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To cite this article: Sergio d’A Sanchez et al 2009 J. Phys.: Conf. Ser. 194 012035

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Transient Ions in Electron and Positron Scattering

Sergio d’A. Sanchez†, Eliane M. de Oliveira†, Josué S. dos Santos†, Romarly F. da Costa†, Márcio H. F. Bettega*, Marco A. P. Lima† and Márcio T. do N. Varella†

† Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, 09210-170, Santo André, São Paulo, Brazil.
‡ Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, 13083-970, Campinas, São Paulo, Brazil.
* Departamento de Física, Universidade Federal do Paraná, CP 19044, 81531-090, Curitiba, Paraná, Brazil
E-mail: marcio.varella@ufabc.edu.br

Abstract. We report on recent advances in studies of transient ions formed in electron and positron scattering by molecules. We briefly discuss elastic electron collisions against pyrrole and glycine, as well as electron affinities of glycine-water clusters. Positron scattering and annihilation on small molecules is also discussed.

1. Introduction

It is well known that secondary electrons generated by ionizing radiation may induce single- and double-strand breaks in nucleic acids. Since the seminal work of Sanche and co-workers [1] it became clear that DNA damage arises from dissociative electron attachment (DEA), a mechanism in which electrons are resonantly trapped by DNA subunits. The resonances responsible for the DEA mechanism usually have either a $\pi^*$ or $\sigma^*$ character. The long-lived $\pi^*$ ions are non-dissociative, while the short-lived $\sigma^*$ ions are often dissociative, giving rise to two dissociation pathways. In the direct mechanism the electron is captured in a $\sigma^*$ resonance, although the formation of a $\pi^*$ ion diabatically coupled to a $\sigma^*$ ion is also possible. The latter indirect mechanism would be dominant in electron interactions with DNA. The complexity of biomolecules poses severe difficulties for the simulation of the DEA process, since the description of the potential surfaces of the relevant metastable ions is computationally demanding even for DNA subunits. The pyrrole molecule, shown in Fig. 1, is an interesting prototype for more detailed studies of dissociation dynamics, since the aromatic ring provides a manifold of $\pi^*$ orbitals, and dissociation along the N–H bond may proceed from the occupation of $\sigma^*$ orbitals. The photochemistry of the $\pi^*$ and $\sigma^*$ excited states of this relatively small and highly symmetric molecule is very similar to the photochemistry of adenine [2], and it may well provide a suitable analog for DEA studies.

Though much of our knowledge on electron attachment to biomolecules has been learned from gas-phase studies, the connection with actual biological systems is not a simple matter. An obvious limitation is the fact that biologically relevant species are found in solution, posing severe difficulties for studies of electron scattering. This drawback is particularly evident in amino-acids, since the neutral form is more stable in the gas phase while the zwitterionic form
is more stable in solution (these two forms are shown in Fig. 1 for glycine). Though gas-phase studies of electron scattering by glycine and other amino-acids in neutral form are relevant, it would also be desirable to survey the connection between electron interactions and solvation effects. We briefly discuss results for electron scattering by neutral glycine (gas-phase) and for adiabatic electron affinities of glycine-water clusters in both neutral and zwitterionic forms.

We also present studies of vibrationally inelastic positron scattering and vibrationally enhanced positron annihilation on small molecules. Our description of these processes is based on the projection operator formalism of Feshbach. This approach has long been applied to resonant electron-molecule collisions and it may as well be useful for the description of low-energy positron scattering and annihilation. The couplings of these states to molecular vibrations strongly enhance the annihilation rates.

Figure 1. The pyrrole molecule (a) is shown along with the neutral (b) and zwitterionic (c) forms of glycine. The color scheme for the atoms is as follows. Blue: hydrogen; yellow: carbon; gray: nitrogen; red: oxygen.

