

## Positron binding to alcohol molecules

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## Positron binding to alcohol molecules

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**Abstract.** Results are presented for positron binding to a selection of molecules containing the hydroxyl functional group. These molecules, which span in the range of carbon atoms from 1 (methanol) to 4 (1-butanol), have moderate permanent dipole moments ranging from about 1.4 to 2.4 D. The dependence of the binding energy on the magnitude of the molecular dipole polarizability and static dipole moment is studied. An effect that appears to be due to the localization of the bound positron is discussed.

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### 1. Introduction

Positron binding is an important topic of study in various fields, ranging from medical applications, such as positron emission tomography, to astrophysics. Much work has been undertaken to better understand the binding of positrons to molecular targets. The study of

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positron interactions with biomolecules is a topic of current research (see, e.g., [1–3]), and the alcohols are an important class of these molecules. Considerable progress has also been made in understanding the observed binding energies as a function of molecular properties [4] as well as the study of annihilation spectra upon which the present work is based (e.g. [5–7]).

Alcohols are an important class of molecules, and methanol, for example, has provided important insights into the nature of resonant annihilation spectra [8]. In this work, energy-resolved annihilation spectra are presented for positron binding to ethanol, 1- and 2-propanol, 1-butanol and 1,2-ethanediol (i.e. ethylene glycol). Positron–alcohol binding energies and other features of the spectra are discussed.

Within the group of molecules studied here, there is a series of linear alcohols, also known as *n*-alcohols, in which the hydroxyl group is located at the end of the carbon chain. They can be thought of as alkane-like molecules with moderate permanent dipole moments. The binding energy  $\epsilon_b$  in alkane molecules is found to increase linearly with the molecular polarizability [4]. Given the relatively constant dipole moments found in the *n*-alcohols, one might expect similar behavior, namely a roughly linear increase in binding energy with increasing carbon chain length. This is consistent with the data presented here.

Evidence that molecular geometry has a substantial impact on the binding energy is provided by a comparison of 1- and 2-propanol (i.e. through the position of the polar OH group, located at the end of the carbon chain in 1-propanol and centrally on 2-propanol). Based on molecular parameters alone, one might anticipate comparable binding energies for these two molecules. However, a significant difference is observed. As discussed in more detail elsewhere [9], this is consistent with other lines of evidence leading to the conclusion that, in the presence of a permanent dipole moment, the bound positron wavefunction tends to be localized near that portion of the molecule. In such cases, the contribution to binding energy from the polarizability can vary with a change in dipole location and hence lead to different binding energies for molecules such as 1- and 2-propanol.

The remainder of this paper is organized as follows. In section 2, we detail the experimental apparatus and explain how the annihilation spectra are obtained. The measured spectra are presented in section 3. This includes a re-evaluation of the spectra for methanol and ethanol. Section 4 has a discussion of the results including an analysis of the measured binding energies versus molecular parameters, and section 5 presents a set of concluding remarks.

## 2. Description of the experiments

The experimental apparatus used here has been discussed in detail previously [6]. The positron source is  $^{22}\text{Na}$ , with a current activity of 12 mCi. Positrons are moderated using solid Ne and then transferred to a buffer gas trap, where they thermalize at the ambient gas temperature. A pulsed beam is extracted from the trap at a rate of 1–3 Hz, with an axial energy spread of  $\sim 20$  meV and a total energy spread of  $\sim 45$  meV. The beam is confined and guided by an axial magnetic field, which is  $\sim 800$  G in the region of measurement.

The beam is magnetically guided through a cell filled with the target gas, typically at pressures in the range 1–20  $\mu\text{torr}$ . Single 511 keV gamma-rays are detected using a CsI detector, located outside of the chamber at the axial center of the cell and surrounded by lead shielding.

The measurements presented here are normalized annihilation spectra,  $Z_{\text{eff}}$ , as a function of incident positron energy. The quantity  $Z_{\text{eff}}$  is defined as

$$Z_{\text{eff}} = \frac{\lambda}{\pi r_0^2 c n_m}, \quad (1)$$

where  $\lambda$  is the measured annihilation rate,  $r_0$  is the classical electron radius and  $n_m$  is the target gas number density.

The primary source of systematic uncertainty in the measurements is the uncertainty in the test-gas pressure, which is about 20%. Other potential sources of systematic uncertainty come from the calibration of the detector efficiency and knowledge of the magnitude of the positron pulse amplitude. However, the detector efficiency was measured using a test source of known activity for several detector positions, with the error estimated to be  $\leq 5\%$ , while the measurement of the positron pulse magnitude is calibrated before each run and is accurate to about 2%.

