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Semiempirical polarization potential for low-energy positron-atom and positron–atomic-ion interactions. II. The halogens

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A previously described model potential for polarization effects in positron-atom interactions is applied to the halogens. The model predicts that (i) each halogen is capable of binding positronium but not a positron, except for iodine, for which the positron affinity has an uncertainty of sign; (ii) no bound excited states for any of the systems exist, except possibly for PsCl; and (iii) the elastic-scattering cross section of positrons off fluorine has a deep Ramsauer minimum at a positron incident energy of about 0.85 eV, as does neon. For (i) results are in substantial agreement with the self-consistent-field results of Cade and Farazdel as corrected for correlation.

INTRODUCTION

We have recently initiated a comprehensive theoretical study of positron/positronium-atom interactions.[1] The study is based upon an empirically determined polarization potential, and it yields phase shifts and cross sections for low-energy (≤ 1 a.u.) positrons scattering off atoms, as well as binding energies for those positron/positronium-atom complexes which have bound states. In the first paper of this series,[1] the theory was described, and applications to the hydrogen atom and to the noble gases were given. In the present paper, applications to the halogens are reported.

The scattering of positrons off halogen atoms has not evoked any interest in the literature except for one paper[2] in which s-wave phase shifts for positrons scattering elastically off fluorine atoms were calculated in the static approximation. On the other hand, bound states of positrons and halide ions have attracted theoretical attention from the earliest days of positronium chemistry. The system which today we call positronium chloride, PsCl, was first mentioned in the literature in 1948.[3] A series of quantum-mechanical studies on this system by Simons[4] culminated in 1953[5] with a calculation of a bound positronic orbital in the field of a static Hartree-Fock chloride ion. The calculation was performed in such a way as to preserve the Ritz variational principal. Thus Simons unambiguously proved the stability of the species PsCl against dissociation.

Experimentally, bound states of PsCl and other positronium halides have been invoked to explain the quenching of triplet positronium in aqueous solutions of halide salts for over ten years.[6] More recent observations of positron lifetimes in solutions containing halogen compounds[7-15] are also interpreted in the same way. Gas-phase observations of positronium interactions with chlorine have also been interpreted by invoking bound PsCl.[16-18] Tao and Green[7] were able to obtain estimates of some positronium affinities from their observations of quenching in solutions of oxyacids. Their values for F and Cl are 2.9 ± 0.5 and 2.0 ± 0.5 eV. The latter value agrees with Tao's[18] gas-phase result.

It is our goal in the present paper to improve our understanding of these bound states.

REVIEW OF THE THEORY

For convenience, we give here a brief description of the theory.[1] We solve a Schrödinger equation for a positronic orbital/scattering wave ϕ_p in the field of a polarizable Hartree-Fock atom:

$$\left(-\tfrac{1}{2}\nabla^2+\frac{Z}{r}-\sum_i J_i(r)+V_{\mathrm{pol}}(r)-\epsilon_p\right)\phi_p=0\,. \qquad (1)$$

J_i is the spherically averaged Coulomb potential for the ith electronic orbital of the isolated atom,

$$J_i(r_p)=\int\int\frac{|\phi_i(r_e)|^2}{|\vec{r}_e-\vec{r}_p|}\,d\vec{r}_e\,d\hat{r}_p\,; \qquad (2)$$

ϵ_p is either (−) the binding energy of the positron to the atom or the positron incident kinetic energy $\frac{1}{2}k^2$, depending upon whether a bound or scattering positron is being considered; and V_{pol} is a semiempirical potential which gives the polarization response of the atom to the positron. The spherical averaging in Eq. (2) introduces a small error for the positron-halogen results, but not for the positronium-halogen results. This error is discussed below.

