DOI: 10.1140/epjd/e2014-40680-y

Eur. Phys. J. D (2014) 68: 65
DOI: 10.1140/epjd/e2014-40680-y

THE EUROPEAN
PHYSICAL JOURNAL D

Regular Article

Elastic scattering of slow electrons by n-pentanol alcohol[⋆]

Eliane M. de Oliveira[1], Márcio T. do N. Varella[2], Márcio H.F. Bettega[3,a], and Marco A.P. Lima[1]

[1] Instituto de Física "Gleb Wataghin", Universidade Estadual de Campinas, 13083-859 Campinas, São Paulo, Brazil
[2] Instituto de Física, Universidade de São Paulo, Caixa Postal 66318, 05315-970 São Paulo, São Paulo, Brazil
[3] Departamento de Física, Universidade Federal do Paraná, Caixa Postal 19044, 81531-990 Curitiba, Paraná, Brazil

Received 31 October 2013 / Received in final form 23 December 2013

Abstract. We report elastic integral (ICS), differential (DCS) and momentum transfer cross sections (MTCS) for low-energy electron scattering by *n*-pentanol alcohol in the gas phase. The Schwinger multichannel method implemented with pseudopotentials was employed in the calculations. The DCSs were computed for energies from 1 to 50 eV and the ICS and MTCS from 1 to 100 eV. Due to the significant value of the electric dipole moment, the DCSs are dominated by strong forward scattering. Despite this fact, the DCS around 10 eV displays a behavior related to a f-wave scattering pattern at intermediate angles which may be associated with shape resonances. This result is consistent with the ICS and the MTCS since they show a pronounced peak near this energy. For energies below 1 eV, the MTCS obtained in the static-exchange plus polarization approximation does not increase, as expected for polar molecules, suggesting that a Ramsauer-Townsend minimum could be present. This finding motivated us to revisit the previously studied methanol, ethanol, *n*-propanol and *n*-butanol molecules and to perform new calculations for impact energies below 1 eV (not addressed before). With the inclusion of polarization effects, the MTCS for the five alcohols suggest a Ramsauer-Townsend minimum coming from the negative to the positive scattering energies. To the best of our knowledge, there are neither experimental nor calculated cross sections for comparison with the present results.

1 Introduction

Reducing the emissions of greenhouse gases has become one of the major challenges of this century. One way of contributing to this task is to reduce the dependence on fossil fuels by replacing them with biofuels from renewable sources. In this context, alcohol molecules, specially ethanol and pentanol ($C_5H_{11}OH$), have attracted increasing attention from the scientific community as renewable energy source [1–4]. This fact, along with the knowledge that electron collisions are relevant to spark ignition and combustion of alcohols used as biofuels, motivated us to investigate electron collisions with alcohols. We already investigated low-energy electron interactions with methanol (CH_3OH), ethanol (C_2H_5OH), *n*-propanol (C_3H_7OH) and *n*-butanol (C_4H_9OH) [5,6]. There are also the investigations of Bettega et al. on electron collisions with the three isomers of C_4H_9OH, isobutanol, 2-butanol and *t*-butanol [7], and with isopropanol [8]; isopropanol and *n*-propanol are isomers of C_3H_7OH. *n*-pentanol would be the natural system to study next.

In this work we employed the Schwinger multichannel method (SMC) [9,10] to obtain elastic cross sections for electron collisions against *n*-pentanol. The calculations were carried out in both the static-exchange (SE) and static-exchange plus polarization (SEP) approximations.

The theoretical formulation is outlined in Section 2 and the numerical aspects are discussed in Section 3. Our results are presented and discussed in Section 4, and the conclusions are summarized in Section 5.

2 Theory

The Schwinger multichannel (SMC) method is a variational approach to the scattering amplitude. The current implementations of the SMC method, employed in the present work, are discussed in detail elsewhere [9–15]. Here we will only present the relevant points to the present calculations. The working expression for the scattering amplitude is given by:

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

[⋆] Contribution to the Topical Issue "Electron and Positron Induced Processes", edited by Michael Brunger, Radu Campeanu, Masamitsu Hoshino, Oddur Ingólfsson, Paulo Limão-Vieira, Nigel Mason, Yasuyuki Nagashima and Hajime Tanuma.

