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Covalent bonds in positron dihalides†

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We report a computational study on homo- and heteronuclear $e^+[X^-Y^-]$ compounds formed by two halide anions ($X^-, Y^- = F^-, Cl^-, Br^-$) and one positron. Our results indicate the formation of energetically stable positronic molecules in all cases. Analysis of the electron and positron densities points out that the formation of positron covalent bonds underlies the stabilization of the otherwise repelling dihalides, revealing that positronic bonding can reach far beyond the previously addressed $e^+[H^-H^-]$ molecule [J. Charry, M. T. do N. Varella and A. Reyes, *Angew. Chem. Int. Ed.*, 2018, 57, 8859–8864.]. To a significant extent, the properties of the positron dihalides are similar to those of the purely electronic analogs, $e^-[A^+B^+]$, molecular cations with isoelectronic atomic cores ($A^+, B^+ = Na^+, K^+, Rb^+$) bound by one electron. The positron bonds in the $e^+[X^-Y^-]$ complexes are however stronger than those in the isoelectronic $e^-[A^+B^+]$ counterparts, as the former have shorter bond lengths and higher bond energies. While an energy decomposition analysis points out that both electronic and positronic bonds essentially arise from electrostatic interactions, the more stable positron bonds are partly due to the higher polarizabilities of the dihalide anions, and partly to more significant contributions from correlation and relaxation effects.

1 Introduction

Fundamental positron and positronium (Ps) chemical physics has long been a reality.^{1,2} Even a place for the Ps atom in the periodic table³ and term symbols for atomic and diatomic positronic species were proposed.⁴ For quite some time, however, the field was often plagued by a gap between the fascinating predictions of new species and phenomena, based on theory and numerical methods, and experimental realization. The situation drastically changed, for better, in more recent years. Unprecedented progress was made possible by the techniques to accumulate and manipulate positrons⁵ and Ps atoms⁶ at very low energies, and by Ps⁻ emission from metal surfaces.⁷ Among many other breakthroughs, one could mention the observation of an optically excited Ps⁻ resonance,⁸ Ps₂ molecules,^{9,10} Ps-molecule transient states,^{11,12} and positronic molecules.¹³ Already in 2010, Gribakin *et al.*¹⁴ pointed out that about 60 positronic molecules were produced by low energy

collisions. In these experiments, positron attachment to vibrationally excited molecules is mainly driven by dipole and induced-dipole interactions,^{15,16} so the binding energies can be viewed as positron affinities, analogues of electron affinities.

Some of us recently reported on the energy stability of a fundamentally different type of positronic molecule,¹⁷ formed by two hydride anions and one positron, $e^+[H^-H^-]$. While the potential energy curves (PECs) undoubtedly pointed out the formation of a molecule, the electron densities around the nuclei were found very similar to those in the isolated atomic species, $H^- + PsH$, where PsH is the same as $e^+[H^-]$. In contrast, the positron density accumulated in the internuclear region, also showing typical signatures of constructive (ground state) and destructive (excited state) interference between atom-centered orbitals, which led to the conclusion that the formation of a positron covalent bond underlies the stabilization of the positron-dihydride compound.

The present study shows that positron bonding is not restricted to the $e^+[H^-H^-]$ molecule. Based on numerical simulations, we provide sufficient evidence of positron covalent bonding in homo- and heteronuclear dihalide anions, $e^+[X^-Y^-]$, with $X^-, Y^- = F^-, Cl^-, Br^-$. The bonding properties of these positron dihalide anions are compared to those of dialkali cations AB^+ , denoted as $e^-[A^+B^+]$, with $A^+, B^+ = Na^+, K^+, Rb^+$. The dialkali molecules are referred to as purely electronic analogs of the positronic dihalides with isoelectronic atomic cores, *e.g.*, $e^+[F^-Cl^-]$ and $e^-[Na^+K^+]$. We present a method to calculate the bond energies along with an energy decomposition scheme that provides a clear physical picture of bond formation. Finally, we

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† Electronic supplementary information (ESI) available: Details of the positron basis set construction, dissociation channels and thermodynamic cycles, a molecular orbital theory model of the positron bond, potential energy curves and densities not shown in the main document, electron binding energies, energy decomposition results and counterpoise correction tables. See DOI: 10.1039/c9sc04433g

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compare the properties of the positronic dihalides with those previously reported for positronic dihydride.