The polarization potential is taken to be

$$V_{\mathrm{pol}}(r)=\begin{cases}-\alpha/2r^4 & r\geq r_0\\ -\alpha/2r_0^4 & r\leq r_0\,,\end{cases} \qquad (3)$$

where α is the dipole polarizability and r_0 is determined from

$$r_0^{-2} = 0.02637 + 0.007308(P_I)^{1.1510} \qquad (4)$$

where P_I is the ionization potential of the atom in electron volts. The numbers in Eq. (4) are obtained by fitting our model potential results for the positronium affinity of the hydrogen atom and the scattering lengths for positrons off hydrogen and helium to their well-known values.[1]

Positronium-atom interactions are studied by solving Eq. (1) for a positron in the field of a polarizable mononegative ion. P_I in Eq. (4) is then the electron affinity (A_e) of the atom, and $(-)\epsilon_p$ obtained from Eq. (1) is the positron affinity of the negative ion. The positronium affinity A_{Ps} of the atom is

$$A_{\text{Ps}} = A_e - \epsilon_p - 6.8 \text{ eV}. \qquad (5)$$

In order to carry out our studies, we need Hartree-Fock wave functions, polarizabilities, and ionization potentials (electron affinities) for the atoms (negative ions). These quantities are all accurately known, except for the polarizability of the iodine atom and of the halide ions, which are known with only modest accuracy.

PREVIOUS WORK ON THE POSITRONIUM HALIDES

Shortly after Simon's work, Millett and Castillo-Bahena[19] interpreted their observations of angular correlation in the alkali-halide crystals by evaluating parameters in an assumed form for the product of electronic and positronic orbitals $\phi_i\phi_p$ in such a way as to fit calculated to experimental curves. The fit achieved was quite good, but no binding information was obtained.

At about the same time, Ferrell, in his famous review article,[20] calculated positron affinities of anions with a procedure which amounts to replacing the potential in Eq. (1) with a simpler parameterized function:

$$\frac{z}{r} - \sum_i J_i + V_{\text{pol}} \to \begin{cases} \infty & \text{for } r < c \\ -1/r & \text{for } r > c\,. \end{cases} \qquad (6)$$

This crude potential was used in conjunction with a simple functional form for ϕ_p containing parameters determined by minimizing the calculated energy. Using the ionic radius of Cl^- for c in Eq. (6), Ferrell obtained $\epsilon_p = 2.37$ eV, which corresponds to a positronium affinity of chlorine of -0.82 eV.

More recently Goldanskii and Prokopev[21] used an approximation which amounts to setting $-J_i = -(z+1)/r$ and $V_{\text{pol}} = 0$ in Eq. (1). With a particular form for ϕ_p, a variational calculation yields $\epsilon_p = -10.2$ eV for all the halides. Positronium affinities are thus differentiated only by the electron affinities of the atoms. The positronium affinities one obtains with this approach are 6.85, 7.01, 6.76, and 6.46 eV for F, Cl, B, and I, respectively.

Then Bussolati, *et al.*[22] presented a theory in which the potential in Eq. (1) is replaced with

$$\frac{z}{r} - \sum_i J_i + V_{\text{pol}} \to -\frac{c^2}{r} + \frac{c}{r^2}, \qquad (7)$$

where c is determined by fitting calculated and observed annihilation rates in alkali-halide crystals. This approach permits an evaluation of positron binding energies. The resulting positronium affinities for the four halogens are 0.07, -0.37, -0.86, and -1.40 eV.

Simon's calculation on positronium chloride[5] consisted of setting V_{pol} in Eq. (1) to zero. For the calculation of the static electronic potential $-\sum_i J_i$ he used the Hartree-Fock wave function of chloride of Hartree and Hartree.[23] The binding energy of the positron obtained by Simons, 3.75 eV, coupled with the modern value of the electron affinity of chlorine, 3.61 eV, and the binding energy of positronium, 6.80 eV, gives a positronium affinity of 0.56 eV for the chlorine atom. This is a lower bound, although a little uncertainity is introduced by inaccuracies in the chloride wave function. A more modern chloride wave function[24] was used by Hautojärvi and Nieminen[25] who found $\epsilon_p = 3.88$ eV, giving the positronium affinity as 0.69 eV. Recently Cade and Farazdel[26] examined the system again and, with a chloride-ion wave function which is essentially the exact solution of the Hartree-Fock equations, obtained $\epsilon_p = -3.86$ eV, which gives the positronium affinity as 0.67 eV. This must be regarded as the exact result for the binding energy of PsCl in the static Hartree-Fock approximation.