[a] e-mail: bettega@fisica.ufpr.br

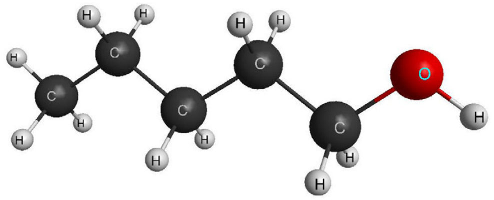

Fig. 1. Structure of n-pentanol.

where

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

and, for electrons,

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

In the expressions above, $S_{\boldsymbol{k}_{i(f)}}$ is a product of a target state and a plane wave with momentum $\boldsymbol{k}_{i(f)}$, which is an eigenstate of the unperturbed Hamiltonian H_0, P is a projector onto the energy-allowed target electronic channels, $G_P^{(+)}$ is the free-particle Green's function projected onto the P space, $\hat{H} = E - H$ is the collision energy minus the scattering Hamiltonian, and V is the projectile-target interaction potential. The $(N + 1)$-particle configuration state functions (CSFs) denoted by χ_m are given by products of target electronic states and projectile scattering orbitals. The CSFs provide the basis set for the expansion of the trial scattering wave function (the scattering orbital is antisymmetrized to the target orbitals for electron collisions). The open electronic collision channels are included in the P space and the dynamical response of the target electrons to the projectile field (polarization effects) are accounted for through virtual single excitations of the target.

3 Computational procedures

The Cartesian Gaussian basis sets used in fixed-nuclei calculations are given elsewhere [5,6]. The symmetric combinations of the d-type functions $[(x^2 + y^2 + z^2)\exp(-\alpha r^2)]$ were not included in the calculations to avoid numerical linear dependency. The target electronic ground state was described at the restricted Hartree-Fock (RHF) level. To represent the particle and scattering orbitals we employed modified virtuals orbitals (MVOs) [16]. The MVOs were generated by diagonalizing a cationic Fock operator with charge +2. The projector P in equation (3) included only the ground state, since we only considered elastic scattering. The pseudopotentials of Bachelet et al. [17] were used to replace the core electrons of the carbon and oxygen atoms. The ground state geometry of n-pentanol was optimized within the C_s group employing density functional theory (DFT) with the hybrid three-parameter Becke-Lee-Yang-Parr (B3LYP) functional and the DZV++$(2d, p)$ basis set, as implemented in the GAMESS package [18]. The optimal structure is shown in Figure 1. The computed value for the dipole moment is 1.63 D, which agrees fairly well with the experimental value of 1.61 D [19]. We also estimated the polarizability for n-pentanol using the GAMESS package with the aug-cc-pVDZ basis set at the optimized geometry. We obtained the value of 10.41 Å^3, which compared well with the experimental value for ethyl propyl ether (another isomer of $C_5H_{12}O$) of 10.68 Å^3 [20].

Scattering calculations at the SE and SEP approximations were carried out. The number of CSFs employed in SE calculation was 171 (92) in the A' (A'') symmetry. The polarization space comprised singlet- and triplet-coupled single-particle excitations from all valence occupied orbitals to the 46 lowest-lying MVOs, and these MVOs were also used as scattering orbitals. The number of CSFs employed in SEP calculation was 14023 (13748) in the A' (A'') symmetry. The total number of CSFs used in the expansion of the scattering wave function was thus 263 for the SE and 27 771 for the SEP approximations.

The differential cross sections (DCSs) at forward scattering angles were improved with the well-known Born-closure procedure [21,22] in order to incorporate the dipole scattering contribution. Smooth matching between the near-forward cross section, which is dominated by dipolar scattering, and the cross section at intermediate and backward angles, dominated by short-range interactions described by the SMC calculation, is achieved by varying $\ell_{\max}$ with energy, where $\ell_{\max}$ is the maximum partial wave retained from the half-expanded SMC amplitude [22]. In the present work, we gradually increased $\ell_{\max}$ from 2 at 1 eV to 14 at 100 eV. Specifically, we used $\ell_{\max} = 2$ at 1 eV, $\ell_{\max} = 3$ at 1.25−2 eV, $\ell_{\max} = 4$ at 2.5 eV, $\ell_{\max} = 5$ at 3−3.5 eV, $\ell_{\max} = 6$ at 4−7 eV, $\ell_{\max} = 7$ at 8−10 eV, $\ell_{\max} = 8$ at 11−15 eV, $\ell_{\max} = 9$ at 16−20 eV, $\ell_{\max} = 10$ at 25−30 eV, $\ell_{\max} = 12$ at 50 eV and $\ell_{\max} = 14$ at 100 eV.