Since covalent bonds are largely responsible for the structure of matter above the atomic level, the similarities between positron and electronic bonds suggest that the former could give rise to a wide variety of exotic molecular systems. The interest on the interactions between positrons and halide anions dates back to early years of positron and Ps Chemical Physics (for a brief review see Saito¹⁸) so we revisit those interactions from a new perspective, hopefully expanding the landscapes of the field.

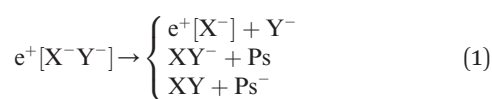
This paper is organized as follows. In Section 2, we summarize the theoretical and computational details of the numerical simulations of positronic and electronic systems. In Section 3, we provide the vibrational parameters, positron and electron densities and binding energies of positronic molecules and contrast them with those of their electronic analogs. In Section 4 we present our concluding remarks and perspectives for future work.

2 Methods

Positronic atoms and molecules are described with the any particle molecular orbital (APMO) approach,^{19,20} considering electrons and positrons as quantum particles and atomic nuclei as point charges. APMO and other multicomponent approaches have been regularly applied to study positron-containing atoms and molecules.^{18,21–34} A summary of APMO expressions can be found elsewhere.²⁰ In this paper, we label the multicomponent methods after the purely electronic ones, *e.g.*, APMO/HF for Hartree–Fock, APMO/CI for configuration interaction, APMO/MP2 for second-order Møller–Plesset perturbation theory, *etc.*

2.1 Energy stability of positronic molecules

Apart from pair annihilation, the following reaction channels are considered to determine the energy stability of the positron dihalides

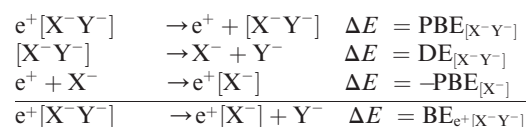


The first decay channel, in which the positron remains bound to the anion with the highest positron affinity (X^-), has the lowest dissociation energy among the reactions separating X and Y. The second channel involves the formation of a Ps atom and a stable XY^- molecular anion, while the third channel leads to the formation of a Ps^- anion and a stable XY molecule. The last two channels exhibit the lowest dissociation energies among the reactions producing Ps and Ps^- , respectively. From top to bottom, the dissociation channels in eqn (1) define the bond energy (BE), the Ps binding energy (PsBE) and the Ps^- binding energy (Ps^- BE) for the positron dihalides.

An accurate description of correlation effects in positronic molecules is a challenging numerical task. To study the energy stability of the $e^+[H^-H^-]$ complex against the dissociation

products $e^+[H^-] + H^-$, it was necessary to resort to the complete basis set limit of high-order CI calculations (up to quadruple excitations, APMO/CISDTQ).¹⁷ While employing such high-level methods for the positronic dihalides of present interest would be computationally prohibitive, we avoid lower levels of theory, such as APMO/MP2 or APMO/CISD, which could lead to erroneous predictions of the stability of positronic molecules, as was seen for the $e^+[H^-H^-]$ system.

To compromise accuracy and effort, we propose thermodynamic cycles as an alternative method to obtain adequate predictions of the positron dihalides energy stability. From the following cycle,



BEs are estimated as,

$$BE_{e^+[X^-Y^-]} = PBE_{[X^-Y^-]} + DE_{[X^-Y^-]} - PBE_{X^-}. \quad (2)$$

Similar cycles, presented in the ESI,[†] are used to estimate PsBEs and Ps^- BEs as,

$$PsBE_{e^+[X^-Y^-]} = PBE_{[X^-Y^-]} + EBE_{XY^-} + E_{Ps} \quad (3)$$

$$Ps^-BE_{e^+[X^-Y^-]} = PBE_{[X^-Y^-]} + EBE_{XY^-} + EBE_{XY} + E_{Ps^-}. \quad (4)$$