One might consider two distortion effects which are ignored in these calculations: self-consistency and correlation-polarization. The former may be viewed as an extension of Hartree-Fock self-consistent-field theory.[26,27] The self-consistency between the positron and electrons is achieved by adding a term $-J_p(r)$ to the usual electronic equations. The complete set becomes

$$\left(-\tfrac{1}{2}\nabla^2 - \frac{z}{r} + \sum_j \left[J_j(r) - \delta(s_i s_j) K_j(r)\right] - J_p(r) - \epsilon_i\right)$$

$$\times \phi_i(\vec{r}) = 0\,,$$

$$\left(-\tfrac{1}{2}\nabla^2 + \frac{z}{r} - \sum_i J_j(r) - \epsilon_p\right)\phi_p(\vec{r}) = 0\,, \qquad (8)$$

where $\delta(s_i s_j)$ is unity if the spins associated with ϕ_i and ϕ_j are the same and zero otherwise, and where

$$K_j(r)\phi_i(\vec{r}) = \phi_j(\vec{r}) \int \frac{\phi_j^*(\vec{r}\,')\phi_i(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,' ,$$

$$J_p(r) = \int \frac{|\phi_p(\vec{r}\,')|^2}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,' . \qquad (9)$$

The second of Eqs. (8) is the same as Eq. (1) with $V_{\rm pol}$ neglected; but ϕ_p in Eq. (8) is coupled to the set $\{\phi_i\}$ and hence will differ from the static solution to the extent to which ϕ_p responds to the relaxation of $\{\phi_i\}$ induced by the additional term $-J_p$. This additional term enables the electrons to see the positron in the form of its orbitally averaged potential. Cade and Farazdel[26] solved Eqs. (8) for the four positronium halides, and from their results we can judge how important the self-consistency error is: they find the positronium binding energy to the halogens increases from the static results, 1.60, 0.67, 0.16, and −0.50 eV, by the amounts 0.09, 0.06, 0.05, and 0.07 eV for F, Cl, Br, and I, respectively. Self-consistency is a small effect.

The other error, correlation-polarization, has two aspects. One has to do with the distortion of the halide by the positron when it is far away (polarization); the other, when it is embedded in the electronic cloud (correlation). The polarization effect is the better understood of the two. This effect, which has been reviewed recently,[28] can be treated accurately by including a long-range effective potential in the positronic equation. This is the basic idea of our present work.

Accurate treatment of the correlation effect is more difficult. It has been considered formerly[27] but never worked out numerically except in a first-order approximation.[28] We do know this about correlation: it introduces a local maximum (cusp) in the many-particle wave function in those regions of space corresponding to close approach of an electron to the positron. An accurate representation of this cusp is necessary for accurate calculations of annihilation rates,[29] but, interestingly, not for calculations of angular correlation curves. Indeed, the most satisfactory contact between theory and experiment to the present in positronium chemistry is the agreement in the angular correlation curves between the calculations of Farazdel and Cade[29] on the positronium halides and the measurements of Mogensen and Jansen[12] on aqueous solutions of halide salts.

One hopes that this agreement is not fortuitous: will it disappear when long-range polarization effects are added to the calculation? Unfortunately, the present work does not provide an answer because the polarization effects are merely parametrized into a specification of $V_{\rm pol}$; the polarization effects are not realized explicitly as shifts of electronic orbitals.

Cade and Farazdel[26] have provided estimates of the correlation-polarization corrections to the positron affinities of the halides. These estimates are based on an analogies between electron-positron correlation-polarization and the much better understood electron-electron correlation-polarization. Two estimates are provided, one conservative and one liberal. The conservative estimates lead to positronium affinities of 1.83, 1.11, 0.55, and −0.19 eV; the liberal estimates, made only for PsF and PsCl, give 3.93 and 2.53 eV. Thus the correlation-polarization errors are estimated to be 1.28 ± 1.05, 1.15 ± 0.71, >0.39, and >0.31 eV, which are considerably larger than the self-consistency errors: 0.09, 0.06, 0.05, and 0.07 eV.