In the discussion of the Ramsauer-Townsend minimum we decided to present MTCSs instead of ICSs. The MTCS is essentially unaffected by the Born-closure procedure at all angles, specially in the forward scattering angles [22]. This would be expected in view of the weighting factor $(1 - \cos\theta)$, where θ is the scattering angle, that makes the contribution of forward scattering angles less important to the MTCS than to the ICS.

4 Results and discussion

DCSs for elastic scattering of electrons by n-pentanol obtained in the SEP approximation are shown in Figure 2, for energies ranging from 1 eV to 50 eV. At 10 eV, the DCS displays an oscillatory pattern characteristic of f-wave [23]. The energy dependence of the DCS is also shown in Figure 3, where the f-wave pattern is seen to progressively increase from 6 eV to 10 eV. As shown in Figure 4, the f-wave behavior in the DCS is also presented in n-propanol and n-butanol [6], although it is barely seen in ethanol and absent in methanol [5]. The f-wave pattern in the DCS of ethanol at 10 eV was confirmed by Fujimoto et al. [24] using the R-Matrix method. This behavior might have a relation with several C−C and/or C−H σ^* resonances, such as in n-propanol and n-butanol [6]. These resonances can be seen as a broad maximum around 10 eV

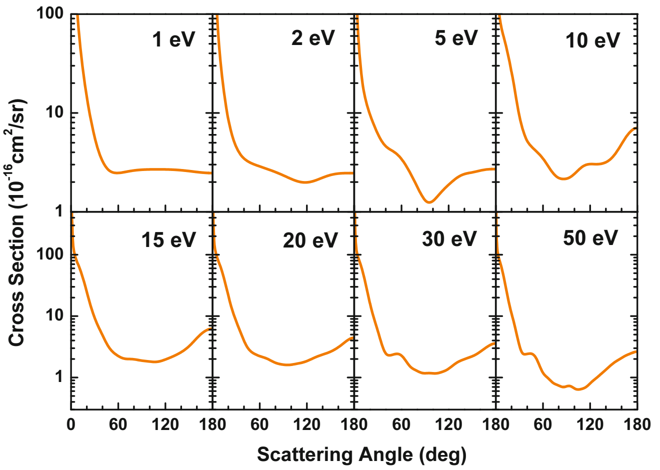

Fig. 2. Differential cross sections for elastic electron scattering by *n*-pentanol alcohol.

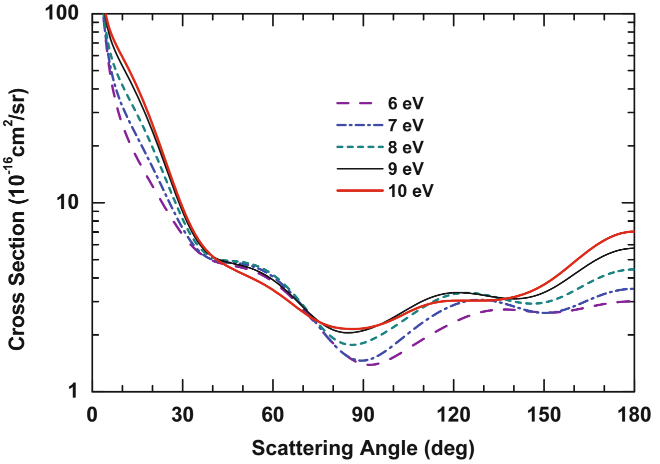

Fig. 3. Comparison between differential cross sections for elastic electron scattering by *n*-pentanol from 6 eV to 10 eV showing the evolution of the oscillatory around the resonance's energy. See text for discussion.

in the ICS and in the MTCS, which are shown in Figure 5 in the SE (line with triangles) and SEP (line with circles) approximations (the SEP peak is found at a lower energy, as expected). We also present in this figure the ICS obtained in the SEP approximation with the Born-closure procedure. The ICS is larger than the MTCS due to the presence of the weighting factor $1 - \cos\theta$, where theta is the scattering angle, in the latter. As the energy decreases, the ICS increases reflecting the long range character of the dipole interaction. At higher energies the ICS also shows the broad shape resonance, whose location is unaffected by the long range interaction.

