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Dependence of positron–molecule binding energies on molecular properties

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Abstract

Positron annihilation on many molecular species occurs via capture into vibrational Feshbach resonances. The study of the downshifts in the energy of these resonances from the vibrational modes in the molecule using a tunable, high-resolution positron beam provides a measure of the positron–molecule binding energy. Regression analysis on data for 30 molecules is used to identify the molecular properties that affect these binding energies. One parameterization that fits the data well involves a linear combination of the molecular dipole polarizability, the permanent dipole moment and the number of π bonds in aromatic molecules. The predictions of this empirical model are compared with those from positron–molecule binding energy calculations. They are also tested in cases where other experimental evidence indicates that molecules do and do not bind positrons. Promising candidate molecules for further experimental and theoretical investigation are discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

While positrons are of scientific and technological use in many areas including astrophysics, materials science, medicine and fundamental physics, the understanding of a number of basic processes involving positrons is lacking [1–4]. The focus of this paper is the binding of positrons to 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 [5–7]. The situation is essentially the reverse in the case of positron binding to molecules. Binding energies have now been measured for 30 molecules [8, 9]. While there is a simple model for alkanes that describes qualitatively the observed increase in binding energies with molecular size, it stops short of predicting their binding energies [10]. There are also a number of quantum-chemistry calculations that predict positron binding to strongly polar molecules such as alkali halides, MgO and HCN [11–16]; however, these molecules are difficult to study experimentally.

This paper describes an analysis that attempts to bridge the gap between theory and experiment for positron–molecule binding energies. A regression analysis is performed 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. This analysis is done with several objectives in mind. One is to identify the molecular properties that are most important in determining ϵ_b. A second objective is to identify molecules that are promising candidates for further experimental and theoretical study. In this regard, one would like to study theoretically molecules with few atoms and relatively simple electronic structure. From the point of view of experiment, one would like to have candidate molecules such that modest density vapours of these species can be created at not too high an ambient temperature. For the benefit of both theoretical and experimental investigations, one would also like to have targets with relatively large binding energies so that they can be determined with high accuracy.

The predictions of the empirical model described here are also related to an extensive body of data for the positron annihilation rates of thermalized positrons interacting with polyatomic gases at 300 K. For most of these species, the binding energies have not been measured (i.e. using a tunable, monoenergetic positron beam). Nevertheless, the magnitudes of the measured thermal annihilation rates are a good indicator of positron binding or lack thereof, in that large annihilation

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rates are associated with positron–molecule attachment [8, 17–19]. The parameterization of ϵ_b developed in this paper is used to predict the binding energies for the species in this data set, and then these predictions are compared with the observed enhancements in annihilation rates (or lack of them).

Other interesting results from this analysis include the identification of chemical trends and predictions of unusually large binding energies. The results described here may also be useful in understanding the interaction of positrons with surfaces and bulk materials as investigated, for example, using techniques such as positron emission tomography (PET), angular correlation of annihilation radiation (ACAR) and positron lifetime spectroscopy (PALS). In a broader sense, the phenomenological model described here can be regarded as a potentially important ingredient in the formulation of a complete and quantitative chemistry of matter and antimatter (i.e. positrons).

2. Measurements of annihilation rates and positron–molecule binding energies

In discussing the annihilation of positrons on atoms or molecules, it is customary to define a normalized rate, Z_eff, which is the measured annihilation rate, λ, normalized to that of a free electron gas [20], specifically

$$Z_\mathrm{eff} = \frac{\lambda}{\pi r_0^2 c n_\mathrm{m}}, \tag{1}$$

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. Thus, the benchmark value, $Z_\mathrm{eff} = Z$, where Z is the number of electrons in the target, corresponds to annihilation in an uncorrelated electron gas with electron density $n_\mathrm{m}Z$.

