Virtual photon exchange and electron transfer in Interparticle Coulombic Electron Capture

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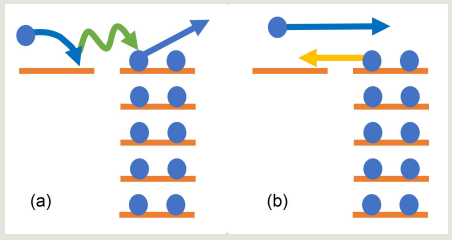
1. Introduction

Interparticle Coulombic Electron Capture (ICEC) is an environment enabled process that involves an electron being captured by an atom, a molecule or a quantum dot [1]. When the electron is captured, the excess energy is released leading to the ionization or excitation of a nearby particle. Here, we focus on ionization:

$$A^+ + B + e^- \rightarrow A + B^+ + e^-$$

Two mechanisms contribute to the overall ICEC process: (a) **virtual photon exchange:** an electron is captured from the continuum and a virtual photon is exchanged; (b) **electron transfer**: the environment (a neighbouring atom or molecule) provides the electron (i.e. no capture of the projectile electron takes place).



ICEC was first predicted in 2009 [2] and can lead to cross sections that are significantly larger than those for conventional photorecombination.

2. Systems investigated

We studied [3] ICEC for:

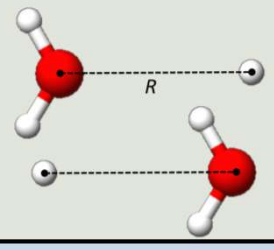
ICEC-P:

$$H^+ \bullet H_2O + e^- \rightarrow H \bullet H_2O^+ + e^-$$

ICEC-W:

$$H \bullet H_2O^+ + e^- \rightarrow H^+ \bullet H_2O + e^-$$

We investigated the dependence of the cross section for ICEC and each mechanism on the inter-neighbour distance R between acceptor and neighbour for two relative orientations:



3. Target states

The ICEC cross sections (see right) are strongly dependent on the distance between electron acceptor and neighbour. We modelled states of $H^+ + H_2O$ and $H + H_2O^+$ up 18 eV for a range of distances R.

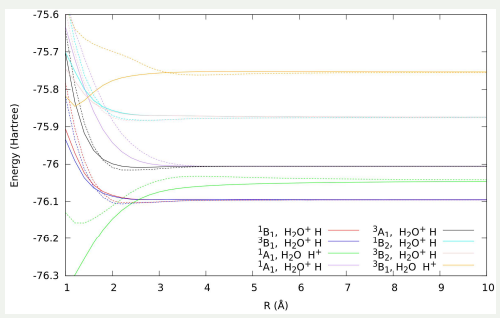


Figure 1: Target state energies as a function of R for lowest 8 target states. Solid lines, H_2OH orientation; dashed, HH_2O.

