. Phys.* **20** 6613
[7] Sohn W, Kochem K-H, Scheuerlein K M, Jung K and Ehrhadt H 1987 *J. Phys. B: At. Mol. Phys.* **20** 3217
[8] Sakamoto Y, Watanabe S, Hoshino M, Okamoto M, Kitajima M, Tanaka H and Kimura M 1999 *Progress Report on Atomic Collision Research in Japan* vol 25 (Jap. Soc. for Atomic Collision Research) p 7
[9] Jones N C, Field D, Ziesel J-P and Field T A 2002 *Phys. Rev. Lett.* **89** 093201
[10] Gutsev G L, Bartlett R J and Compton R N 1998 *J. Chem. Phys.* **108** 6756
[11] Zubek M 2002 *Chem. Phys. Lett.* **364** 64
Gackowska J, Olszewski R and Zubek M 2003 *Radiat. Phys. Chem.* **68** 133
Zubek M, Gackowska J and Snegursky A 2003 *Radiat. Phys. Chem.* **68** 323

[12] Morrison M A 1982 *Phys. Rev.* A **25** 1445
[13] Morgan L A 1998 *Phys. Rev. Lett.* **80** 1873
[14] Lee C-H, Winstead C and McKoy V 1999 *J. Chem. Phys.* **111** 5056
[15] Rescigno T N, Byrum D A, Isaacs W A and McCurdy C W 1999 *Phys. Rev.* A **60** 2186
[16] Bettega M H F, Lima M A P and Ferreira L G 2004 *Phys. Rev.* A **70** 062711
[17] Takatsuka K and McKoy V 1981 *Phys. Rev.* A **24** 2473
Takatsuka K and McKoy V 1984 *Phys. Rev.* A **30** 1734
[18] Lima M A P, Brescansin L M, da Silva A J R, Winstead C and McKoy V 1990 *Phys. Rev.* A **41** 327
[19] Bettega M H F, Ferreira L G and Lima M A P 1993 *Phys. Rev.* A **47** 1111
[20] D R Lide (ed) 1998 *CRC Handbook of Chemistry and Physics* 79th edn (Boca Raton, FL: CRC Press)
[21] Bachelet G B, Hamann D R and Schlüter M 1982 *Phys. Rev.* B **26** 4199
[22] Bettega M H F, Natalense A P P, Lima M A P and Ferreira L G 1996 *Int. J. Quantum Chem.* **60** 821
[23] Fripiat J G, Barbier C, Bodart V P and Andre J 1986 *J. Comput. Chem.* **7** 756
[24] Rescigno T N, Byrum D A, Isaacs W A and McCurdy C W 1999 *Phys. Rev.* A **60** 2186
[25] Bauschlicher C W 1990 *J. Chem. Phys.* **72** 880
[26] Winstead C and McKoy V 1998 *Phys. Rev* A **57** 3589
[27] Newton R G 2002 *Scattering Theory of Waves and Particles* 2nd edn (Mineola, NY: Dover)
[28] Joachain C J 1983 *Quantum Collision Theory* (Amsterdam: North-Holland)