Positron annihilation rates for molecules have been studied using two techniques. One is to measure Z_eff (denoted here as $Z_\mathrm{eff}^\mathrm{th}$) for test species, with typical number densities $n_\mathrm{m} \sim 1$ amagat [21, 22], using a thermal (Maxwellian) distribution of positrons that is typically at 300 K. Measurements of $Z_\mathrm{eff}^\mathrm{th}$ have also been made at much lower densities (e.g. $< 10^{-7}$ amagat) in the presence of gases of thermal positrons confined in a Penning–Malmberg trap [23–25]. Using this latter method, a wider range of chemical species could be studied, including those with low vapour pressures at 300 K.

The advent of high-quality, trap-based positron beams enabled experiments that measure the entire $Z_\mathrm{eff}(\epsilon)$ spectrum, resolved as a function of the incident positron energy, ϵ [26]. These experiments provided more microscopic information about the annihilation process, including elucidating the role of molecular vibrations in producing large annihilation rates. Details of the techniques used for these measurements are described in [8, 9] and references therein. These experiments use a tunable, 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 [8, 19].

The energy-resolved annihilation measurements show that the $Z_\mathrm{eff}(\epsilon)$ spectra for many molecular species exhibit vibrational Feshbach resonances (VFR). In this process of resonant annihilation, the incident positron excites a molecular vibration and makes a transition from the continuum into a positron–molecule bound state [26, 27]. This process, in fact, *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 $\epsilon_\mathrm{res} + \epsilon_\mathrm{b} = \epsilon_\nu$, 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 [19]:

$$\Delta\epsilon = \epsilon_\nu - \epsilon_\mathrm{res} \equiv \epsilon_\mathrm{b}. \tag{2}$$

The resulting complex formed in this two-body process is a resonance and not a true bound state in that the vibrational energy in the molecule can subsequently eject the positron. Estimates for molecular gases indicate that these resonances can last as long as ~ 1 ns before annihilation occurs [17, 18]. The shift of the VFR from the energy of the vibrational mode that produced it is found to be independent of the mode energy. Thus, the binding energies measured using this technique are independent of the vibrational energy added by positron capture, and hence they are also valid measures of the binding energy for the ground-state molecule.

For a wide variety of molecules, the magnitude of this C–H stretch peak in Z_eff is found to depend predominantly on the number of atoms, N, in the molecule [28, 8], namely

$$Z_\mathrm{eff} = 2.3(\epsilon_\mathrm{b}/\epsilon_\mathrm{res})^{1/2} N^{4.1}. \tag{3}$$

Here, the dependence on N is interpreted as reflecting the dependence of Z_eff on the number of vibrational degrees of freedom of the molecule. Thus, the magnitude of Z_eff in species that exhibit VFR is largely independent of details of the chemical structure and depends only weakly on ϵ_b and ϵ_res.

Theory indicates that the intrinsic energy spreads, $\delta\epsilon$, of the resonances are much narrower than that of the positron beam (e.g. $\delta\epsilon \lesssim 1$ meV) [19, 29]. As a consequence, the measured widths are completely dominated by the energy spread of the positron beam. Thus, while the measurements are absolute and the integral over the resonances is determined by the energy-resolved measurements, the true heights of the peaks are not.

The absolute accuracies of the binding energy measurements vary. For binding energies $\geqslant 20$ meV, ϵ_b was determined using $Z_\mathrm{eff}(\epsilon)$ and equation (2). In this case the estimated error in peak positions is $\sim$ 10–15 meV. For small molecules, with smaller apparent binding energies, ϵ_b can be determined by fitting to theoretical expressions for $Z_\mathrm{eff}(\epsilon)$ [9, 19, 30].

A summary of data for molecules used in the analysis presented here is shown in table 1. Measurements of ϵ_b obtained from $Z_\mathrm{eff}(\epsilon)$ spectra for smaller molecules are taken from [9] and for larger molecules from [8]. Also included in table 1 are the molecular parameters relevant to the analysis taken from the literature [31–33].