	Symmetry	State	R = 3 Å		R = 8 Å		R = 25 Å		R=∞
			H_2O-H	H-H_2O	H_2O-H	H-H_2O	H_2O-H	H-H_2O	
1	$^3B_1$	H(1s) $H_2O^+(\tilde{X}^2B_1)$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
2	$^1B_1$	H(1s) $H_2O^+(\tilde{X}^2B_1)$	0.0035	0.0108	0.0000	0.0000	0.0000	0.0000	0.0000
3	$^1A_1$	H^+ $H_2O(\tilde{X}\,^1A_1)$	0.5513	1.5665	1.2960	1.4970	1.3880	1.4080	1.0430
4	$^3A_1$	H(1s) $H_2O^{+*}(^2A_1)$	2.3717	2.4161	2.4390	2.4500	2.4460	2.4470	2.1300
5	$^1A_1$	H(1s) $H_2O^{+*}(^2A_1)$	2.5102	3.0279	2.4390	2.4500	2.4460	2.4470	2.1300
6	$^3B_2$	H(1s) $H_2O^{+*}(^2B_2)$	6.0979	5.9543	6.0190	5.9920	6.0070	6.0040	5.9400
7	$^1B_2$	H(1s) $H_2O^{+*}(^2B_2)$	6.1011	5.9646	6.0190	5.9920	6.0070	6.0040	5.9400
8	$^3B_1$	H^+ $H_2O^*(^3B_1)$	9.2026	9.5559	9.3040	9.2620	9.2950	9.2910	7.0000
9	$^1B_1$	H^+ $H_2O^*(^1B_1)$	9.8144	10.170	9.9090	9.8630	9.8980	9.8940	7.4000
10	$^3A_1$	H^+ $H_2O^*(^3A_1)$	11.992	12.135	11.847	11.776	11.816	11.809	9.3000
11	$^1A_1$	H^+ $H_2O^*(^1A_1)$	13.005	13.248	12.905	12.882	12.882	12.876	9.7000
12	$^3B_2$	H^+ $H_2O^*(^3B_2)$	14.192	14.302	14.196	14.154	14.172	14.169	11.040
13	$^1B_2$	H^+ $H_2O^*(^1B_2)$	15.191	15.018	14.950	14.886	14.909	14.902	11.050
14	$^3B_2$	H^+ $H_2O^*(^3B_2)$	15.017	15.341	14.982	14.960	14.973	14.971	11.410
15	$^1B_2$	H^+ $H_2O^*(^1B_2)$	15.683	16.380	15.882	15.879	15.891	15.890	11.500
16	$^3B_1$	H(1s) $H_2O^{+*}(^4B_1)$	15.770	15.505	15.982	16.023	16.003	16.007	14.778
17	$^3A_1$	H^+ $H_2O^*(^3A_1)$	16.526	17.011	16.642	16.682	16.659	16.663	11.100
18	$^1A_1$	H^+ $H_2O^*(^1A_1)$	16.490	16.127	16.642	16.682	16.659	16.663	11.130
19	$^3B_1$	H^+ $H_2O^*(^3B_1)$	16.967	17.227	17.198	17.243	17.220	17.225	9.9800
20	$^1B_1$	H^+ $H_2O^*(^1B_1)$	17.015	17.440	17.198	17.243	17.220	17.225	10.010

4. R-Matrix Method and model

The R-Matrix method solves the time independent Schrödinger equation by splitting the problem into two regions, separated by a sphere of radius a. Here, the UKRMol+ [4] suite of codes is used. The inner region multi-electronic scattering $(N+1)$ wavefunction can be expanded using the Close-Coupling approximation:

$$\Psi^{N+1} = \mathcal{A} \sum_{i,j} a_{i,j} \phi_i^N \eta_{i,j} + \sum_j b_j \phi_j^{N+1}$$

$a_{i,j}, b_j$ = Expansion coefficients obtained from the diagonalization of the N+1 Hamiltonian.
ϕ_i^N = N-electron target electronic wavefunction.
$\eta_{i,j}$ = Continuum orbital.
ϕ_j^{N+1} = L^2 functions built from occupied and virtual orbitals (VOs). Used to describe polarization effects.

A complete active space consisting of 9 active orbitals and 8 active electrons and HF orbitals generated with the cc-pVDZ basis set were used for the target. The close-coupling included 20 target states. The continuum contained BTOs only with the parameters presented below.

a=20 a_0	No. BTOs: 20	No. partial waves:6	BTO order: 6	1/2-el Legendre expansion: 85/30

6. R-dependence

The asymptotic formula [2] models the virtual photon exchange when there is no interaction between acceptor and neighbour:

$$\sigma_{ICEC}(E) = \frac{3\hbar^4c^4}{4\pi} \frac{\sigma_{PI}^B(E')}{R^6(h\nu)^4} \sigma_{PR}^{A^+}(E) = \frac{3\hbar^4c^2}{8\pi m_e} \frac{g_A}{g_{A^+}} \frac{\sigma_{PI}^A(E)\sigma_{PI}^B(E')}{ER^6(h\nu)^2}$$

- Electron transfer depends on orbital overlap [5] so is proportional to $\exp(-R^2)/R^2$
- **R-dependence is stronger for electron transfer**
- **Orientation dependence is stronger for electron transfer**