Bettega and co-workers investigated electron collisions with three isomers of C_4H_9OH [7], namely isobutanol, 2-butanol and *t*-butanol. They compared the cross sections of these systems and of *n*-butanol and observed that for the isomers with linear chains, as *n*-butanol, the DCSs around 10 eV presented an *f*-wave behavior; the branched systems, as isobutanol, presented a *d*-wave character. The same behavior was observed in the DCSs of *n*-propanol and isopropanol [8] and in the DCSs of the alcanes (except methane).

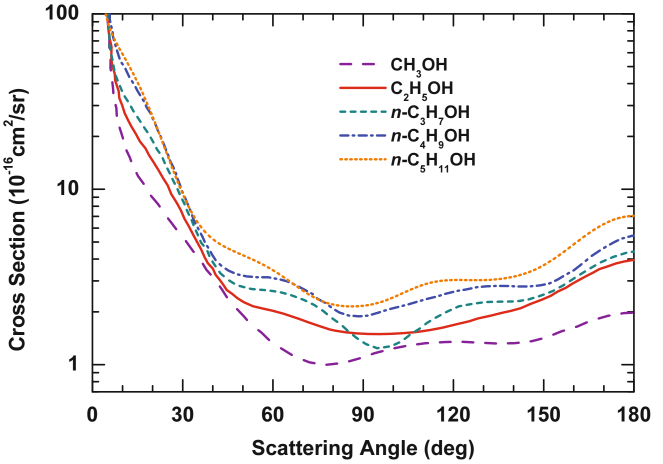

Fig. 4. Comparison between the differential cross sections for elastic electron scattering by methanol, ethanol, *n*-propanol, *n*-butanol, and *n*-pentanol at 10 eV. The results for methanol, ethanol, *n*-propanol, and *n*-butanol were previously calculated [5,6]. See text for discussion.

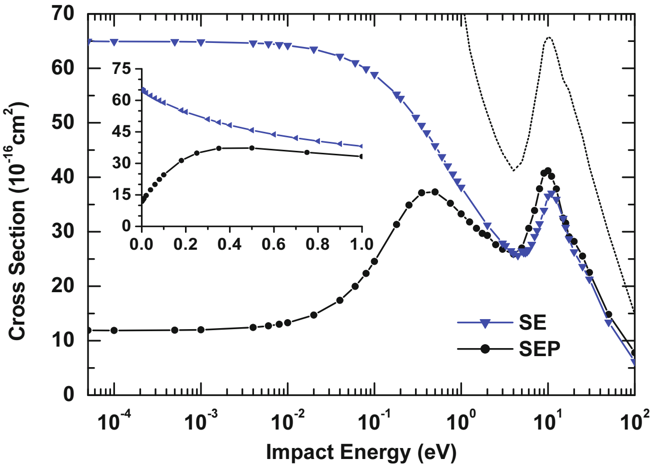

Fig. 5. Momentum transfer cross sections for electron scattering by *n*-pentanol molecules. The line with circles (triangles) is the static-exchange plus polarization (static-exchange) result. The dotted line is the integral cross section obtained in the static-exchange plus polarization approximation with the Born-closure procedure.