3. Relationship of binding energies with molecular properties

The goal of the analysis presented here is to find a robust parameterization of ϵ_b in terms of selected molecular

Table 1. The values of binding energy, ϵ_b (meV), are tabulated for all molecules where ϵ_b has been measured [8, 9], and they are compared with the predictions of equation (5). Also listed are the number of electrons, Z, on the molecule; thermal annihilation rates, $Z_{\text{eff}}^{\text{th}}$, normalized rates, $Z_{\text{eff}}^{\text{th}}/Z$ [24, 25]; dipole polarizability, α (Å^3) [31, 32]; permanent dipole moment μ (D) [31, 33] and the ionization energy, E_i (eV) [31]. Values in parentheses are lower bounds for molecules that lack known values for μ.

Molecule name	Formula	ϵ_b (meV)	Equation (5) (meV)	Z	$Z_{\text{eff}}^{\text{th}}$	$Z_{\text{eff}}^{\text{th}}/Z$	α (Å^3)	μ (D)	E_i (eV)
Alkanes									
Ethane	C_2H_6	$\geqslant 0$	−14	18	660	37	4.4	0	11.5
Propane	C_3H_8	10	10	26	3,500	135	6.3	0.1	11.1
Butane	C_4H_{10}	35	31	34	11 300	330	8.1	0	10.6
Pentane	C_5H_{12}	60	54	42	37 800	900	10.0	0	10.4
Hexane	C_6H_{14}	80	77	50	120 000	2,400	11.8	0	10.2
Heptane	C_7H_{16}	105	100	58	242 000	4,200	13.7	0	9.9
Octane	C_8H_{18}	115	123	66	585 000	8,800	15.5	0	10.0
Nonane	C_9H_{20}	145	146	74	643 000	8,700	17.4	0	10.0
Dodecane	$C_{12}H_{26}$	220	214	98	1,780 000	18 000	22.9	0	9.9
Tetradecane	$C_{14}H_{30}$	260	261	114	–	–	26.6	0	–
Hexadecane	$C_{16}H_{34}$	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	1,930 000	8,700	17.4	0	–
Alkane related molecules									
Acetylene	C_2H_2	$\geqslant 0$	−28	14	3,160	230	3.3	0	11.4
Ethylene	C_2H_4	20	−17	16	1,200	75	4.2	0	10.5
Isopentane	C_5H_{12}	60	57	42	50 500	1,200	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	20 000	420	11.1	0	9.9
Aromatics (N_π term included in equation (5))									
Benzene	C_6H_6	150	149	42	15 000	360	10.4	0	9.3
Benzene-d6	C_6D_6	150	149	42	30 500	730	10.4	0	9.3
Naphthalene	$C_{10}H_8$	300	296	68	494 000	7,300	16.6	0	8.2
Alcohols									
Methanol	CH_3OH	2	5	18	1,510	84	3.3	1.7	10.9
Ethanol	C_2H_5OH	45	27	26	–	–	5.1	1.7	10.5
Partially halogenated hydrocarbons									
Methyl fluor.	CH_3F	$\geqslant 0$	−3	18	1,390	77	2.4	1.85	12.9
Methyl chlor.	CH_3Cl	25	23	26	15 000	580	4.4	1.9	11.2
Methyl brom.	CH_3Br	40	35	44	–	–	5.6	1.8	10.5
1-fl.propane	C_3H_7F	35	45	34	–	–	6.0	2.0	11.3
2,2-difl.prop.	$C_3H_6F_2$	25	51	42	8,130	190	5.9	2.4	11.4
1-fl.butane	C_4H_9F	70	(27)	42	–	–	7.8	–	–
1-fl.hexane	$C_6H_{13}F$	80	(73)	58	269 000	46 000	11.5	–	–
1-fl.nonane	$C_9H_{19}F$	145	(141)	82	–	–	17.0	–	–
1-chl.hexane	$C_6H_{13}Cl$	175	138	66	–	–	13.6	2.0	10.3