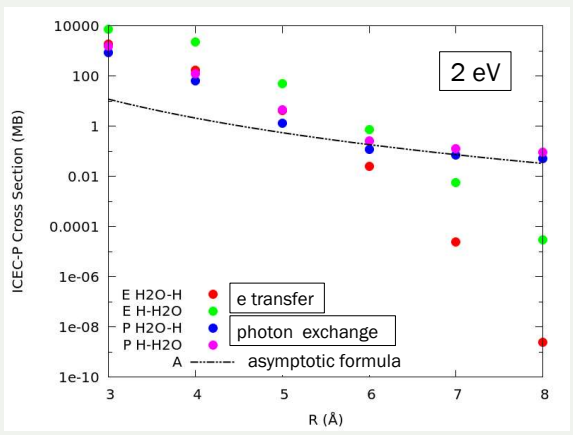


Figure 4: R dependence of the electron transfer and virtual photon exchange cross sections for 2 eV and both orientations.

5. Mechanisms

- *Approximate* separation (neglecting interference) of the mechanisms in R-matrix calculations enables the evaluation of a virtual photon exchange and an electron transfer cross section.
- As R ↘, electron transfer increases faster than virtual photon exchange
- Electron transfer dominates for R < 6
- Electron transfer more effective if H^+ is on the H end of H2O (HH2O)
- Geometry effect larger for larger R: strong effect on electron transfer when R ↗, much smaller on photon exchange for all R
- In ICEC-W ratios are all > 1

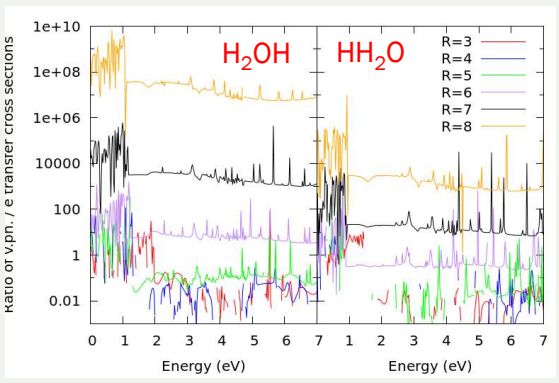


Figure 2: Ratio of the virtual photon exchange and electron transfer cross sections for **ICEC-P** for both relative orientations for the acceptor-neighbour distances , in Å , indicated in the panels.