2. Methods
2.1. Fixed-nuclei scattering calculations
Elastic scattering cross sections were obtained in the fixed nuclei approximation with the Schwinger Multichannel Method (SMC). This approach is discussed in detail elsewhere for electrons [3] and positrons [4]. The working expression for the scattering amplitude is given by

\[ f_{i,f} = -\frac{1}{2\pi} \sum_{\nu,\mu} \langle S_{\vec{k}_i} | V | \chi_\nu \rangle (d^{-1})_{\nu\mu} \langle \chi_\mu | V | S_{\vec{k}_f} \rangle , \]  

(1)

with

\[ d_{\mu\nu} = \langle \chi_\mu | A^{(+)} | \chi_\nu \rangle . \]  

(2)

The operator \( A^{(+)} \) takes the forms

\[ A^{(+)} = \frac{1}{2} (PV + VP) + \frac{1}{2} \left( \hat{H}P + P\hat{H} \right) + \frac{\hat{H}}{N+1} - V G_P^{(+)} V , \]  

(3)

and

\[ A^{(+)} = PV P + Q\hat{H}Q - V G_P^{(+)} V \]  

(4)

for electron and positron scattering, respectively. In the above expressions, \( S_{\vec{k}} \) is a solution of the free Hamiltonian, given by the product of a plane wave (free electron or positron) by the
where $T$ is the $e^\pm$-target scattering potential; $\chi_\nu$ is a configuration state function, the product of a target electronic state by a scattering orbital (antisymmetrized to the target orbitals for electron collisions); $\hat{H} = E - H$ denotes the collision energy minus the scattering Hamiltonian; $P$ is a projection operator onto the open (energy-allowed) electronic states of the target; $G^{(+)}_P$ is the free Green’s function projected onto $P$ space and $Q = (1 - P)$ is the closed-channel space.

The SMC approach accounts for exchange (electron scattering) and polarization effects in a fully ab initio fashion, and electronic excitation may be incorporated in the $P$ projector. The present applications are restricted to elastic collisions, such that $P = \langle \Phi_0 | \Phi_0 \rangle$, where the target ground state $\Phi_0$ is described at the restricted Hartree-Fock level. Target polarization is described with single-particle virtual excitations $| \nu \rangle \Phi_\nu$ for the finite lifetime of the temporary ion state.

2.2. Positron-impact vibrational excitation and annihilation

The Feshbach projection operator (FPO) approach has long been employed in resonant electron-molecule collisions [6] and was recently applied to positron scattering [7] and annihilation [8]. The formalism relies on a discrete state $| \phi_\nu \rangle$, parametrically dependent on the nuclear coordinates in the Born-Oppenheimer sense, that describes the electronic capture of the positron (e.g., in a virtual or bound state). This discrete component is assumed orthogonal to a set of continuum states $| \{ \phi_k \} \rangle$, thus defining the projection operators $Q = | \phi_\nu \rangle \langle \phi_\nu |$ and $P = (1 - Q)$ that allow for a decomposition of the scattering wave function according to $| \Psi^{(+)}_k \rangle = | \Psi_P \rangle + | \Psi_Q \rangle$, with $| \Psi_P \rangle = P | \Psi^{(+)}_k \rangle$ and $| \Psi_Q \rangle = Q | \Psi^{(+)}_k \rangle$. The vibrational excitation integral cross section is given by

$$\sigma_{\nu_i \rightarrow \nu_f} = \frac{2 \pi}{E} | T_{\nu_i \nu_f}^{bg} + \langle \eta_{\nu_f} | \Gamma(E_f) \frac{1}{E - K - V_{opt}(E - H_N)} \Gamma(E) | \eta_{\nu_i} \rangle |^2 ,$$

where $T_{\nu_i \nu_f}^{bg}$ is the background ($P$ space) $T$-matrix element, $\eta_\nu$ is a vibrational eigenstate of the target, $E_f = E - (\epsilon_{\nu_f} - \epsilon_{\nu_i})$ is the final positron energy, $K$ is the nuclear kinetic energy, $\Gamma(E)$ and $\Gamma(E_f)$ are capture and decay widths, respectively, and $V_{opt}$ is the complex, non-local and energy-dependent potential energy surface of the transient [6, 7, 8]. Though a mathematical description of this complex potential is avoided here, it may be observed that positron attachment is a fast process in the time scale of nuclear motion, thus suddenly launching the nuclei onto the transient potential surface. To a first approximation, this potential would arise from the discrete positron-electron state, $\langle \phi_\nu | H | \phi_\nu \rangle$, but the coupling to the continuum gives rise to a potential energy shift (real part of the complex potential) and to an imaginary potential (width $\Gamma$) that accounts for the finite lifetime of the temporary ion state.