parameters. Regarding the choice of parameters to include in the analysis, it is well known that the molecular dipole polarizability, α, can provide an attractive potential to bind positrons. For example, calculations of positron binding to *atoms* for $E_i > 6.8$ eV (i.e. the case relevant here in which the positronium-formation channel is closed) indicate an unambiguous increase in ϵ_b with increasing atomic dipole polarizability [5]. Shown in figure 1 are measured positron–molecule binding energies for a variety of molecules as a function of α. Also shown are the predicted binding energies for three atoms from [5]. Here and elsewhere in this paper, α is expressed in units of Å^3. As shown in figure 1, there is a trend in the data for molecules such that increasing polarizability leads to increased binding energy, albeit with considerable scatter.

Alkane molecules (C_nH_{2n+2}), for which the molecular size (and hence polarizability) can be varied without changing the chemical structure, are a logical choice to begin the analysis. As shown in figure 1, the alkane binding energies are, to good accuracy, linear in the molecular polarizability, α. A linear fit to the alkane data, shown as the solid line in figure 1, is given by

$$\epsilon_b = 12.4(\alpha - 5.6) \quad (\text{meV}). \tag{4}$$

Note that, in figure 1, almost all molecules that do not lie on or near the alkane-fit line, lie above it, indicating that the fit to α alone underestimates the binding. In particular, molecules with non-zero values of permanent dipole moment, μ, lie above the curve; this is most apparent for the molecules with relatively small values of ϵ_b. Also the fit significantly underestimates ϵ_b for the two aromatic molecules in the data set, benzene and naphthalene.

It is known that a sufficiently large static point dipole moment, μ, can bind positrons [34, 35]. Furthermore, the potential role of a permanent dipole moment in binding positrons to molecules such as alkali hydrides has been

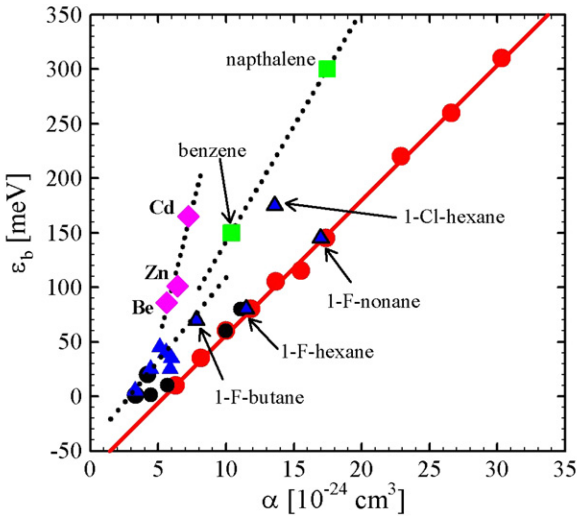

Figure 1. Measured positron binding energies, ϵ_b, as a function of molecular dipole polarizability, α. Alkane molecules used in fit (circles); alkane related molecules (dark circles); molecules with permanent dipole moments (triangles); and aromatics with π bonds (squares). The solid line is a best fit to the alkane data (cf equation (4)). The dotted lines are guides to show the linearity of ϵ_b to α for the different series. Also, shown for comparison are binding energies calculated for several metal atoms (pink diamond) [5].

discussed in some detail [36]. Thus, to accommodate molecules with permanent dipole moments, an additive term linear in μ is included to model its effect on ϵ_b. In this paper, the permanent dipole moment, μ, is expressed in units of debye (D). In fitting μ, the datum for 1-chlorohexane was excluded. Including it in the fit for μ significantly distorts the fit to the other data while not improving very significantly the agreement for 1-chlorohexane.

It turns out that this fit to α and μ leaves a significant, remaining discrepancy for the two aromatic molecules in the data set, benzene and naphthalene. While there appears to be no particularly obvious choice of a parameter to remedy this deficiency, one might 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. This could be expected to be particularly important in these aromatic molecules where the electron density in π orbitals lies roughly in the planes above and below the plane carbon ring. For the aromatics, the number of π bonds, N_π, turns out to be a convenient parameter ($N_\pi = 3$ for benzene and 5 for naphthalene). We note that including the number of π bonds bears some similarity to the approach used by Miller who predicted the molecular polarizability, α, for molecules in terms of the characteristics of individual molecular bonds [32].

