

Analysis of experimental positron-molecule binding energies

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Abstract. Experiments show that positron annihilation on molecules frequently occurs via capture into vibrational Feshbach resonances. In these cases, the downshifts in the annihilation spectra from the vibrational mode spectra provide measures of the positron-molecule binding energies. An analysis of these binding energy data is presented in terms of the molecular dipole polarizability, the permanent dipole moment, and the number of π bonds in aromatic molecules. The results of this analysis are in reasonably good agreement with other information about positron-molecule bound states. Predictions for other targets and promising candidate molecules for further investigation are discussed.

1. Introduction

While positrons are of use in many areas of science and technology, a quantitative understanding of their behaviour in many physical situations is lacking [1, 2, 3]. One example is the binding of positrons to ordinary matter (e.g., atoms and molecules). There are calculations that are believed to be quite accurate for the binding of positrons to atoms, however there are as yet no experimental measurements of positron-atom binding energies [4, 5, 6]. The situation is essentially the reverse in the case of positron binding to molecules. Binding energies have now been measured for thirty molecules [7, 8], but few calculations are available and those that have been done are generally for molecules with large permanent dipole moments.

Here, we conduct an analysis to express the positron-molecule binding energy, ϵ_b , in terms of physical properties of the molecule including the dipole polarizability, the permanent dipole moment, and the number of π bonds in aromatic molecules. The predictions of this analysis are tested with other available data. They are also used to make a number of predictions, including the identification of molecules with unusually large binding energies and interesting chemical trends and candidates for further study.

2. Measurements of positron-molecule binding energies

Annihilation rates on atoms and molecules are usually expressed as a normalized rate, Z_{eff} , which is the measured annihilation rate, λ , normalized to that of a free electron gas [9], specifically

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

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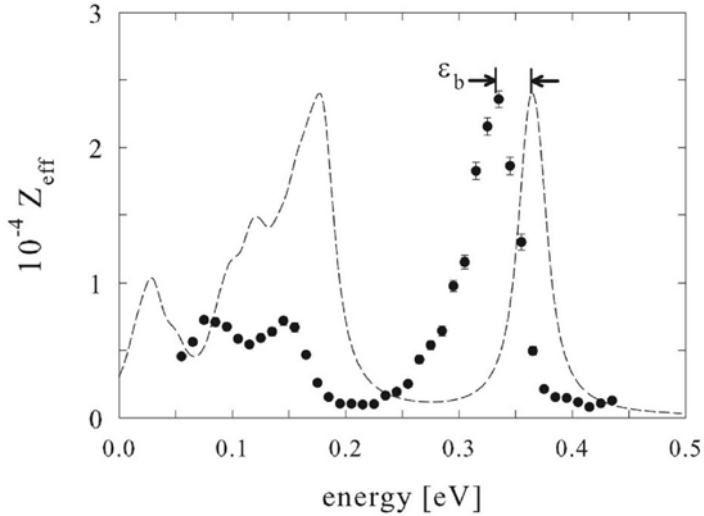


Figure 1. The normalized annihilation spectrum, $Z_{\text{eff}}(\epsilon)$, for butane (C_4H_{10}) is shown as a function of incident positron energy. Also shown (- -) is the spectrum of vibrational modes, in arbitrary amplitude units, with each mode arbitrarily broadened in energy by 10 meV FWHM. The shift of ~ 35 meV between the two spectra is a measure of the positron-binding energy, ϵ_b .

where r_0 is the classical electron radius, c is the speed of light, and n_m is the number density of the target atoms or molecules. In this representation, the value $Z_{\text{eff}} = Z$, where Z is the number of electrons in the target, corresponds to annihilation in an uncorrelated electron gas with electron density $n_m Z$.

High-quality, trap-based positron beams have enabled measurements of $Z_{\text{eff}}(\epsilon)$ as a function of the incident positron energy, ϵ [10]. The techniques used for these measurements are described, for example, in Refs. [7, 8]. They use a tuneable, cold positron beam magnetically guided through a gas cell. The result is an asymmetric distribution in total positron energy with a width ~ 40 meV FWHM [7, 11]. An example of such a measurement is shown in Fig. 1. It is typical of the spectra for many molecules in that $Z_{\text{eff}}(\epsilon)$ shows evidence of vibrational Feshbach resonances (VFR). In this resonant annihilation process, the incident positron excites a molecular vibration and makes a transition from the continuum into a positron-molecule attached state [10, 12]. This process *requires* the existence of a positron bound state on the molecule. The observed energy of the resonance, ϵ_{res} , is determined by energy conservation, namely

$$\epsilon_{\text{res}} + \epsilon_b = \epsilon_\nu, \quad (2)$$

where ϵ_ν is the energy of the molecular vibration. Hence the downshift, $\Delta\epsilon$, of the resonance with respect to ϵ_ν is a direct measure of the binding energy [11]. The attached state is a resonance and not a true bound state in that the vibrational energy in the molecule can subsequently eject the positron.