This is not hard to understand on the basis of the sizes of the orbitals calculated by Cade and Farazdel. For PsCl, Fig. 2 of the paper of Cade and Farazdel[26] shows that the probability distribution for the positron, $r^2\phi_p^2$, has a maximum about four times farther from the nucleus than that for the $3p$ electrons. This tells us that the positron spends more time in the long-range polarization region than the short-range correlation region.

PRESENT RESULTS FOR THE POSITRONIUM HALIDES PsX

Accurate Hartree-Fock wave functions for the halides X^-, are available.[30] The electron affinities of Massey[31] give, from Eq. (4), r_0 values of $4.20a_0$, $4.14a_0$, $4.23a_0$, and $4.35a_0$ for F^-, Cl^-, Br^-, and I^-, respectively.

The polarizabilities of these ions are less well known than the other quantities needed for our theory. Perturbed Hartree-Fock calculations of polarizabilities for negative ions are unreliable and tend to be too high (except for H^-, for which the Hartree-Fock results are much too low).[32-34] Fortunately there is a reasonably accurate calculation for F^- in the literature: An eight-term configuration interaction calculation of Donath[35] gives a value for the polarizability of $8.14a_0^3$. Winslow[36] has made careful semiempirical determinations of the polarizabilities of the halides: $7.24a_0^3$, $25.9a_0^3$, $28.3a_0^3$, and $41.8a_0^3$ for F^-, Cl^-, Br^-, and I^-, respectively. These values are probably a little too small since they are close to older values determined from refractive indices of alkali-halide crystals and aqueous solutions[37-40] which are known to be smaller than gas-phase ionic values.[41] Winslow's value for the polarizability of F^- is 11% less than Donath's; we therefore take this to be the range of uncertainty in all the polarizabilities, and adopt for our calculations the values $(7.69 \pm 0.45)a_0^3$, $(27.4 \pm 1.4)a_0^3$, $(29.8 \pm 1.6)a_0^3$, and $(44.1 \pm 2.3)a_0^3$.

Integration of Eq. (1) yields $-\epsilon_p = 5.21 \pm 0.02$,

TABLE I. Positronium binding by the halogens.[a]

	F	Cl	Br	I
Present work	1.86 ± 0.02	1.40 ± 0.04	0.83 ± 0.04	0.25 ± 0.05
Static approximation[b]	1.60	0.67	0.16	−0.50
Self-consistent approximation[b]	1.69	0.73	0.21	−0.43
Contribution from self-consistency[c]	0.09	0.06	0.05	0.07
Contribution from polarization[d]	0.26	0.73	0.67	0.75
Estimates of Cade and Farazdel (Ref. 26)	2.88 ± 1.05	1.82 ± 0.71	>0.55	>−0.19
Tao and Green (Ref. 7)	2.9 ± 0.5	2.0 ± 0.5		
Positronium affinities for a $2p$-positronic state: Present work	−0.22 ± 0.02	−0.04 ± 0.02	−0.42 ± 0.02	−0.84 ± 0.04
Cade and Farazdel (Ref. 26)	−0.35	−0.50	−0.85	−1.29

[a] Energies are in eV.

[b] Calculated from Eq. (5) with ϵ_p from Cade and Farazdel (Reference 26).

[c] The fourth line is the difference between lines 2 and 3.

[d] The fifth line is the difference between lines 1 and 2.

4.59 ± 0.04, 4.27 ± 0.04, 3.99 ± 0.05 eV which gives positronium affinities of 1.86 ± 0.02, 1.40 ± 0.04, 0.83 ± 0.04, 0.25 ± 0.05 eV for F, Cl, Br, and I, respectively. Thus our prediction is that all the halogens will bind positronium.

Our positronium affinities are within the limits estimated by Cade and Farazdel[26] for F and Cl (2.88 ± 1.05 and 1.82 ± 0.71 eV), and greater than their lower limits for Br and I (0.55 and −0.19 eV). Our values for F and Cl are 0.5 and 0.1 eV less than the lower limits of Tao and Green.[7] These data are collected in Table I, which lists also the effects of self-consistency and polarization. The latter is seen to be larger by about an order of magnitude, and makes the difference between binding and not binding in the case of iodine.