With these considerations, the fit described in equation (4) was augmented by terms linear in μ, and N_π (i.e. the latter for the two aromatic molecules only), with the constraint that the coefficients for the slope and offset in equation (4) were held constant. The result is

$$\epsilon_b = 12.4(\alpha + 1.6\mu + 2.4N_\pi - 5.6) \quad (\text{meV}), \tag{5}$$

where ϵ_b is in meV. This fit to the binding energy data is shown in figure 2, with the numerical values given in table 1. Generally, the agreement between the predictions of equation (5) and the measurements is quite good. The most significant discrepancies are 1-chlorohexane, acetylene (C_2H_2), ethylene (C_2H_4) and 2,2-difluoropropane. For all but 2,2-difluoropropane, equation (5) underestimates the binding energy, which may indicate that a relatively small attractive mechanism or higher order parameter is still missing. With the exception of 1-chlorohexane, the outliers are molecules containing double and triple bonds. However, if the N_π term in equation (5) is included for these molecules, the result overestimates ϵ_b. Thus, a similar mechanism may well be operating for these species as for the aromatics, but to a lesser extent.

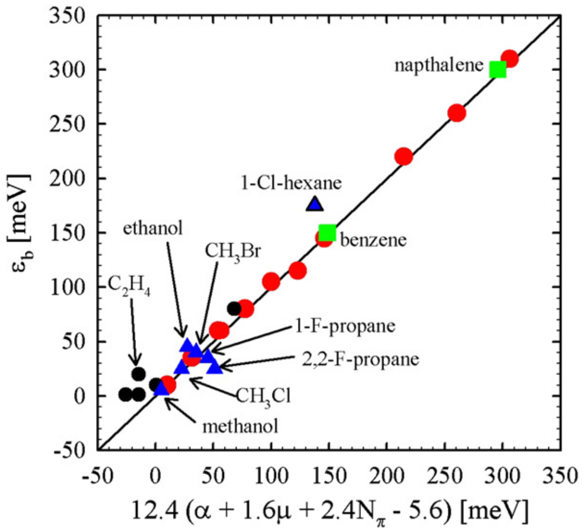

Figure 2. Binding energy fit as described by equation (5), using the polarizability α, permanent dipole moment, μ, and the number of π bonds, N_π, for aromatic molecules. Symbol notation is as in figure 1.

For completeness, we note that we have found other parameterizations of the data that work about as well as equation (5). One involves including an additional multiplicative factor of E_i instead of the additive N_π term to describe ϵ_b for aromatics. However, α already has a strong dependence on E_i and so this fit is more difficult to interpret and was not pursued further.

Thus, in the following, *we focus on the implications of equation* (5), which represents an empirical fit to the existing data, and its relationship with other available information about positron–molecule binding. While equation (5) can be regarded as a lowest order Taylor expansion in terms of physical parameters that are expected to aid in producing binding (i.e. dipole polarizability, the permanent dipole moment, and N_π), there is at present no obvious reason why such a linear expansion should be valid, particularly over such a large range of α and μ. We note, however, that there is at least one analogous case in VFR-mediated electron attachment, namely the attachment to (spherical) CO_2 clusters [37]. In this case, the observed binding energies also have an approximately linear dependence upon polarizability, namely $\epsilon_b \approx 4.0\ (\alpha - 7.5)$ (meV).