For each molecule studied, multiple experimental runs were performed, varying the target-gas pressure and positron pulse size in order to minimize the impact of systematic effects such as scattering and detector saturation.

Error bars shown below indicate one standard deviation of statistical error. Depending on the spectrum and energy range within the spectrum, these errors range from 5 to 40% of the measured magnitudes. The largest uncertainties occur at higher energies where the magnitude of  $Z_{\text{eff}}$  is due to direct annihilation and a recently discovered, generic form of multimode annihilation that will be discussed elsewhere [10].

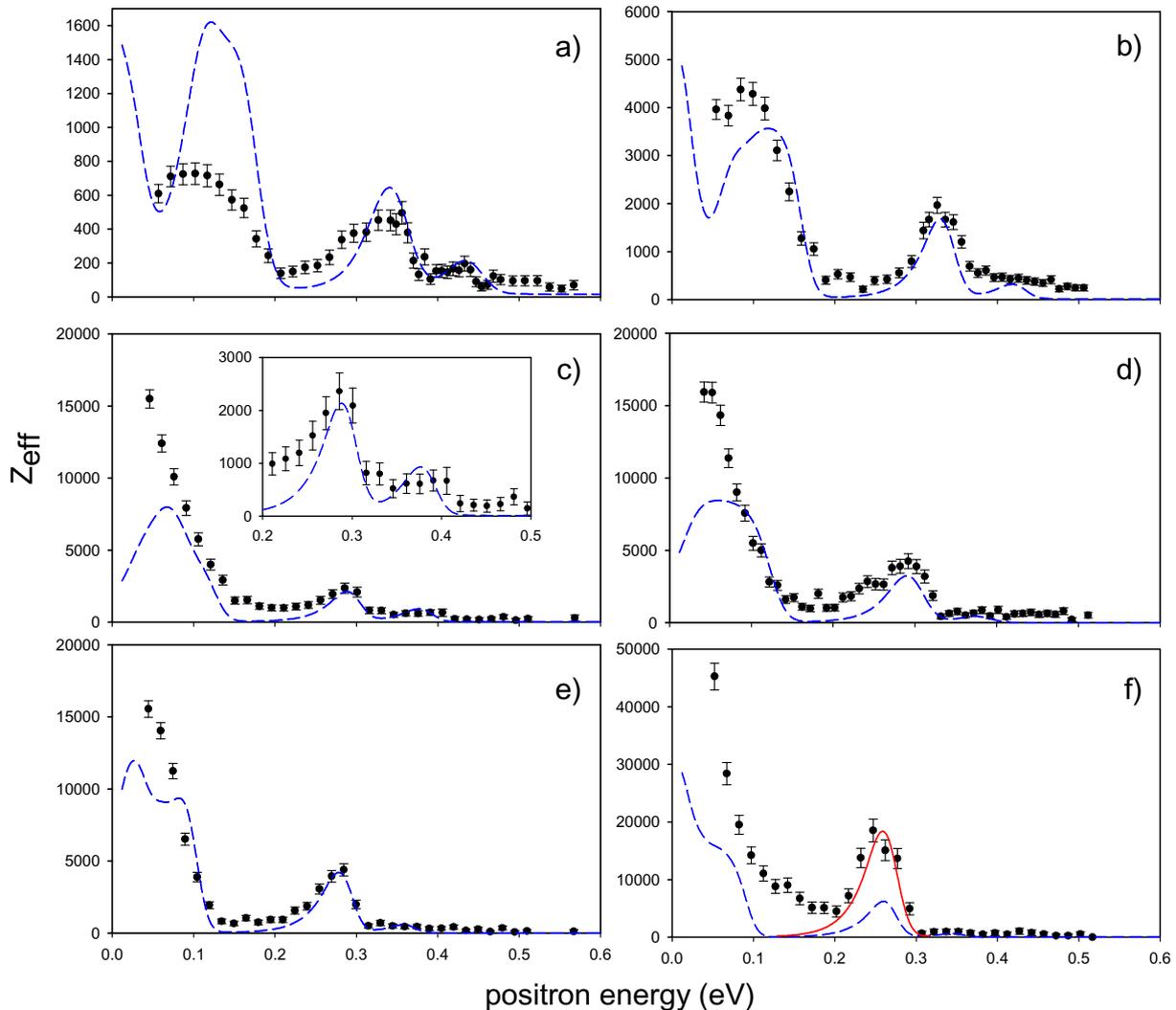
Annihilation spectra are compared with theoretical predictions for the vibrational Feshbach resonances (VFR) by Gribakin and Lee [5]. For small molecules, where there are no enhancements due to intramolecular vibrational redistribution (IVR), the VFR model has just one free parameter, the binding energy. In the data presented here, binding energies are determined from the downshifts in the position of resonances from the known vibrational modes. Vibrational mode data were typically obtained from the NIST Chemistry WebBook<sup>2</sup>. Where experimental data are not available, calculated mode positions are taken from the related CCCBDB repository, using the scaled results of the density functional theory B3LYP ultrafine, with a 6-31G\* basis set<sup>3</sup>.