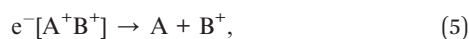
The above expressions relate the decay channels of the positronic dihalides, defined in eqn (1), to positron binding energies (PBEs), electron binding energies (EBEs), dissociation energies (DE) of the purely electronic molecular anions ($[X^-Y^-]$), as well as Ps and Ps^- ground state energies (E_{Ps} and E_{Ps^-}). In eqn (2)–(4), the DEs, EBEs and PBEs are defined with respect to the equilibrium internuclear distances, except for the unstable $[X^-Y^-]$ system, which is assumed to remain at the equilibrium geometry of the $e^+[X^-Y^-]$ complex.

The key aspect of the cycles is the fact that the EBEs, DEs, E_{Ps^-} and E_{Ps} in eqn (2)–(4) can be calculated with high-level correlated methods, or even taken from the literature, while the best available approximations are employed for the PBEs. In the present study, the EBEs and DEs of the purely electronic systems are evaluated with the coupled cluster method with single, double and perturbative triple excitations (CCSD(T)).³⁵ For Ps and Ps^- we employ the exact ground state energies (-656 kJ mol^{-1} and -688 kJ mol^{-1} ,³⁶ respectively), while the atomic and molecular PBEs are calculated with the APMO/REN-PP3 propagator method, a renormalized third-order approximation to the diagonal elements of the self energy.²⁹ An additional set of BEs, referred to as BE_{ib} , is obtained from eqn (2) and the atomic PBEs reported in ref. 18, which were calculated in the full-CI limit of the multi-reference configuration-interaction (MRCI) method. Replacing the APMO/REN-PP3 estimates by the MRCI counterparts serves as a more stringent stability test, since the energies of the positronic dihalides are compared to the best available atomic PBEs. BE_{ib} estimates should thus be viewed as *lower bounds* (the molecular APMO/



REN-PP3 PBEs underestimate the electron–positron correlation²⁹). The BEs computed only from APMO/REN-PP3 PBEs are expected to be more accurate because the positron–electron correlation is more balanced between the molecular and atomic species.

The energy stability of the purely electron analogs is established in terms of the lowest energy dissociation channel



where A represents the alkali atom with the highest EBE. Similarly to positronic dihalides, we employ a thermodynamic cycle

$$BE_{e^{-}[A^{+}B^{+}]} = EBE_{[A^{+}B^{+}]} + DE_{[A^{+}B^{+}]} - EBE_{A^{+}}, \quad (6)$$

to compute the BEs of $e^{-}[A^{+}B^{+}]$ in terms of CCSD(T) EBEs and DEs. The unstable $[A^{+}B^{+}]$ system is assumed to remain at the equilibrium geometry of the $e^{-}[A^{+}B^{+}]$ complex.

2.2 Potential energy curves

The positron dihalides PECs, $E_{e^{-}[X^{-}Y^{-}]}$, were computed with the following expression at different internuclear separations R ,

$$E_{e^{-}[X^{-}Y^{-}]}(R) = E_{[X^{-}Y^{-}]}(R) - PBE_{[X^{-}Y^{-}]}(R). \quad (7)$$

To obtain PECs consistent with eqn (2) results, we have employed APMO/REN-PP3 estimates of $PBE_{[X^{-}Y^{-}]}$ and CCSD(T) energies for the purely electronic systems, $E_{[X^{-}Y^{-}]}$.

Ground state PECs were obtained from PBEs calculated as in ref. 29, applying APMO/REN-PP3 self-energy corrections to the occupied positron orbitals generated with APMO/HF calculations for the $e^{-}[X^{-}Y^{-}]$ system. For the first excited state PECs we employed a technique previously used to estimate the excitation energies of radicals as EBE differences between cation virtual orbitals.^{37–40} In this scheme, virtual positron orbitals are obtained by including ghost positronic basis functions in APMO/HF calculations for the $[X^{-}Y^{-}]$ purely electronic system. The APMO/REN-PP3 self-energy corrections are then applied to the second positronic virtual orbital, which allows for estimates of the first excited state PBE of the $e^{-}[X^{-}Y^{-}]$ complex.