There are three candidates for the first excited state of these systems: a $2p$ positron and an unexcited halide; a $2s$ positron and an unexcited halide; and a $1s$ positron and a halide with a valence np electron excited to the $(n+1)s$ orbital. All three of these were considered for PsF and PsCl by Cade and Farazdel[26] who found the 2s positron state to be higher than the $2p$-state by about 1.05 eV for both PsF and PsCl. One expects this inversion of levels for positrons: a p positron is farther from the repulsive nucleus than an s positron. The electronically excited states calculated by Cade and Farazdel for PsF and PsCl are 4.29 and 4.65 eV above their ground states and 2.27 and 3.44 eV above their $2p$-positron states. Although correlation errors will be different for these states, it seems unlikely that the order of levels obtained by Cade and Farazdel is incorrect. Therefore we conclude that the $2p$-positron state is the first excited state for these systems.

We can study this state with our model by solving Eq. (1) for the lowest p wave. We find all the excited systems to be unstable to dissociation to Ps $+X$, although PsCl comes very close to having a bound excited state according to our model. Equation (5) gives for the positronium affinities for these states the values −0.22 ± 0.02, −0.04 ± 0.02, −0.42 ± 0.02, and −0.84 ± 0.04 eV. From their positronic $2p$ eigenvalues, we infer that Cade and Farazdel's values are −0.36, −0.50, −0.85, and −1.29 eV. The numerical agreement is only fair, but the qualitative conclusions are the same. No bound excited state for any of these species exists.

RESULTS FOR THE POSITRONIC HALOGENS e^+X

These systems have not been studied theoretically and they appear to play an insignificant role in annihilation mechanisms. Exceptions are Malik's work[2] on positron-fluorine scattering, and a conjecture by Tao[9] that a bound state of e^+I rather than PsI might be involved as an intermediate in annihilations where I_2 is present. Knowledge of all these systems is needed, however, to improve our understanding of molecular interactions with e^+ and Ps.[42]

The ionization potentials give, from Eq. (4), $r_0 = 2.12a_0$, $2.45a_0$, $2.56a_0$, and $2.72a_0$ for F, Cl, Br, and I respectively. The polarizabilities of F, Cl, and Br are known[43] from the theoretical work of Werner and Meyer[44] and Reinsch and Meyer[45] to within 2%. This we regard as less than the effects of uncertainties of our model. For the polarizability of iodine, Miller and Bederson[43] attempt to calibrate the uncoupled Hartree-Fock values of Fraga, *et al.*[46] by comparing other calculated quantities with their known values. The value given by Miller and Bederson, $26a_0^3$, is said by them to be uncertain by 50%. The polarizabilities used in our calculation are $3.75a_0^3$, $14.7a_0^3$, $20.6a_0^3$. and $(26 \pm 13)a_0^3$, respectively.

Values of r_0 and α define our polarization potential, Eq. (3). Equation (1) is then solved for $l = 0$. We find no bound state for any system except e^+I for the higher limit of polarizability, $39a_0^3$. The scattering lengths obtained are listed in Table II, along with the positron affinities. Negative affinities are calculated as outlined in our earlier work.[1]

The spherical average in Eq. (2) is not required for any PsX system nor for any system considered earlier[1,27] because all the atoms and ions considered have closed electronic shells and therefore have spherically symmetrical charge distributions. For a positron scattering off a halogen atom, however, there is a small error. This arises in neglecting the effect of the angular momentum coupling of the positron to the *np* hole in the outer subshell. For an *s*-wave positron, the positron-hole coupling produces only *P* multiplets. There are two: ^1P and ^3P, and these are separated only by a very small fine-structure splitting, presumably of the order of that which separates ortho- and parapositronium in the ground state.