The positron annihilation rate in a molecular gas ($\lambda$) is given by the well-known relation

$$\lambda = \pi r_0^2 cn Z_{eff} ,$$

where $r_0$ is the classical electron radius, $c$ is the velocity of light, and $n$ is the gas density. The annihilation parameter is given by

$$Z_{eff}(E) = \frac{\pi}{k_i} \langle \Psi^{(+)}_{k_i} | \sum_{j=1}^{Z} \delta(\mathbf{r}_j - \mathbf{r}_p) | \Psi^{(+)}_{k_i} \rangle ,$$

where $Z$ is the number of target electrons and $\Psi^{(+)}_{k_i}$ is the scattering wave function. Since a positron in the continuum ($P$ space) has a small density at the target electrons and is weakly
coupled to nuclear vibrations, it may be assumed that annihilation only takes place in the \( Q \) space, thus leading to the following expression,

\[
Z_{\text{eff}} = \pi \frac{\langle \eta_i | \Gamma^{1/2}(E) \rangle}{[E - K - V_{\text{opt}}]} \frac{1}{[E - K - V_{\text{opt}}]} \rho_d \frac{1}{[E - K - V_{\text{opt}}]} \Gamma^{1/2}(E) |\eta_i \rangle,
\]

(8)

where

\[
\rho_d = \langle \phi_d | \sum_{\alpha=1}^{N} \delta(r_p - r_{\alpha}) |\phi_d \rangle.
\]

(9)

is the electronic density at the positron.

2.3. Adiabatic electron affinities

Adiabatic electron affinities (AEA) are defined as the difference between the neutral (\( N \)-electron) and the anion ((\( N + 1 \))-electron) species,

\[
AE A = E_{\text{min}}^{N} - E_{\text{min}}^{N+1}
\]

(10)

calculated at the minima of the respective potential surfaces. Schaefer and co-workers suggested a computationally efficient scheme [9] for valence AEA calculations based on density functional theory (DFT) [10]. An even-tempered DZP++ basis set was used with several generalized gradient approximations (GGA) for the exchange-correlation potential built in the Gaussian03 code [11], and the results were compared with experimental data for DNA bases. The B3LYP functional provided the best agreement with experiment, while BHLYP and B3P86 systematically under- and over-estimated the experimental results, respectively. This approach was called a bracketing scheme, since the experimental data lies between the DFT computations in the sense that \( AEA_{\text{BHLYP}} < AEA_{\text{B3LYP}} \simeq AEA_{\text{exp}} < AEA_{\text{B3P86}} \). We applied the same technique to glycine-water clusters, employing BHLYP, B3LYP, B3P86 and PBE1PBE functionals, since the latter has been suggested to provide a better description of hydrogen bonding than B3LYP [12]. PBE1PBE and B3LYP always resulted in similar AEA estimates, lying between BHLYP and B3P86.

