Comparisons of Positron and Electron Binding to Molecules

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Positron binding to molecules is compared to the analogous electron-molecule bound states. For both, the bound lepton density is diffuse and remains outside the valence shell. Positron binding energies are found to be one to two orders of magnitude larger than those of the negative ions due to two effects: the orientation of the molecular dipole moment allows the positron to approach it more closely and, for positrons, lepton correlations (e.g., via dipole polarizability) contribute more strongly.

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Although positrons are important in many areas of science and technology, including materials science, medicine, and astrophysics [1–3], many facets of their interactions with matter are poorly understood [4]. Studies of resonant positron annihilation on molecules provide evidence that positrons bind to these targets. They also provide measures of positron-molecule binding energies [5], and data are now available for some sixty molecules.

These attached states are similar to a subset of negative ions (electrons bound to molecules), frequently referred to as dipole-bound anions [6–8]. Short-range repulsion and longer-range attractive interactions lead to diffuse bound states in which the lepton is excluded from the valence shell. The permanent dipole moment often plays a primary role in forming the attractive potential for electrons [9–11]. In contrast, for positron bound states, the molecular dipole polarizability has also been shown to play an important role [5].

While there are reasonably accurate calculations of electron binding to molecules, and there is much known about the structure of the resulting anions [7,8], understanding of the analogous positron case is at a more primitive stage [12,13]. Similarities and contrasts between these molecular ions are investigated here with the aim of providing added insight into positron attachment to atoms and molecules and the structure of the resulting cations.

The present study compares positron and electron binding for molecules in three chemical families (aldehydes, ketones, and nitriles). For all of the species studied, values of the lepton-molecule binding energy ε_b for positrons are found to be at least one order of magnitude greater than those for the analogous negative ions. This is due predominantly to two effects. Typically, molecules with large permanent dipole moments have the negative end of the dipole at the periphery of the molecule. As such, the positron can approach it more closely, leading to an enhanced attractive potential. In addition, lepton correlations (e.g., mediated by dipole polarizability) are much more strongly attractive for positrons. Both these features lead to enhanced positron binding. This is to be expected generally when comparing positron-molecule attachment to the analogous negative ions [8], namely those in which the extra electron is in a diffuse state, as is typically the case for molecules with closed valence shells.

Positron binding energies were measured by studying vibrational Feshbach-resonant annihilation spectra as a function of incident positron energy. This technique is described in detail elsewhere [5]. The energies ε_ν of the observed resonant peaks in the annihilation spectra, relative to the energies $\hbar\omega_\nu$ of the vibrational modes, provide a measure of the positron-molecule binding energy ε_b through the relationship $\varepsilon_b = \hbar\omega_\nu - \varepsilon_\nu$. These resonances are distinguishable from true bound states in the sense that the molecule has sufficient vibrational energy to subsequently eject the positron. However, theory and experiment indicate that measurements made on these resonant states do provide reliable binding energies for the actual bound states [5].

Electron binding energies for analogous dipole-bound anions have been measured using a number of techniques [9,11]. A relatively comprehensive set of measurements using Rydberg-state charge exchange can be found in Ref. [11], and these data are used for comparison. Considered here are a selection of aldehyde, ketone, and nitrile molecules, shown schematically in Table I. They have appreciable permanent dipole moments that arise from the inclusion of CO double bonds in the aldehydes and ketones and CN triple bonds in the nitriles.

Positron and electron data for ε_b are shown in Table I (from Refs. [14,15], and [11], respectively). Also tabulated are the molecular permanent dipole moments μ and the dipole polarizabilities α of the parent molecules [16]. The dipole moment, where nonzero, provides the lowest order static attractive potential for both leptons. The polarizability, which appears to be more important in the positron case, can contribute both statically and dynamically and might be regarded as a proxy for attractive electron-positron correlations.

Shown in Fig. 1 are the positron and electron binding energies plotted as a function of μ and α. Also included for comparison are positron data for alkanes

TABLE I. Positron- and electron-molecule binding energies ε_b (meV), permanent dipole moments μ (D), and dipole polarizabilities α (10^{-24} cm^3) for selected molecules. Positron data for ε_b are from Refs. [14,15], electron data are from Ref. [11], and values for μ and α are from Ref. [16].

	Molecule	μ	α	$\varepsilon_b(e^+)$	$\varepsilon_b(e^-)$
Aldehydes					
	Acetaldehyde C_2H_4O	2.8	4.6	90	0.6
	Propanal C_3H_6O	2.5	6.5	120	1.0
	Butanal C_4H_8O	2.7	8.2	142	1.2
Ketones					
	Acetone C_3H_6O	2.9	6.4	173	2.6
	2-butanone C_4H_8O	2.8	8.1	195	1.8
	Cyclopentanone C_5H_8O	3.3	9.3	230	2.8
Nitriles					
	Acetonitrile CH_3CN	3.9	4.4	180	19
	Propionitrile C_2H_5CN	4.1	6.5	245	15
	2-methylpropionitrile C_3H_7CN	4.3	8.1	275	12

(C_nH_{2n+2}, $\mu = 0$), methyl halides (CH_3X, where X is F, Cl, and Br; $\mu \sim 1.8$ D), and alcohols (CH_3OH and C_2H_5OH; $\mu \sim 1.7$ D). Cursory inspection of Table I and Fig. 1 indicates that the magnitudes of ε_b for positrons and electrons are remarkably different. Positron binding energies range from 90 to 275 meV. In contrast, the analogous electron ε_b values range from 0.6 to 19 meV—from one to two orders of magnitude smaller. The possible origins of this difference are a focus of this Letter.