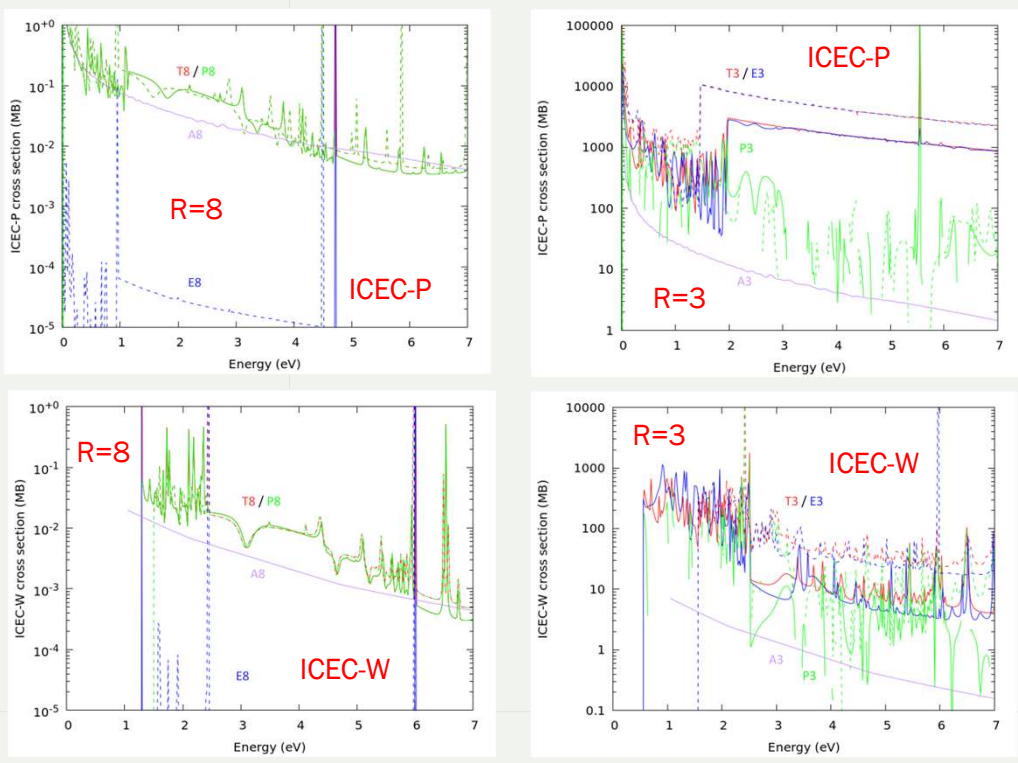


Figure 3: Cross sections for virtual photon exchange (**P**), electron transfer (**E**) and 'total' ICEC (**T**) for R=8 Å (left) and R=3 Å (right) for both orientations: H2OH (solid line(), HH2O (dashed line)

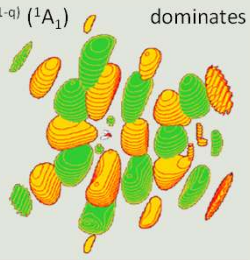
7. Resonances

Many resonances are seen in the ICEC cross section, mainly associated to Rydberg states of H_2O. We identified [6] two $^2A_1$ and two $^2A_2$ resonances with a strong dependence on R at approximately the same energy for ICEC-P and ICEC-W and both orientations.

R-dependence indicates partial ion-pair character

Dyson orbitals indicate partial $H + H_2O^*$ ($^3B_1$) and $H^{q+} + H_2O^{-(1-q)}$ ($^1A_1$) character at small R whereas at large R, $H^{q+} + H_2O^{-(1-q)}$ ($^1A_1$) dominates completely

R=8
1^1A_1
Norm=1



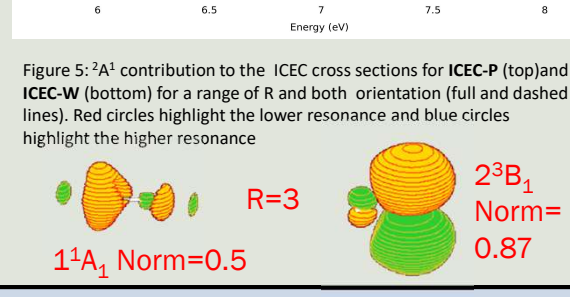


Figure 5: $^2A^1$ contribution to the ICEC cross sections for **ICEC-P** (top)and **ICEC-W** (bottom) for a range of R and both orientation (full and dashed lines). Red circles highlight the lower resonance and blue circles highlight the higher resonance

R=3
1^1A_1 Norm=0.5

2^3B_1
Norm=
0.87

8. Conclusions

- Both virtual photon exchange and electron transfer are sensitive to the energetics of the system.
- The electron transfer mechanism is significant for a range of acceptor-neighbour distances and makes the largest contribution to the ICEC cross section at smaller R
- The magnitude of the electron transfer cross section depends strongly on the relative position of acceptor and neighbour. The photon transfer cross section t is fairly insensitive to it.
- Although the orientation dependence of the electron transfer is stronger for larger R, its smaller contribution to ICEC means the ICEC cross section is more orientation dependent for small R.
- The difference between the asymptotic cross section and the *ab initio* cross section is due almost completely to the electron transfer process.
- The electron transfer mechanism doesn't change the spin of the target whereas virtual photon exchange does. This points at a potential way of establishing experimentally whether virtual photon exchange takes place.
- A rich resonance spectrum is visible in the ICEC cross section, including resonances with ion-pair character that deserve further investigation.

References & Acknowledgments

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