Studies of resonances from different vibrational modes and from deuterated hydrocarbons indicate that the presence of the positron does not alter the vibrational mode energy [7]. Thus the binding energies measured using this technique are valid measures of the binding energy for the ground-state molecule.

The measurements of ϵ_b obtained from $Z_{\text{eff}}(\epsilon)$ spectra for smaller molecules are taken from Ref. [8] and for larger molecules from Ref. [7]. The absolute accuracies of the binding energy measurements for those in which the shifts were resolved directly are typically $\sim 10 - 15$ meV. A summary of data for molecules used in the analysis presented here are shown in Table I, together with the molecular parameters relevant to the analysis.

3. Fit to molecular parameters

The goal of the present analysis is to find a simple parameterization of the binding energy in terms of molecular properties. Two effects that can give rise to binding include the dipole

Table 1. The values of binding energy, ϵ_b [meV], are tabulated for all molecules where ϵ_b has been measured [7, 8], along with the predictions of Eq. (3). Also listed are the number of electrons, Z , on the molecule; dipole polarizability, α [\AA^3] [13, 14]; permanent dipole moment μ [D] [13, 15]; and the ionization energy, E_i [eV] [13]. Values in parentheses are lower bounds for molecules that lack known values for μ .

Molecule Name	Formula	ϵ_b [meV]	Eq. (3) [meV]	Z	α [\AA^3]	μ [D]	E_i [eV]
Alkanes							
Ethane	C_2H_6	≥ 0	-14	18	4.4	0	11.5
Propane	C_3H_8	10	10	26	6.3	0.1	11.1
Butane	C_4H_{10}	35	31	34	8.1	0	10.6
Pentane	C_5H_{12}	60	54	42	10.0	0	10.4
Hexane	C_6H_{14}	80	77	50	11.8	0	10.2
Heptane	C_7H_{16}	105	100	58	13.7	0	9.9
Octane	C_8H_{18}	115	123	66	15.5	0	10.0
Nonane	C_9H_{20}	145	146	74	17.4	0	10.0
Dodecane	$\text{C}_{12}\text{H}_{26}$	220	214	98	22.9	0	9.9
Tetradecane	$\text{C}_{14}\text{H}_{30}$	260	261	114	26.6	0	—
Hexadecane	$\text{C}_{16}\text{H}_{34}$	310	306	130	30.3	0	9.9
Deuterated alkanes							
Butane-d10	C_4D_{10}	35	31	34	8.1	0	—
Nonane-d20	C_9D_{20}	145	146	74	17.4	0	—
Alkane related molecules							
Acetylene	C_2H_2	≥ 0	-28	14	3.3	0	11.4
Ethylene	C_2H_4	20	-17	16	4.2	0	10.5
Isopentane	C_5H_{12}	60	57	42	10.0	0.1	10.3
Cyclopropane	C_3H_6	10	1	24	5.7	0	9.9
Cyclohexane	C_6H_{12}	80	68	48	11.1	0	9.9
Aromatics [N_π term included in Eq. (5)]							
Benzene	C_6H_6	150	149	42	10.4	0	9.3
Benzene-d6	C_6D_6	150	149	42	10.4	0	9.3
Naphthalene	C_{10}H_8	300	296	68	16.6	0	8.2
Alcohols							
Methanol	CH_3OH	2	5	18	3.3	1.7	10.9
Ethanol	$\text{C}_2\text{H}_5\text{OH}$	45	27	26	5.1	1.7	10.5
Partially halogenated hydrocarbons							
Methyl fluoride	CH_3F	≥ 0	-3	18	2.4	1.85	12.9
Methyl chloride	CH_3Cl	25	23	26	4.4	1.9	11.2
Methyl bromide	CH_3Br	40	35	44	5.6	1.8	10.5
1-fluoropropane	$\text{C}_3\text{H}_7\text{F}$	35	45	34	6.0	2.0	11.3
2,2-difluoropropane	$\text{C}_3\text{H}_6\text{F}_2$	25	51	42	5.9	2.4	11.4
1-fluorobutane	$\text{C}_4\text{H}_9\text{F}$	70	(27)	42	7.8	—	—
1-fluorohexane	$\text{C}_6\text{H}_{13}\text{F}$	80	(73)	58	11.5	—	—
1-fluorononane	$\text{C}_9\text{H}_{19}\text{F}$	145	(141)	82	17.0	—	—
1-chlorohexane	$\text{C}_6\text{H}_{13}\text{Cl}$	175	138	66	13.6	2.0	10.3

polarizability and the permanent dipole moment of the molecule. It turns out that this will leave an unexplained deficit in binding energy for aromatic molecules, and so an additional parameter, the number of molecular π bonds in aromatic molecules, is also included.