3. Electron interactions with pyrrole

The scattering calculations indicate three resonances in the elastic cross section of pyrrole, belonging to the \( A_1 (\sigma^*) \), \( B_2 (\pi^*) \) and \( A_2 (\pi^*) \) irreducible representations of the \( C_{2v} \) group. The \( \pi^* \) anion states were found at lower energies, namely 3.2 eV (\( B_2 \)) and 4.4 eV (\( B_2 \)), while the \( \sigma^* \) resonance lies around 4.8 eV. The latter is very broad and its width overlaps the \( \pi^* \) states. Both direct and indirect DEA mechanisms would be operative in pyrrole, validating this system as a prototype for studies of dissociation dynamics in DNA bases. These dynamical studies would be very challenging since they should account for three diabatically coupled temporary ion states and at least three reaction coordinates, namely the symmetry-preserving N-H stretch mode and symmetry-breaking modes of \( B_2 \) and \( A_2 \) symmetry to describe the conical intersections \( \sigma^*(A_1)\pi^*(B_2) \) and \( \sigma^*(A_1)\pi^*(A_2) \). Fig. 2 shows partial results for the real part of the \( \sigma^* \) potential surface as a function of the N-H bond length. Though the \( \sigma^* \) potential has a typical dissociative behavior, the \( \pi^* \) resonances are insensitive to the N-H distance, since they are strongly located on the ring atoms. The isoelectronic molecule furan was recently studied in our group [13] and two \( \pi^* \) resonances were found in the \( B_2 \) and \( A_2 \) irreducible representations, lying slightly below the respective \( \pi^* \) resonances of pyrrole. While these two molecules are similar as long as the \( \pi \) electron moiety is concerned, replacement of the polar N-H bond in pyrrole by the oxygen atom in furan closes the dissociation channel.
4. Electron interactions with glycine

Small organic acids have well-known sharp $\pi^*$ resonances located on the C=O bond. It was believed that DEA leading to hydrogen elimination would be triggered by the formation of this $\pi^*$ ion [14] (indirect mechanism), but the role played by a higher lying though much broader $\sigma^*$ resonance was recently pointed out [15] (direct mechanism). Gallup et al. [15] suggest that the $\sigma^*$ anion would also be responsible for resonant hydrogen elimination in glycine. Our partial results indeed support the existence of $\pi^*$ and $\sigma^*$ resonances in neutral glycine, though the inclusion of polarization effects in the $A'$ symmetry is not fully converged (we cannot assign the position of the $\sigma^*$ state at present). Our calculations indicate a $\pi^*$ anion state around 3.2 eV, in good agreement with recent scattering calculations [16].

As previously observed, the zwitterionic form of glycine is not stable in the gas phase, though it prevails in solution. To investigate the impact of microsolvation on electron attachment to glycine, we performed AEA calculations for a number of Gly-(H$_2$O)$_n$ clusters, employing the DFT-based technique proposed by Schaefer and co-workers [9]. We stress that we are not particularly concerned with estimates of electron affinities, but with a qualitative view of the interplay between solvation and electron attachment. In this sense, these computationally inexpensive calculations may provide insight into this complex problem and raise interesting questions to be answered with scattering calculations. In Fig. 3 we show density plots of the singly occupied molecular orbitals (SOMO) for Gly-(H$_2$O)$_3$ anions, obtained from the lowest-energy neutral clusters reported by Bachrach [17]. In general the water molecules preferably solvate the carboxyl (carboxylate) group in both the neutral and zwitterionic forms, though the orbital densities markedly differ. Electron attachment to the neutral glycine cluster is highly probable on the solvent molecules, while the positively charged NH$_3^+$ group strongly attracts the electron in the zwitterion cluster. We observed the same trends in other clusters for $n = 2, 3, 4$ (it takes at least two water molecules to stabilize the zwitterion [17]). Electron attachment to water molecules may induce H–OH dissociation, and a competition between charge transfer from electrons or hydroxyl radicals to glycine would be expected. The present results suggest that solvated neutral and zwitterionic glycine could differ in this respect, since electron attachment to the solvent molecules would be more effective in the neutral form.
5. Positron scattering and annihilation