Beyond the data in Table I, further insight can be gained from theoretical calculations of the bound positron and electron wave functions. In the absence of a dipole moment, the attached leptons are expected to be in diffuse orbitals surrounding the entire molecule. An example of this is the model wave function for positrons bound to alkanes described in Ref. [17]. For these molecules (with $\mu = 0$), the positron wave function extends over the entire molecule, and ε_b is seen to increase ~linearly with molecular size. On the other hand, of particular relevance here is the case of nonzero μ; it has long been known that the type of binding considered here, with diffuse lepton density remaining outside the valence shell, can be mediated by a permanent molecular dipole moment [18]. First considered for electrons, similar behavior is expected for positrons. Shown in Fig. 2 is a comparison of the calculated wave functions for positrons and electrons bound to acetonitrile, from Refs. [13,19], respectively. Due to the relatively strong permanent dipole moment, the wave function is quite anisotropic (i.e., localized adjacent to one end of the molecule) for both the positive and negative species.

Given this type of wave function, a chemical effect appears to play a potentially important role in modulating the strength of the bound lepton interaction with μ. In particular, the negative end of the dipole (e.g., the nitrogen atom) is nearest the periphery of the molecule. This allows the positron to be in close proximity to the permanent moment, leading, in turn, to a relatively strong contribution of μ to the binding. In contrast, the excess electron is attracted to the other end of the dipole. In this case, the (repulsive) exchange interaction with electrons in the methyl group, which is located between the excess electron and the dipole, prevents the electron density from coming close to the permanent moment; this results in a reduction of ε_b. This geometrical effect occurs for all species listed in Table I; namely, the negative end of the dipole is at the periphery of the molecule. This, generally, favors stronger positron binding, as is observed.

Considering further the dependence of ε_b on μ and α shown in Fig. 1, there appears to be little correlation between the negative ions and the analogous positron-attached states. This is due to the fact that increasing α results in a significant increase in ε_b for positrons, while it has little effect on ε_b for electrons. As shown in Fig. 1(c), in the electron case, all ε_b data lie reasonably close to one curve, with ε_b increasing rapidly beyond $\mu \sim 2.5$ to 3 D. Data for other negative ions from Ref. [11] (not shown) also exhibit this trend.

For positrons, however, the dependence of ε_b on μ is quite different. This is likely due to the interplay between the static dipole potential and the effect of correlations. As illustrated in Fig. 1(b), the slope $\partial\varepsilon_b/\partial\alpha$ is large and positive for all chemical families, including the alkanes. The consequence of this is that, while μ sets a minimum value for ε_b for positrons, increasing molecular size by adding alkyl groups further increases ε_b due to increased α. The dotted line in Fig. 1(a) (drawn as a guide to the eye) illustrates this minimum-ε_b effect; the minimum binding energy for positrons is set by both μ and α of the smallest molecule in a particular chemical series.

In Fig. 1(c), the fact that the electron data lie on a single curve as a function of μ illustrates the relatively weak dependence of ε_b on α [11]. In addition, the slope $\partial\varepsilon_b/\partial\alpha$ is considerably weaker for all molecules studied. It is larger and negative for nitriles, but, as discussed below, this is likely due to a different effect than the increase in α. Two effects likely contribute to this weaker dependence of ε_b on α for electrons. One is that the potential energy contribution due to $\alpha \propto 1/r^4$, where r is the distance from the lepton density to the molecular center. Since the