### 3. Results

The experimental data for positron annihilation on methanol are presented in figure 1(a). The statistical error in the spectral amplitude is between 8 and 40% of the measured magnitudes. The spectrum is compared with the VFR model of Gribakin and Lee (GL). A previous analysis of these data used the GL theory and IR absorption data for combination and overtone modes to fit to the spectrum using  $\epsilon_b$  as an adjustable parameter. A good fit was obtained for  $\epsilon_b = 2$  meV [8]. In figure 1(a), a different approach is used. The peak positions of the observed resonances associated with the CH and OH stretch modes, at about 350 and 420 meV, respectively, are fitted, which results in a substantially larger binding energy of 20 meV. The motivation for this new approach is discussed in more detail below.

<sup>2</sup> <http://webbook.nist.gov/>

<sup>3</sup> NIST Computational Chemistry Comparison and Benchmark Database, <http://cccbdb.nist.gov/>



**Figure 1.** ●: Experimental  $Z_{\text{eff}}$  data for annihilation on alcohols: (a) methanol; (b) ethanol; (c) 1,2-ethanediol (i.e. ethylene glycol); the inset shows an expanded view of the CH and OH stretch mode resonances; (d) 1-propanol; (e) 2-propanol; (f) 1-butanol. --: VFR model; —: IVR enhanced VFR model.

The present results for ethanol are shown in figure 1(b), together with the prediction of the VFR model using a 43 meV binding energy. Statistical errors range between 5 and 30%. These data have been discussed previously [11], with a binding energy of 45 meV proposed, in close agreement with the present analysis. In figures 1(c) and (d), the experimental measurements are shown for annihilation on 1,2-ethanediol and 1-propanol, alongside the VFR predictions. The inset in figure 1(c) provides a closer look at the spectra in the region of the CH and OH stretch mode resonances. The binding energy found for both molecules is approximately 70 meV. Statistical errors typically lie in the range 5–30%.

The data for 2-propanol are presented in figure 1(e). The VFR fit yields a binding energy of approximately 87 meV. The final data set, shown in figure 1(f), is that of 1-butanol. The binding energy found is approximately 102 meV. Statistical errors again lie in the range

**Table 1.** Comparison of the binding energy with important molecular properties and the predicted binding energy, based on (2).

	$\epsilon_b$ Expt (meV)	$\alpha$ ( $10^{-24}$ cm <sup>3</sup> )	$\mu$ (D)	$\epsilon_b$ equation (meV)
Methanol	20	3.08	1.69	2.29
Ethanol	43	5.11	1.44	22.5
1,2-Ethenediol	70	5.71	2.36	48.1
1-Propanol	70	6.74	1.55	44.9
2-Propanol	87	6.97	1.58	48.3
1-Butanol	102	8.77	1.66	72.2

5–30% for both data sets. Shown in red is a fit to the CH stretch peak indicating substantial IVR enhancement [6].

#### 4. Discussion

Table 1 lists the molecular dipole polarizability,  $\alpha$ , the permanent dipole moment,  $\mu$ , and the binding energy,  $\epsilon_b$ , together with the prediction of an empirical formula for  $\epsilon_b$  developed previously (cf equation (5) of [4]), namely

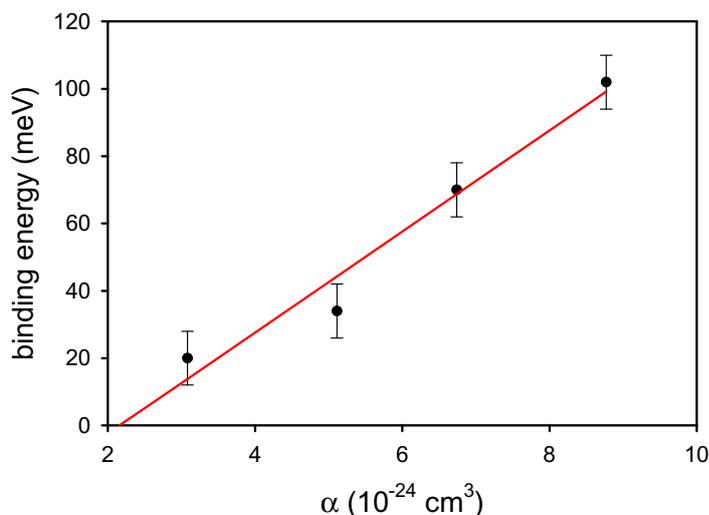
$$\epsilon_b \text{ (meV)} = 12.4 (\alpha + 1.6\mu - 5.6), \quad (2)$$