5.1. Vibrational excitation

The development of high resolution (∼ 25 meV) positron beams allowed for measurements of vibrational excitation cross sections in recent years [18]. Our group employed the FPO formalism to vibrationally resolve fixed-nuclei calculations obtained with the SMC approach, and results for 0 → 1 excitations for H₂ and C₂H₂ (C–C stretch mode) are shown in Fig. 4. The present results for hydrogen (see also Varella and Lima [7]) agree well with other calculations (Sur and Ghosh [19], Gianturco and Mukherjee [20]) and with the experimental data of Sullivan et al. [18]. The positron-hydrogen interaction is interesting since the potential is too attractive to allow for a simple adiabatic (fast collision) treatment of the vibrational excitation, though it is not attractive enough to give rise to a low lying virtual state. In this sense the cross section behavior would be intermediate between typical background and “resonant” (virtual-state driven) scattering. The positron-acetylene potential is much more attractive, having a low-lying virtual state at the equilibrium geometry of the target, which becomes a bound state as the C–C bond is stretched. As a result, the vibrational excitation cross section has a very narrow resonance at the threshold, which is not very clearly seen in the close-coupling calculations of Franz and Gianturco [20]. We had previously calculated this cross section with an energy spacing of 10⁻² eV and the results were in much closer agreement with the calculations of Franz and Gianturco (the present results were obtained with an energy spacing of 10⁻⁶ eV, since the resonance width is ∼ 10⁻⁴ eV). We believe that agreement with the close-coupling calculations would be improved if a finer energy mesh was used (the insets in the figures of Ref. [20] suggest that a 10⁻² eV spacing was employed).

5.2. Annihilation

The straightforward application of Eq. (8) is difficult because the complex potential is energy-dependent and non-local in configuration space. As discussed elsewhere [8], a much simpler model that neglects this non-locality and energy dependence is able to describe the essentials of vibrationally enhanced annihilation rates. The underlying mechanism is the electronic capture of the positron (in a bound or virtual state), which launches the nuclei onto the potential surface of the positron-molecule transient and generates a non-stationary vibrational wave packet. Long-lived transients allow for constructive interference at the vibrational eigenstates of the transient, giving rise to sharp vibrational resonances. A crucial aspect of the dynamics is how different are the potential surfaces of the transient and of the isolated target. If these potentials differ by no more than a constant (vertical shift) the vibrational eigenstates of the target will also be vibrational eigenstates of the positron-molecule compound. As a result, a stationary wave packet will be found on the compound surface, giving rise to a single resonance at the vibrational entrance channel. If, on the other hand, these potentials significantly differ, the vibrational entrance channel (vibrational eigenstate of the target) will couple several resonances.
Figure 4. Positron-impact vibrational excitation cross sections. Left panel: $0 \rightarrow 1$ excitation of hydrogen. Black line: present; green line: Sur and Ghosh [19]; blue line: Gianturco and Mukherjee [20]; red circles: experimental data of Sullivan et al. [18]. Right panel: $0 \rightarrow 1$ excitation of the C–C stretch mode of acetylene. Green line: present; blue dotted line: Franz and Gianturco [20].

\[ |\eta_i\rangle = \sum_{\nu} c_{i\nu} |\eta_{\nu}^{\text{res}}\rangle, \]

where $\eta_i$ is the entrance channel, $\eta_{\nu}^{\text{res}}$ are eigenstates of the transient and $c_{i\nu} = \langle \eta_i | \eta_{\nu}^{\text{res}} \rangle$ are Franck-Condon overlaps. In the simplest version of the theory, the compound and target potentials are assumed to differ linearly,

\[ \Delta V(Q) \simeq \Delta V(0) - F \cdot Q, \]

where $Q$ are the vibrational coordinates of the target and $Q = 0$ denotes the equilibrium geometry. This approximation essentially couples the $0 \rightarrow 1$ resonances of each vibrational mode, in addition to the $\nu = 0$ (ground state) resonance. The model was applied to acetylene and ethylene and could describe the most intense annihilation peaks [21], as shown in Fig. 5.

Figure 5. Annihilation parameter $Z_{\text{eff}}$ for acetylene (left panel) and ethylene (right panel). The thin black lines are the present results. The green thick lines are the present results convoluted over Gaussian profiles of 35 meV (full width at half maximum). The red bullets are the experimental data of Gilbert et al. [21].

Acknowledgments
The authors acknowledge financial support from the Brazilian agencies CNPq, CAPES and FAPESP, and a scholarship grant from UFABC. Part of the calculations were performed at
CENAPAD-SP.

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