We have made extensive studies of alkane molecules ($\text{C}_n\text{H}_{2n+2}$). They represent a case in which the molecules do not have either a permanent dipole moment or π bonds. Further, the molecular size (and hence polarizability) of these molecules can be varied without changing the chemical structure. Thus we fix the dependence upon the molecular polarizability by fitting to these molecules. As shown in Fig. 2, the alkane binding energies are, to good accuracy, linear in the molecular polarizability, α . To accommodate molecules with permanent dipole moments,

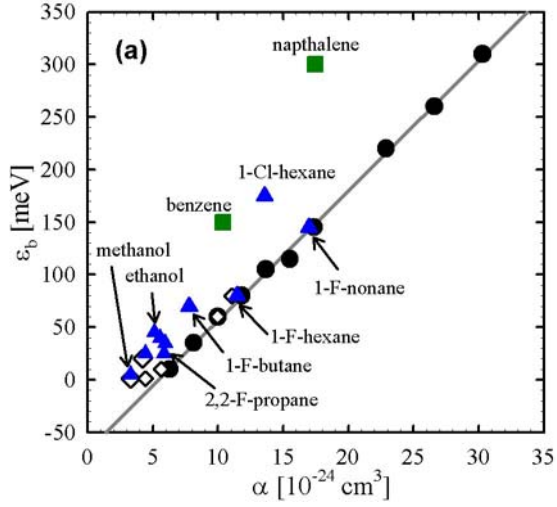


Figure 2. Measured positron binding energies, ϵ_b , as a function of the molecular dipole polarizability, α . Alkane molecules used in fit (\bullet); alkane related molecules (\diamond); molecules with permanent dipole moments (\blacktriangle); and aromatics with π bonds (\blacksquare).

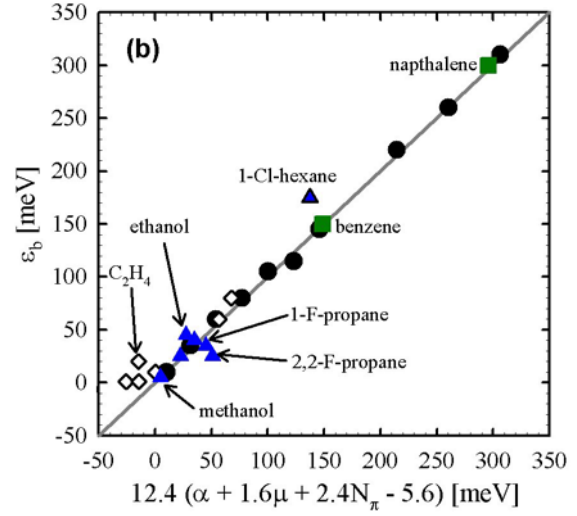


Figure 3. Binding energy fit as described by Eq. (3), using the polarizability α , permanent dipole moment, μ , and the number of π bonds, N_π , for aromatic molecules.

an additive term linear in μ is included to model its effect on ϵ_b . In this paper, α is expressed in units of 10^{-24} cm^{-3} , and the permanent dipole moment, μ , is expressed in units of debye (D).

As mentioned above, the fit to α and μ leaves a significant discrepancy for the two aromatic molecules in the data set, benzene and naphthalene. We speculate that double bonds involving π orbitals can attract the positron more strongly, since the electron density in these bonds is farther from the (repulsive) cores of the carbon atoms. For these aromatics, the number of π bonds, N_π , turns out to be a convenient parameter ($N_\pi = 3$ for benzene and 5 for naphthalene).

The fit to alpha for alkanes was augmented by terms linear in μ , and N_π (i.e., the latter for the two aromatic molecules only) while the coefficients for the slope and offset from the alkane fit are held constant. The result is

$$\epsilon_b = 12.4(\alpha + 1.6\mu + 2.4N_\pi - 5.6) \text{ [meV]}. \quad (3)$$

This fit to the binding energy data is shown in Fig. 3, with the numerical values given in Table I. As indicated in Fig. 3 and Table I, the binding energies for most molecules are in reasonably good agreement with the predictions of Eq. (3). The most notable exceptions are 2,2 difluoropropane, ethylene and 1-chlorohexane.

4. Discussion

A number of checks on the model can be made. For example, studies of a number of small molecules indicate the absence of VFR and this is interpreted as evidence that these molecules do not bind positrons. Generally, Eq. (3) predicts that this is the case. For example, H_2 , O_2 , CO , NO , CO_2 , CH_4 and CF_4 do not exhibit VFR. They are predicted to have $\epsilon_b < -30 \text{ meV}$, which is consistent with the model. As can be seen in Table I, disagreements include acetylene and ethylene.