In contrast to the previous studies on alcohols [5,6], here we decided to investigate the collision of electrons with *n*-pentanol for energies below 1 eV. In this low-energy regime, the MTCS obtained in the SE approximation presents the expected behavior, i.e., it increases as the energy decreases. On the other hand, the SEP MTCS starts to decrease, instead of increasing, for energies below 0.5 eV. This behavior suggests the presence of a Ramsauer-Townsend minimum, although the MTCS presents no minimum at positive energies. This unexpected behavior of the MTCS for low-impact energies

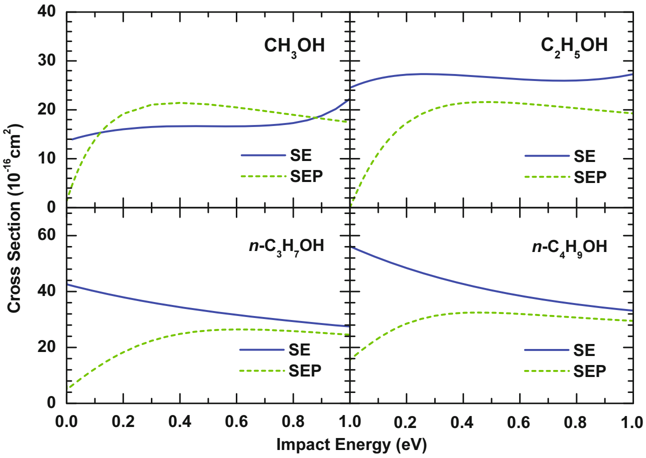

Fig. 6. Momentum transfer cross sections for electron scattering by methanol (upper left panel), ethanol (upper right panel), n-propanol (lower left panel) and n-butanol (lower right panel). The dashed line (straight line) is the static-exchange plus polarization (static-exchange) result.

motivated us to revisit the four previously investigated alcohol molecules, namely methanol, ethanol, n-propanol and n-butanol, and to calculate the cross sections for energies below 1 eV. The results obtained in the SE (straight line) and SEP (dashed line) approximations are shown in Figure 6. For methanol, the simplest alcohol, the polarization space comprised singlet- and triplet-coupled single-particle excitations from all occupied orbitals to all MVOs (87 orbitals), and these MVOs were also used as scattering orbitals. The number of CSFs employed in the SEP calculations for methanol was 27 992 (25 078) in the A' (A'') symmetry. The total number of CSFs used in the expansion of the scattering wave function was 53 070 for the SEP approximation. The idea here is to ensure that all relevant configurations (CSF) to describe a possible Ramsauer-Townsend minimum "formation" are included in the calculation. For the other molecules, namely, ethanol, n-propanol and n-butanol, the calculations followed exactly the same procedure adopted before [5,6]. The total number of CSFs used in the expansion of the scattering wave function, in the SEP approximation, was 10 787, 11 851 and 17 658 for ethanol, n-propanol and n-butanol, respectively. As shown in Figure 6, the MTCS for methanol, ethanol, n-propanol and n-butanol behaves essentially in the same way as that for n-pentanol, showing minimum at zero-energy with the inclusion of polarization effects. We believe that the presence of this minimum is due to the cancelation of the attractive part of the potential (static plus polarization) with the repulsive one (orthogonality condition imposed by the anti-symmetrization of the $(\mathrm{N}+1)$-particle wave function, assuring that the incoming electron can not visit the doubly occupied orbitals). This type of cancelation gives rise to a Ramsauer-Townsend minimum in several molecular systems, and it is present (not fully for positive energies) in all molecules investigated here [25,26].

5 Conclusions

We performed calculations for elastic scattering of low-energy electrons by n-pentanol alcohol. The present ICS and MTCS show a broad structure around 10 eV, which is related to several C-C and/or C-H σ^* resonances, in agreement with previous studies of electron collisions with methanol, ethanol, n-propanol and n-butanol. The effect of this resonance is also seen in the behavior of the DCS at 10 eV, which shows a f-wave pattern. The MTCS for n-pentanol obtained in the SEP calculation for energies below 1 eV shows an unexpected behavior, i.e., it decreases instead of increasing. We surveyed the MTCS for the previously studied alcohol molecules in this energy range (not investigate before) and found, for these molecules, the same behavior observed in the MTCS of n-pentanol.

E.M. de O., M.T. do N.V. and M.A.P.L. acknowledge support from *Fundação de Amparo à Pesquisa do Estado de São Paulo* (FAPESP). M.T. do N.V., M.H.F.B and M.A.P.L. acknowledge support from *Conselho Nacional de Desenvolvimento Científico e Tecnológico* (CNPq). M.H.F.B. acknowledges support from FINEP (under project CT-Infra) and computational support from Prof. Carlos de Carvalho. The present calculations were performed at CENAPAD/SP, IFGW/UNICAMP, LFTC-DFis/UFPR, LCPAD/UFPR and CTBE/CNPEM.