However, for a *p*-wave positron, the positron and hole have the same angular momentum quantum number *l*, and a larger multiplet splitting can be expected. As for two nonequivalent *p* electrons, this coupling will produce singlet and triplet *S*, *P*, and *D* terms, of which the *D* will be the most stable and *S* the least. We neglect this coupling by simply spherically averaging the *np* hole in integrating over the positron angle in Eq. (2). Consequently our *p*-wave phase shifts tend to be less accurate than our *s* wave. But the *p*-wave contribution to the cross section is generally small compared to that of the *s* wave, so this error is probably not numerically important.

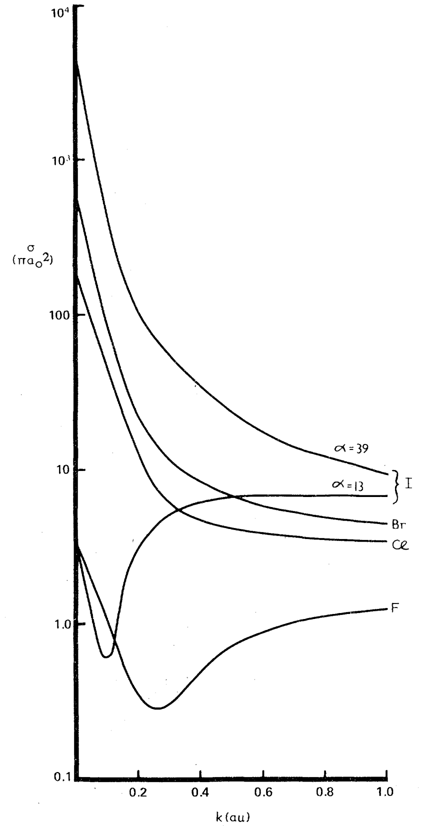

FIG. 1. Cross sections for positron-halogen elastic scattering. Two curves for iodine result from the two choices of the polarizability: $13a_0^3$ and $39a_0^3$.

As one proceeds to higher *l* waves beyond *p*, one expects the multiplet splittings to decrease because the positron and hole have different angular momenta. The error in these higher waves should therefore be less important than that for the *p* wave.

The elastic-scattering cross sections for F, Cl, Br, and I are presented in Fig. 1 for $k = 0$ to 1 a.u. The ambiguity for iodine is strikingly apparent in

TABLE II. Results for positronic halogens e^+X.

				I	
	F	Cl	Br	$\alpha = 13a_0^3$	$\alpha = 39a_0^3$
Scattering length (a_0)	−0.901	−6.42	−11.5	−0.969	+33.3
Positron affinity (eV)	−12.62	−0.50	−0.15	−2.93	+0.010

Fig. 1 and Table II. The uncertainty in the polarizability is the difference between binding and not binding; consequently there is a qualitative difference between the calculated cross sections for these two polarizabilities. Presumably a measurement of the elastic cross section would enable us to improve our estimate of the polarizability of iodine.

The shapes of the cross sections are quite similar to those previously calculated for the adjacent noble gases,[1] and about two to three times larger. Fluorine, like neon, exhibits a very large Ramsauer minimum which is absent in chlorine, argon, bromine, and krypton. The cross section for the more polarizable iodine has a shape similar to that of xenon.

CONCLUSIONS

For the positronium affinities of the halogens, our model is in substantial agreement with the calculations and correlation estimates of Cade and Farazdel.[26] We predict the positronium affinities of F, Cl, Br, and I to be 1.86, 1.40, 0.83, and 0.25 eV, respectively, and we predict no bound excited states of these systems exist, although the prediction for chlorine is very uncertain. The small uncertainties in these values appearing in Table I are less than the uncertainties inherent in our model, which are difficult to estimate. The principle source of uncertainty in the model is the shape of the polarization potential at short range.

The positron-halogen scattering cross sections predicted by our model are much like those of the adjacent noble gases. Fluorine should exhibit a deep Ramsauer minimum at $k \sim 0.25$ a.u., as neon. Uncertainties in the polarizability of iodine vitiate any predictive power of our model for that atom; however, it may be possible to improve our information about the polarizability of iodine by comparing measured elastic cross sections with the data of Fig. 1.

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