The ground state PECs of the purely electronic dialkali molecules are constructed from CCSD(T) total energies, while their first excited state PECs from equation of motion coupled cluster with single and double excitations (EOM-CCSD) excitation energies.³⁵ First excited state properties are denoted by the “*” superscript. The bond energy of a stable excited state (BE^{*}) is calculated as the difference between energy of the dissociation products and the potential energy minimum.

2.3 Energy stability analysis

According to eqn (2)–(4), the energy stability of the positronic complexes can be related to the DEs, EBEs and PBEs. To better understand the mechanisms underlying electronic and positronic bonding, we decompose each of those energy terms as follows.

The DEs of the repulsive $[X^{-}Y^{-}]$ dianions and $[A^{+}B^{+}]$ dications are expressed in terms of a modified Coulomb equation that accounts for polarization

$$DE(R) = \frac{1}{R} - \frac{\alpha_1 + \alpha_2}{2R^4}, \quad (8)$$

where R is the internuclear distance and the α 's are the polarizabilities of the ions. The PBEs are decomposed with a scheme previously employed for proton binding energies.⁴¹ The PBE of $e^{-}[Z]$ is decomposed into electrostatic (E_{el}), relaxation (E_{rlx}) and correlation (E_{cor}) contributions. E_{el} is defined as the PBE calculated with the frozen electronic density approximation using the Hartree–Fock wave function of Z . E_{rlx} , which accounts for the electronic density change induced by positron binding, is obtained from the difference between the APMO/HF PBE and E_{el} . Finally, E_{cor} is obtained as the difference of the PBE estimates from a correlated method (APMO/REN-PP3) and APMO/HF. The EBEs are likewise decomposed into the same energy components using CCSD(T) in place of APMO/REN-PP3.

2.4 Computational details

A positron basis set with 6s4p3d2f Gaussian-type functions (GTFs) was used in all calculations. The GTF exponents of this basis set, which is referred to as PsX-TZ, were generated by following the Dunning correlation consistent scheme,⁴² as described in the ESI.† Calculations for the $e^{-}[X^{-}]$ atomic species employed a single basis set centred at the $[X^{-}]$ nucleus. For the $e^{-}[X^{-}Y^{-}]$ molecular complexes, three basis sets were used, with expansion centers at the X^{-} and Y^{-} nuclei, and also at their midpoint. The def2-TZVPPD electronic basis set⁴³ was employed in all calculations. Ground-state electronic and positronic densities were obtained from CISD and APMO/CISD wave functions calculated at equilibrium distances. In the reported calculations, all electrons and all orbitals were taken into account. Counterpoise corrections were considered in the DE, Δ PBE, Δ EBE and BE calculations to account for the basis set superposition error. The calculations for the positronic systems were carried out with the LOWDIN software,⁴⁴ while those for the purely electronic systems were performed with the ORCA computational package.⁴⁵

3 Results and discussion

3.1 Positron halides

The PBEs of the $e^{-}[F^{-}]$, $e^{-}[Cl^{-}]$ and $e^{-}[Br^{-}]$ positronic atoms, obtained with the APMO/REN-PP3 method, are shown in Table 1. There is good agreement, within 4–8% (mean error of 35 kJ mol^{−1}), with the multi-reference configuration-interaction (MRCI) calculations,¹⁸ obtained in the full CI limit. The CCSD(T) EBEs of the alkali atoms are within 1–2% of the experimental values (mean error of 7 kJ mol^{−1}).⁴⁶ While both the PBEs and EBEs decrease with the ionic core size, the PBEs are always higher comparing the analog systems (*i.e.*, those with isoelectronic ionic cores).



Table 1 Positron binding energies (PBE/kJ mol⁻¹) of the positronic atoms, e⁺[X⁻], and electron binding energies (EBE/kJ mol⁻¹) of the alkali atoms, A

e ⁺ [X ⁻]	APMO/REN-PP3 ^a	MRCI ^b
e ⁺ [F ⁻]	574	600
e ⁺ [Cl ⁻]	497	532
e ⁺ [Br ⁻]	472	516
A	CCSD(T) ^a	Exp ^c
Na	491	496
K	410	419
Rb	395	403

^a def2-TZVPPD electronic and PsX-TZ positronic basis sets. ^b Multi-reference configuration-interaction (MRCI) results from ref. 18. ^c Experimental results from ref. 46.