where  $\alpha$  is the dipole polarizability, expressed in units of  $10^{-24}$  cm<sup>3</sup>, and the dipole moment,  $\mu$ , is expressed in units of Debye. The uncertainties in the measured binding energies are dominated by systematic effects and are estimated to be  $\pm 8$  meV.

The present re-evaluation of the positron affinity of methanol is based on the positions of the resonances, which are better represented using a larger binding energy than assumed in the previous analysis [8]. However, a good fit then requires significant adjustment of the VFR magnitudes, namely a factor of  $\sim 0.4$  attenuation of the low-energy modes (i.e. those below 200 meV) and a more modest 0.8 reduction of the CH stretch peak.

The OH stretch peak appears to be reduced by as much as 50%, based upon the observed magnitude of the feature, which lies in what may be described as a broad spectral background, clearly visible at higher energies and between the two primary peaks of the spectrum. Recent analysis, introducing a generic multimode spectral component, requires suppression of peaks below the VFR model for molecules with small binding energies (i.e.  $\epsilon_b$  up to  $\sim 30$  meV). The larger binding energy proposed here is in better agreement with the prediction of (2). Future work is planned to re-analyze resonant annihilation spectra, including methanol and several of its deuterated analogues, with the aim of elucidating further the behavior of annihilation spectra in cases of weak binding.

In figure 2, the experimentally determined binding energies of the *n*-alcohols (i.e. methanol, ethanol, 1-propanol and 1-butanol) are plotted as a function of polarizability. A linear regression is also shown, which indicates a dependency on the polarizability about 20% stronger than that given in (2), i.e.  $\epsilon_b \approx 15\alpha - 32$ . Additionally, the  $\epsilon_b$  offset found in this analysis indicates that either the zero offset in (2) of 5.6 is instead about 5.15 in the case of the alcohols, or alternatively there is an increased dependence on the dipole moment



**Figure 2.** Experimentally determined binding energies of the linear alcohols as a function of molecular polarizability,  $\alpha$ . Also shown is the result of a linear regression.

of approximately 20% (i.e.  $1.6 \rightarrow 1.9$ ). Although the expression used to predict the binding energies has been determined using the full array of molecules studied to date and represents a more general dependency, it is instructive to see how individual families of molecules differ in their dependencies, and may provide useful insight into the dependency of binding on molecular geometry.

The comparison of 1-propanol with 2-propanol indicates a strong dependence of the binding energy on the geometry of the molecule. Based on the parametric equation employed to estimate the binding energies, the positron affinities for these two molecules are expected to differ by less than 4 meV, yet the observed binding energies differ by almost 20 meV, with both in excess of the predicted values. The underlying mechanism or mechanisms responsible for the observed difference in positron affinity is a topic of ongoing investigation.

The molecule 1,2-ethanediol is an alcohol with a moderately strong dipole moment due to an approximate alignment of the two hydroxyl groups from internal hydrogen bonding [12]. The observed binding energy is in approximate agreement with the value predicted by (2), although better agreement is found with the trend observed in the linear alcohols (i.e. see figure 2). The observed OH stretch mode, in contrast with the prediction of the VFR model, is only weakly visible in the spectra, as shown in the inset of figure 1(c). Although the magnitude of  $Z_{\text{eff}}$  in the region of the resonance is not inconsistent with the VFR predictions, the observed shape is significantly shallower.

In 1-butanol, clear signs of IVR enhancement of the CH stretch peak at 250 meV are observed, with the peak exceeding the VFR prediction by a factor of  $\sim 3$ , slightly less than half the enhancement seen in butane [13]. The process of IVR enhancement is thought to occur due to redistribution of the molecule's vibrational energy into so-called dark states, where the escape rate is greatly reduced.

There are two effects common to all the spectra presented here. One is the weak magnitude of the OH stretch feature. While this might be the result of an inelastic escape process

depopulating the resonance, it is at present unclear why this effect is much stronger for the OH stretch mode as compared with the CH stretch.