According to equation (5), binding is assured if $\alpha > 5.6\,\text{Å}^3$. This can be compared with that identified for binding to a polarizable atom, namely $\alpha > 3.5\,\text{Å}^3$ [5]. As shown in figure 1, the dependence of ϵ_b on α (i.e. as parameterized by the slope, $\Delta\epsilon_b/\Delta\alpha$) is approximately a factor of 3 larger for atoms as compared to alkane molecules. Given that equation (5) relates to more extended targets (i.e. molecules, and not atoms), the increased binding thresholds and the weaker dependence on α in the case of molecules is not unreasonable. For molecules with similar chemical composition, α increases with molecular size. However, the linear increase of ϵ_b with α predicted by equation (5) is expected to saturate at some point (e.g. when the positron de Broglie wavelength becomes smaller than the size of the molecule).

As another point of comparison, equation (5) is in complete agreement with the fact that binding energies for fully deuterated hydrocarbons are close to their hydrogenated analogues (cf table 1, deuterated butane, benzene and nonane), and that isomers also have similar values of ϵ_b (cf pentane and isopentane).

Equation (5) indicates that binding is assured if $\mu > 3.6$ D. The criterion for binding to a static, point dipole is $\mu \geqslant 1.625$ D [34, 35]. However, studies of electron–molecule binding indicate that, for binding energies of millielectron volts or greater, $\mu \gtrsim 2.5$ D [38]. Given the differences between electron and positron interactions with molecules, these values are reasonably consistent.

4. Relationship of binding energies with annihilation rates for thermalized positrons

There is also an extensive set of annihilation-rate measurements taken with thermal positrons at 300 K that can be compared to predictions from equation (5) [24, 25]. Many of these species are listed in tables 2 (small molecules, alkanes and alkane variants) and 3 (other aromatics and oxygen-containing molecules). These data are not spectral measurements, and thus they do not provide direct evidence of VFR and hence positron binding. However, these annihilation rates, $Z_{\text{eff}}^{\text{th}}$, can provide a strong indication as to whether positrons do or do not bind to the molecular species. Namely, large values of $Z_{\text{eff}}^{\text{th}}/Z$ correlate well with the observation of VFRs (and hence nonzero positron binding energies) [8, 17–19]. As another independent criterion for nonzero binding, we use the fact that theory indicates that the maximum possible value of $Z_{\text{eff}}^{\text{th}}$ without VFRs is ~ 1000 [39].

Experiments have shown that, in the absence of positron binding, positron–atom and positron–molecule correlations can increase $Z_{\text{eff}}^{\text{th}}/Z$ from the free-electron-gas value from 1 to about 10, but not more (e.g. largest values are 7 for H_2 and 8 for Xe) [24]. Thus, we take $Z_{\text{eff}}^{\text{th}}/Z = 10$ as a guide, namely $Z_{\text{eff}}^{\text{th}}/Z > 10$ for a given molecule implies that the positron likely binds to it and vice versa. The predictions of equation (5) are also listed in tables 2 and 3. Generally, molecules with relatively large values of $Z_{\text{eff}}^{\text{th}}/Z$ are predicted correctly by equation (5) to have positive binding energies. The criterion of $Z_{\text{eff}}^{\text{th}} \geqslant 1000$ for binding, and hence VFRs, is in similar agreement with equation (5). However, there are a few exceptions: perfluoroalkanes violate both criteria; ethane binds positrons but has $Z_{\text{eff}}^{\text{th}} = 660$; and methane does not bind, yet $Z_{\text{eff}}^{\text{th}}/Z = 14$.

As shown in tables 2 and 3, the criterion from equation (5) that molecules will bind for $\alpha > 5.4$ has the consequence that most larger molecules will bind positrons whether they have a permanent dipole moment or not. From tables 1 and 2, the alkanes are an example of this, where only methane does not bind. For non-aromatic molecules, due to the relative weights of the α and μ terms in equation (5), and the fact that most values of μ are $\leqslant 2.5$, the α term dominates for all but relatively small molecules with small values of α. A related trend is seen in halogen substitution, where ϵ_b rises rapidly as the size (and hence the polarizability) of the halogen is increased. For example, as shown in table 2, CF_4 does not bind positrons, while CBr_4 has a predicted binding energy in excess of 120 meV.