3.2 Positron dihalides potential energy curves

The ground-state PECs of the positron complexes e⁺[F⁻F⁻] and e⁺[F⁻Cl⁻], shown in Fig. 1, display potential energy minima which clearly indicate that the addition of a positron to the otherwise repulsive dianions leads to the formation of stable molecular species. Similar stabilization is also found for the other positron dihalides, e⁺[Cl⁻Cl⁻], e⁺[Br⁻Br⁻], e⁺[F⁻Br⁻] and e⁺[Cl⁻Br⁻], as shown in Fig. S1.† Likewise, the ground-state PECs of the purely electronic complexes e⁻[A⁺B⁺] display

potential energy minima consistent with the formation of the stable alkali diatomic molecules e⁻[Na⁺Na⁺] and e⁻[Na⁺K⁺]⁴⁷⁻⁴⁹ (Fig. 1), as well as e⁻[K⁺K⁺], e⁻[Rb⁺Rb⁺], e⁻[Na⁺Rb⁺] and e⁻[K⁺Rb⁺] (Fig. S1†), by the addition of one electron to the repulsive [A⁺B⁺] systems.

Fig. 1 also presents the PECs of first excited states of e⁺[F⁻F⁻], e⁻[Na⁺Na⁺] e⁺[F⁻Cl⁻] and e⁻[Na⁺K⁺]. The PECs of the homonuclear systems (top panel) display repulsive behaviour and their dissociation limits coincide with those of the respective ground states. In contrast, the PECs of heteronuclear systems (bottom panel) present shallow minima and their dissociation limits manifest the energies required to transfer either the positron from F⁻ to Cl⁻, or the electron from Na⁺ to K⁺, as discussed in the next section. Similarly to the cases discussed above, the homonuclear PECs of the remaining positronic and electronic molecules display repulsive behaviour, while the heteronuclear systems exhibit potential energy minima (see Fig. S1†).

The ground-state equilibrium internuclear distances, shown in Table 2, increase with the size of the ionic cores for all systems, while the corresponding force constants decrease. It is worth noting that the positronic systems exhibit shorter bond lengths (0.5–0.8 Å) and larger force constants (3–6 N m⁻¹) compared to their purely electronic analogs (isoelectronic ionic cores). The latter results, which suggest more stable positronic bonds, are consistent with the BEs presented in Table 2, obtained from eqn (2) and (6). The BEs of the positronic molecules exceed those of their purely electronic analogs by 4–16 kJ mol⁻¹.

The present ground state calculations indicate stable positronic dihalides with respect to the atomic dissociation products described at the same level of theory. A more rigorous check of their energy stability is provided by the BE_{ib} values shown in Table 3, obtained from the most accurate PBEs reported for the atomic fragments.¹⁸ The BE_{ib} estimates corroborate the stability of the positronic dihalides and provide lower bounds, in view of the more thorough description of positron–electron correlation in the dissociation products (full CI limit of MRCI) than in the molecules (APMO/REN-PP3). The PsBE and Ps⁻BE values reported in Table 3 also point out that dissociation into e⁺[X⁻] + Y⁻ is always the lowest-energy decay channel.

For completeness, we mention that the excited states of the heteronuclear molecules show similar trends as their ground states. As evident from Table 2, the first excited states of the positronic complexes present shorter bond lengths (1.0–1.4 Å) and stronger force constants (0.7–1.0 N m⁻¹) than those of the purely electronic analogs.

For the ground state BEs of all complexes, the basis set superposition error did not exceed 4 kJ mol⁻¹, while for the excited states, having larger internuclear separations, the maximum calculated error was 0.4 kJ mol⁻¹. Counterpoise corrections are presented in Table S5 in the ESI.†

3.3 Positron bond densities and orbitals

To gain further insight into bond formation in the ground states, we computed the electron (ρ_{e^-}) and positron (ρ_{e^+}) densities of the e⁺[X⁻Y⁻] systems, along with the electron and spin