Calculations for binding to molecules have been conducted for several molecules, all of which have appreciable dipole moments. The predictions from these theoretical calculations are listed

Table 2. Comparisons of theoretical predictions for positron-molecule binding energies with those from Eq. (3).

Name	Formula	α [\AA^3]	μ [D]	ϵ_b , Eq. (3) [meV]	ϵ_b , th [meV]
Cyanide	HCN	2.5	3.0	21	35 ^a
Formaldehyde	H ₂ CO	2.8	2.3	11	18 ^b
Urea	(NH ₂) ₂ CO	9.7	4.6	140	13 ^c
Acetone	(CH ₃) ₂ CO	6.4	1.6	42	4 ^c
Lith. hydride	LiH	3.8	5.9	95	1000 ^d

^aRef. [17]. ^bRef. [16]. ^cRef. [18]. ^dRefs. [19, 20, 21, 22].

in Table II, and they are also in reasonable agreement with those from Eq. (3). Cyanide and formaldehyde agree to within a factor of two. While the theoretical values for urea and acetone are about an order of magnitude smaller than those from Eq. (3), it is believed that these calculations likely underestimate ϵ_b [16], in agreement with the present comparison.

The predictions of Eq. (3) can also be compared with electron-molecule attached states (i.e., negative ions). There are two classes of negative molecular ions. When the molecule has an open valence shell, the electron forms a strong bond with the molecule, and this typically results in electron-volt binding energies; these states have no positron analogue. If, on the other hand, the valence shell is closed, the electron can be weakly bound to the molecule due to the forces associated with the dipole polarizability and/or the permanent dipole moment of the molecule. These latter states approximate closely the positron-attached states described here. In fact, (spherical) atomic clusters of CO₂ have been shown to exhibit VFR, and the spectra of the resulting negative ions that are formed as a function of incident electron energy have been used to measure the electron binding energies [23]. This is very similar to the procedure for the positron-molecule VFR measurements described here. Further, the binding energy is also found to be an approximately linear function of atomic polarizability, consistent with Eq. (3), namely $\epsilon_b \approx 4.0(\alpha - 7.5)$ [meV]. It is interesting that the coefficient of proportionality $\Delta\epsilon_b/\Delta\alpha$ is a factor of three smaller in the case of electrons. This appears to be an important clue that the linear dependence of ϵ_b reflects more than simply long-range electrostatic coupling (i.e., which would be the same for electrons and positrons). In the positron case, it is possible that the (closed) positronium channel plays a role in enhancing the binding of the positron to the target.

Another point of comparison between electron- and positron-attached states is the case of molecules with permanent dipole moments. Again, in the case of molecules with closed valence shells, a permanent dipole moment on a molecule is found to produce a weakly bound negative ion. Examples of such negative ion states include acetone ($\mu = 2.9$; $\epsilon_b = 1.5$ meV) and acetonitrile ($\mu = 3.9$; $\epsilon_b = 11.5$ meV) [24]. Theoretically, a permanent moment of 1.625 D will bind an electron or positron [25]. Experimentally, to bind an electron with greater than 1 meV binding energy requires a moment in excess of ~ 2.5 D [24]. This experimental result is in reasonable agreement with the critical value for positrons of 3.5 D obtained from Eq. (3).

Equation (3) can also be used to make a number of interesting predictions. Large targets typically have large dipole polarizabilities and hence they will generically tend to bind positrons. Examples include the larger fluoroalkanes such as fluorohexane ($\alpha = 12.4$ cm⁻³, $\epsilon_b = 84$) and C₆₀ ($\alpha = 76$ cm⁻³, $\epsilon_b = 880$). In this regard, if ϵ_b is greater than the most energetic fundamental mode frequency, then the primary VFR will be shut off. This has been observed for the case of fully deuterated naphthelene [7]. The cluster C₆₀ is also expected to be such a case.

5. Concluding remarks

We describe here an empirical parameterization of positron-molecule binding energies in terms of molecular parameters. It indicates that the dominant contributions come from the molecular

dipole polarizability and permanent dipole moment, augmented by an additional term for aromatic molecules. In large molecules, the first and last terms dominate. The positron-molecule complexes discussed here have close analogues of a certain class of weakly bound electron-molecule attached states (i.e., molecules with closed valence shells). One interesting feature of this comparison is the fact that the polarizability term appears to be much stronger in the positron case.

The parameterization in Eq. (3) is expected to be useful in identifying targets for future study. One important example is small molecules that appear to have appreciable binding energies and can both be studied experimentally and calculated using currently available theoretical tools. Other interesting targets include large perfluoroalkanes, larger polycyclic aromatic molecules such as anthracene and pyrene, and atomic clusters such as C_{60} . A more detailed description of this analysis and its implications, including the relationship between the predictions of Eq. (3) and the extensive body of data for molecular annihilation rates using thermal positrons at 300 K, will be published elsewhere [26].

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