In testing the predictions for molecules that do not appear to bind positrons, we restrict comparison to cases where equation (5) predicts $\epsilon_b < -15$ meV (i.e. in deference to the likely error bars for the model). Similarly, we consider that molecules are 'too close to call' when equation (5) predicts $|\epsilon_b| < 15$ meV. As shown in table 2, equation (5) predicts negative binding energies (and hence no binding) for almost all small molecules, including methane and carbon tetrafluoride, in agreement with the interpretation of their small $Z_{\text{eff}}^{\text{th}}/Z$ values [24]. Further, as indicated in table 1, molecules for which the predicted binding energies are 'too close to call,' consistent with their measured $\epsilon_b < 15$ meV, include ethane, propane, cyclopropane, methanol and methyl fluoride [9].

There are some disagreements between the predictions of equation (5) and experiment (perhaps not surprisingly) in cases where the binding energy is predicted and/or observed to be reasonably small. From table 2, the only molecule that violates the $|\epsilon_b| \geqslant 15$ meV criterion is NO_2 with a $Z_{\text{eff}}^{\text{th}}/Z$ ratio of 50 and yet a predicted binding energy of -26 meV. Like benzene, NO_2 has two resonant electronic states involving π bonds, but the geometry of its valence orbitals differs greatly from that of aromatics.

As mentioned above, an alternative description to equation (5) involves including a term with the ionization energy E_i as a parameter, such that smaller values of E_i correspond to larger values of ϵ_b. The two representations are similar in that they associate larger binding energies with more electron density further away from the atomic cores. For example, in the description involving E_i, H_2O and NO_2 are predicted to be more likely to bind positrons than H_2O or CO_2, since the former have lower E_i values, and this is in accord with experiment [40]. However, including all of the currently available data, this alternative parameterization and equation (5) give about the same results. Additional experiments are needed to better distinguish the effects of different types of electronic bonds and E_i, particularly in small molecules.

5. Comparison with theoretical predictions and further discussion

The positron–molecule binding energies discussed here can also be compared with available *calculations* for positron

Table 2. Values of $Z_{\mathrm{eff}}^{\mathrm{th}}$ and $Z_{\mathrm{eff}}^{\mathrm{th}}/Z$ for small molecules, alkanes and alkane variants and the predictions of equation (5) for their binding energy are compared for molecules where $|\epsilon_b|$ has not been measured. Also given are values of Z, α, μ and E_i [31–33]. Data for $Z_{\mathrm{eff}}^{\mathrm{th}}$ are from [24, 25]; see the text for details. As in table 1, values in parentheses are lower bounds for molecules that lack known values for μ.