The second common effect is that, in the comparison of the VFR model, there appears to be an additional contribution to  $Z_{\text{eff}}$  that is not at present accounted for. This is most evident in the spectra of 1,2-ethanediol, 1- and 2-propanol and 1-butanol (i.e. substantial spectral weight in regions where fundamental modes are absent) at low energies, where the experimental data rise substantially above the predicted magnitudes. It is also evident at higher energies, away from the primary resonant features. We have become aware of a generic multimode process that contributes a broad component to the spectra that diminishes with increasing positron energy. This phenomenon is currently under investigation and will be discussed elsewhere [10].

## 5. Concluding remarks

We have presented  $Z_{\text{eff}}$  spectra for a selection of alcohol molecules. The behavior of the observed binding energies for linear alcohols is found to be in reasonable agreement with a previously developed parametric equation (cf (2)), although a somewhat stronger dependence on molecular dipole polarizability is observed.

An alternative analysis is presented for methanol that results in a substantially larger binding energy. In this new analysis, the VFR model produces a theoretical curve that is substantially larger than the experimental data, which then requires suppression of the observed resonances. Work is currently in progress on methanol and its deuterated analogues to better understand positron annihilation in them, as is work towards establishing a more general framework with which to understand the suppression and enhancement of resonances in the VFR model.

In the comparison of 1- and 2-propanol, molecules with comparable polarizabilities and dipole moments, we observe a substantial difference in the binding energies. This difference is attributed to the effect of the dipole moment, which appears to localize the bound positron wavefunction. Similar studies have been carried out with comparable molecules, such as propanal and acetone (i.e. which have similar geometries) and comparable effects are observed. This is discussed in more detail elsewhere [14]. More work is planned in order to further elucidate this effect.

In each of the molecules studied, there is evidence that the resonances due to the OH stretch mode are suppressed below the predicted VFR level. The expected peaks are difficult to resolve from the background annihilation, indicating diminished contributions. The origin of this effect remains to be explained. In contrast, at lower energies most of the spectral peaks rise well above the VFR predictions. While IVR enhancement might account for some of this intensity, the observed behavior is thought to result primarily from a new, generic resonant annihilation mechanism, which has been observed more clearly in studies of other molecules. To understand this new mechanism is the focus of ongoing research and will be discussed elsewhere [10].

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## References

- [1] Surdutovich E, Setzler G, Kauppila W E, Rehse S J and Stein T S 2008 Measurements of total cross sections for positron scattering by uracil molecules *Phys. Rev. A* **77** 054701
- [2] Zecca A, Chiari L, Sarkar A, Nixon K L and Brunger M J 2008 Low-energy positron scattering from methanol and ethanol: total cross sections *Phys. Rev. A* **78** 022703
- [3] Makochekanwa C *et al* 2009 Total and positronium formation cross sections for positron scattering from H<sub>2</sub>O and HCOOH *New J. Phys.* **11** 103036
- [4] Danielson J R, Young J A and Surko C M 2009 Dependence of positron–molecule binding energies on molecular properties *J. Phys. B: At. Mol. Opt. Phys.* **42** 235203
- [5] Gribakin G F and Lee C M R 2006 Positron annihilation in molecules by capture into vibrational Feshbach resonances of infrared-active modes *Phys. Rev. Lett.* **97** 193201
- [6] Gribakin G F, Young J A and Surko C M 2010 Positron–molecule interactions: resonant attachment, annihilation, and bound states *Rev. Mod. Phys.* **82** 2557–607
- [7] Danielson J R, Gosselin J J and Surko C M 2010 Dipole enhancement of positron binding to molecules *Phys. Rev. Lett.* **104** 233201
- [8] Young J A, Gribakin G F, Lee C M R and Surko C M 2008 Role of combination vibrations in resonant positron annihilation *Phys. Rev. A* **77** 060702(R)
- [9] Danielson J R, Jones A C L, Natisin M R and Surko C M 2011 Comparisons of positron and electron binding to molecules, in preparation
- [10] Jones A C L, Danielson J R, Natisin M R, Surko C M and Gribakin G F 2011 Ubiquitous nature of multimode vibrational resonances in positron-molecule annihilation, submitted
- [11] Young J A and Surko C M 2008 Feshbach-resonance-mediated positron annihilation in small molecules *Phys. Rev. A* **78** 032702
- [12] Caminati W and Corbelli G 1981 Conformation of ethylene glycol from the rotational spectra of the nontunneling O-monodeuterated species *J. Mol. Spectrosc.* **90** 572–8
- [13] Young J A and Surko C M 2008 Feshbach-resonance-mediated annihilation in positron interactions with large molecules *Phys. Rev. A* **77** 052704
- [14] Danielson J R, Jones A C L, Gosselin J J, Natisin M R and Surko C M 2011 Interplay between permanent dipole moments and polarizability in positron-molecule binding, submitted