Comment on "Semiempirical Approach to Positron Annihilation in Molecules"

One of the outstanding results of positron scattering is the very large annihilation rates for the organic molecules [1]. In a recent Letter, Laricchia and Wilkin [2] postulated that the large values of Z_{eff} were caused by two mechanisms. First, the length of time a virtual positronium (Ps) cluster would remain in the vicinity of an atom or molecule during the collision was estimated to get increasingly larger as the ionization potential approached 6.80 eV. This aspect of their Letter is not discussed in this Comment.

The discussion of the second factor can be simplified by referring to the electron that is part of a real or virtual Ps cluster as the cluster electron. The other electrons of the atom or molecule can be called the spectator electrons. Laricchia and Wilkin suggested that the pickoff annihilation rate Γ_{po} , with the spectator electrons, was much larger than the direct annihilation rate with the cluster electron due to strong electron-positron correlations with the spectator electrons. The cluster annihilation rate Γ_c is the spin-averaged rate of Ps ground state, i.e., $2 \times 10^9 \text{ s}^{-1}$. The pickoff rate (in s^{-1}) was estimated to be

$$\Gamma_{\text{po}} = 1.2 \times 10^{10} \alpha N, \quad (1)$$

where N was the number of valence electrons and α was the dipole polarizability in units of 10^{-30} m^3 . For most values of N and α , Γ_{po} is 1–4 orders of magnitude larger than Γ_c . Equations similar to (1) have been used to describe free positrons interacting with an electron gas, but it is difficult to use Eq. (1) to justify an annihilation rate enhancement for a neutral Ps atom interacting with an electron gas. There is little support for this idea and much contradictory evidence.

For example, while short range electron-positron correlations enhance positron annihilation rates in metals, the known annihilation rates range from 3×10^9 to $11 \times 10^9 \text{ s}^{-1}$ [3]. Nonconducting materials typically have slower annihilation rates of the order $2 \times 10^9 \text{ s}^{-1}$ [4]. Laricchia and Wilkin predict values of Γ_{po} larger than 10^{13} s^{-1} .

There are also a number of exotic systems that bind a positron, and explicit calculations show no sign of an enhancement in Γ_{po} . Since the introduction of Eq. (1) by Laricchia and Wilkin makes no reference to scattering theory, Eq. (1) should be applicable to bound states. Applying Eq. (1) to Bee^+ , Mge^+ , LiPs, NaPs, and KPs implies pickoff annihilation rates of 10^{11} s^{-1} or greater. LiPs [5], NaPs [5], and KPs [6] all have annihilation rates of about $2 \times 10^9 \text{ s}^{-1}$, while those of Bee^+ [5] and Mge^+

[5] are smaller than 10^9 s^{-1} . Other systems such as HPs [5] and Ps_2O [7] have annihilation rates (per positron) of 2.45×10^9 and $2.3 \times 10^9 \text{ s}^{-1}$, respectively. Pickoff annihilation contributes for both systems, but leads only to an annihilation rate slightly larger than Γ_c .

The evidence for exotic systems that bind a positron suggests that positron annihilation is dominated by direct annihilation with the cluster electron [5,6,8]. The cluster annihilation rate Γ_c represents a natural upper limit to the annihilation rate in an atomic or molecular environment since the positron can form a cluster with only one electron. While pickoff annihilation can slightly increase the annihilation rate, the annihilation rate is largely determined by the extent to which a Ps cluster forms part of the total wave function, and none of these positron binding systems have an annihilation rate (per positron) larger than $2.5 \times 10^9 \text{ s}^{-1}$ [5–9].

The idea that the pickoff annihilation rate can be more than 2 orders of magnitude larger than Γ_c is untenable and the very large values of Z_{eff} observed for organic molecules require an alternate explanation.

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