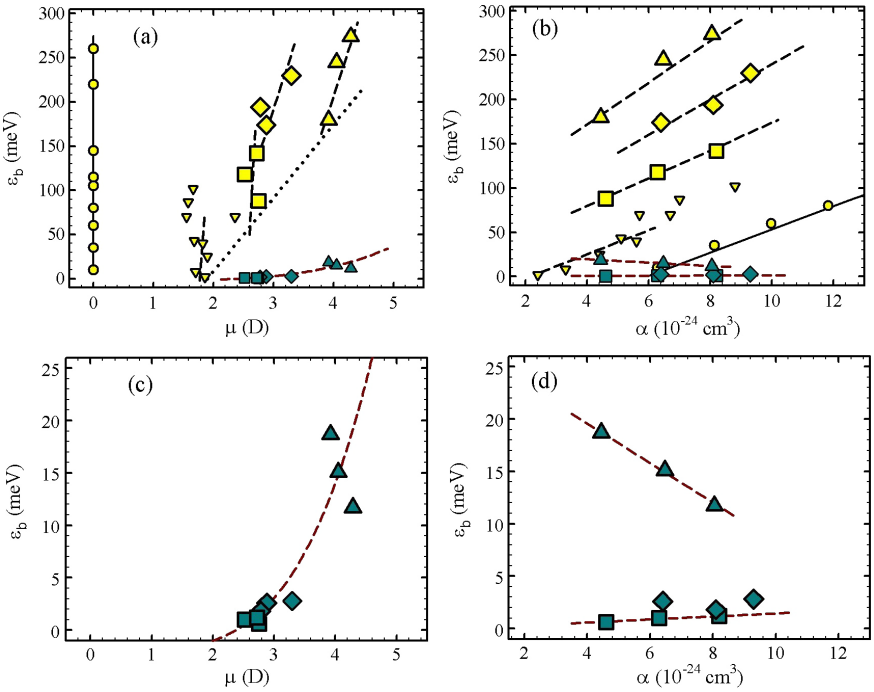

FIG. 1 (color online). Binding energies ε_b as a function of molecular parameters: (a) ε_b vs μ for positrons [light (yellow) symbols] and electrons [dark (cyan) symbols]; (b) positron and electron ε_b vs α; (c),(d) analogous plots showing only electron data but on an expanded scale. Symbols are aldehydes (□), ketones (◇), and nitriles (△). Also shown in (a),(b) are positron data for alkanes (○) and methyl halides and alcohols (▽). Dashed and dotted lines are guides to the eye. The solid line for the alkanes is a fit as described in Ref. [20].

electron is more weakly bound to the molecule than the positron, the average electron-molecule distance is correspondingly larger, and hence the contribution to ε_b is correspondingly smaller. Secondly, while the static, long-range, lepton-molecule potential due to α is attractive for both electrons and positrons, at shorter ranges, lepton correlations are strongly repulsive for electrons (i.e., due to the exchange interaction). Thus, the tendency for ε_b to increase with α may be partially cancelled by an increased short-range repulsion for electrons.

As mentioned above, the slope $\partial\varepsilon_b/\partial\alpha$ is negative for electron attachment to nitrile molecules, while it is positive for positrons. The former dependence may not be an effect attributable to α but (indirectly) to μ. In this case, as the size of the molecule is increased, there is more alkyl chain located between the bound electron and the permanent dipole. Thus, the repulsion of the electrons (on the alkyl chain) tends to keep the bound electron farther away from the dipole. This, in turn, can lead to a further reduction of the contribution of the permanent dipole potential to the binding energy. For positron binding to nitriles, the effect is the opposite. Lengthening the alkyl chain increases α and tends to draw the positron density even closer to the permanent dipole. The positron binding energy is thus increased due both to the larger polarization potential and the closer proximity of the positron density to the dipole moment.

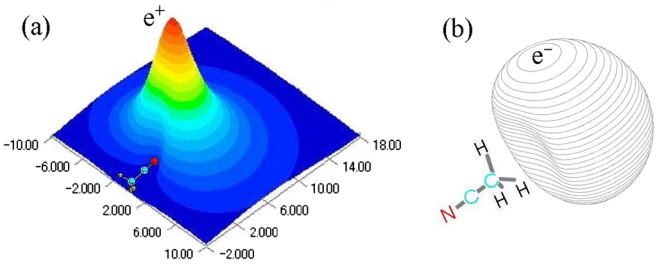

FIG. 2 (color online). Contour plots of calculated bound (a) positron [13] and (b) electron [19] wave functions for the positive and negative acetonitrile (CH_3CN) molecular ions.

Beyond the localization due to the permanent dipole moment, there are other geometry-dependent effects, such as the permanent quadrupole moment and anisotropic molecular polarizability, that can also be expected to affect lepton binding (e.g., see Ref. [10]). While there do not appear to be obvious trends in ε_b with these parameters in the present positron data set, further consideration of such effects is warranted.

In summary, we focused here on a class of lepton-molecule attached states in which the lepton is in a diffuse bound state, with the lepton density localized predominantly outside the valence shell. In the positron case, both the permanent dipole moment and the molecular dipole polarizability contribute significantly to the binding, whereas, in the electron case, the effect of μ is much larger

than that due to α. In all of the examples discussed here, electron binding is much weaker. The stronger positron binding is likely due to a combination of the absence of the exchange interaction, attractive lepton-lepton correlation effects, and an important steric effect: for the molecules studied, the negative end of the dipole is at the periphery of the molecule, leading to a much stronger, attractive dipole potential for positrons. This stronger binding for positrons is likely to have important practical consequences, such as the stabilization of the complex against thermal detachment, and this, in turn, increases the probability of annihilation.

It is hoped that the analysis presented here will be of help in identifying the mechanisms that contribute most significantly to positron-molecule binding. It can also be used as a guide to predicting, at least qualitatively, which molecules will bind positrons and roughly at what magnitude. Finally, these results highlight the paramount importance of developing accurate theoretical methods to treat electron-positron correlations, which appear to be a key factor in determining positron-molecule binding energies.

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