References

1. L. Zhao, L. Ye, F. Zhang, L. Zhang, J. Phys. Chem. A **116**, 9238 (2012)
2. K.A. Heufer, S.M. Sarathy, H.J. Curran, A.C. Davis, C.K. Westbrook, W.J. Pitz, Energy Fuels **26**, 6678 (2012)
3. C. Tang, L. Wei, X. Man, J. Zhang, Z. Huang, C.K. Law, Combust. Flame **160**, 520 (2013)
4. T. Tsujimura, W.J. Pitz, F. Gillespie, H.J. Curran, B.W. Weber, Y. Zhang, C.-J. Sung, Energy Fuels **26**, 4871 (2012)
5. M.A. Khakoo, J. Blumer, K. Keane, C. Campbell, H. Silva, M.C.A. Lopes, C. Winstead, V. McKoy, R.F. da Costa, L.G. Ferreira, M.A.P. Lima, M.H.F. Bettega, Phys. Rev. A **77**, 042705 (2008)
6. M.A. Khakoo, J. Muse, H. Silva, M.C.A. Lopes, C. Winstead, V. McKoy, E.M. de Oliveira, R.F. da Costa, M.T. do N. Varella, M.H.F. Bettega, M.A.P. Lima, Phys. Rev. A **78**, 062714 (2008)
7. M.H.F. Bettega, C. Winstead, V. McKoy, Phys. Rev. A **82**, 062709 (2010)
8. M.H.F. Bettega, C. Winstead, V. McKoy, A. Jo, A. Gauf, J. Tanner, L.R. Hargreaves, M.A. Khakoo, Phys. Rev. A **84**, 042702 (2011)
9. K. Takatsuka, V. McKoy, Phys. Rev. A **24**, 2473 (1981)
10. K. Takatsuka, V. McKoy, Phys. Rev. A **30**, 1734 (1984)
11. M.A.P. Lima, V. McKoy, Phys. Rev. A **38**, 501 (1988)
12. M.A.P. Lima, L.M. Brescansin, A.J.R. da Silva, C.L. Winstead, V. McKoy, Phys. Rev. A **41**, 327 (1990)
13. M.H.F. Bettega, L.G. Ferreira, M.A.P. Lima, Phys. Rev. A **47**, 1111 (1993)
14. R.F. da Costa, F.J. da Paixão, M.A.P. Lima, J. Phys. B **37**, L129 (2004)

15. J.S. dos Santos, R.F. da Costa, M.T. do N. Varella, J. Chem. Phys. **136**, 084307 (2012)
16. C.W. Bauschlicher Jr., J. Chem. Phys. **72**, 880 (1980)
17. G.B. Bachelet, D.R. Hamann, M. Schlüter, Phys. Rev. B **26**, 4199 (1982)
18. M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S.J. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, J. Comput. Chem. **14**, 1347 (1993)
19. A. D'Aprano, D.I. Donato, V. Agrigento, J. Solution Chem. **10**, 673 (1981)
20. *CRC Handbook of Chemistry and Physics*, 79th edn., edited by D.R. Lide (CRC, Boca Raton, 1998)
21. T.N. Rescigno, B.I. Schneider, Phys. Rev. A **45**, 2894 (1992)
22. E.M. de Oliveira, R.F. da Costa, S.d'A. Sanchez, A.P.P. Natalense, M.H.F. Bettega, M.A.P. Lima, M.T. do N. Varella, Phys. Chem. Chem. Phys. **15**, 1682 (2013)
23. F.H. Read, J. Phys. B **1**, 893 (1968)
24. M.M. Fujimoto, W.J. Brigg, J. Tennyson, Eur. Phys. J. D **66**, 204 (2012)
25. M.A.P. Lima, K. Watari, V. McKoy, Phys. Rev. A **39**, 4312 (1989)
26. B.M. Nestmann, K. Pfingst, S.D. Peyerimhoff, J. Phys. B **27**, 2297 (1994)