Molecule Name	Formula	Equation (5) (meV)	Z	$Z_{\mathrm{eff}}^{\mathrm{th}}$	$Z_{\mathrm{eff}}^{\mathrm{th}}/Z$	α (Å^3)	μ (D)	E_i (eV)
Small molecules								
Hydrogen	H_2	−60	2	15	7.3	0.8	0	15.4
Deuterium	D_2	−60	2	15	7.4	0.8	0	15.5
Nitrogen	N_2	−45	14	31	2.2	1.9	0	15.6
Oxygen	O_2	−51	16	37	2.3	1.5	0	12.1
Carbon monoxide	CO	−43	14	39	2.8	2.0	0.1	14.0
Nitric oxide	NO	−45	15	34	2.3	1.7	0.2	9.3
Carbon dioxide	CO_2	−36	22	55	2.5	2.7	0	13.8
Sulfur hexafluoride	SF_6	−14	70	86	1.2	4.5	0	15.3
Water	H_2O	−15	10	319	32	1.5	1.9	12.6
Nitrous oxide	N_2O	−29	22	78	3.5	3.0	0.2	12.9
Nitrogen dioxide	NO_2	−26	23	1,090	47	3.0	0.3	9.8
Ammonia	NH_3	−12	10	1,600	160	2.3	1.5	10.2
Methane	CH_4	−37	10	142	14	2.6	0	12.7
Alkane rings and isomers								
Isobutane	C_4H_{10}	34	34	14 400	420	8.1	0.1	10.6
Neopentane	C_5H_{12}	54	42	21 100	500	10.0	0	10.4
Cyclodecane	$C_{10}H_{20}$	160	80	369 000	4,600	18.5	0	10.0
Bicyclodecane	$C_{10}H_{18}$	151	78	389 000	5 000	17.7	0	9.4
Alkenes and alkynes								
1-Hexene	C_6H_{12}	81	48	185 000	3,900	11.6	0.3	9.5
trans 3-Hexene	C_6H_{12}	74	48	196 000	4,100	11.6	0	8.9
1,3-Hexadiene	C_6H_{10}	(72)	46	389 000	8,500	11.4	–	8.5
1,3,5-Hexatriene	C_6H_8	69	44	414 000	9,400	11.2	0	8.3
Perhalogenated alkanes								
Carbon tetrafl.	CF_4	−34	42	54.4	1.2	2.9	0	16.2
Hexafl.ethane	C_2F_6	−10	66	149	2.3	4.8	0	14.6
Perfluoropropane	C_3F_8	(13)	90	152	1.7	6.7	–	–
Perfluorohexane	C_6F_{14}	84	162	535	3.3	12.4	0	12.8
Perfluorooctane	C_8F_{18}	131	210	1,064	5.1	16.2	0	12.6
Carbon tetrachl.	CCl_4	58	74	9,530	130	10.3	0	11.3
Hexachloroethane	C_2Cl_6	129	114	68 600	600	16.0	0	11.2
Carbon tetrabrom.	CBr_4	120	146	39 800	270	15.3	0	10.3
Carbon tetraiodide	CI_4	235	218	7,990	37	24.5	0	–
Dichl.-difl.methane	CCl_2F_2	20	58	750	13	6.4	0.1	12.3
Partially fluorinated alkanes								
Difluoromethane	CH_2F_2	0.4	26	799	31	2.5	1.8	12.6
Trifluoromethane	CHF_3	−4	34	247	7.3	2.7	1.7	14.8
Fluoroethane	C_2H_5F	21	26	3,030	120	4.2	2.0	12.4
1,1,1-Trifl.ethane	$C_2H_3F_3$	29	42	1,600	38	4.2	2.3	13.3
1,1,2-Trifl.ethane	$C_2H_3F_3$	14	42	1,510	36	4.2	1.6	–
1,1,1-Trifl.propane	$C_3H_5F_3$	52	50	3,350	67	5.9	2.5	–

binding to atoms and molecules. Predictions from calculations of positron binding to atoms [5], which are believed to be quite accurate, are shown in figure 3 as a function of the ionization potential of the target. Also shown is the positron binding energy expected for a 'model alkali atom' [5] in which the ionization potential can be varied. In this case, there is a maximum in ϵ_b at the threshold for positronium formation, namely at $E_i = 6.8$ eV. These calculations indicate that for molecules such that $E_i > 6.8$ eV, the bound state is qualitatively that of a positron loosely attached to a neutral target, whereas for $E_i < 6.8$ eV, the physical picture is closer to that of a (pseudo) Ps atom bound to a positive ion.

Also shown in figure 3 are the values of ϵ_b measured for the molecules described here. As illustrated in the figure, these molecules correspond to the physical picture in which a positron is loosely bound to a neutral molecule. Further, there is quantitative agreement between the measured values of ϵ_b for both aromatics and small alkanes with the atomic data plotted in this way. The larger alkane molecules depart from the atomic trend due to the fact that, for these molecules, alpha increases with molecular size while the ionization potential remains roughly constant.

Positron–molecule binding energies have been calculated for several small molecules (all with substantial dipole moments). These data are listed in table 4 and compared with the predictions of equation (5). All of these molecules are predicted by equation (5) to bind positrons in agreement with the theoretical calculations. The absolute values of ϵ_b predicted by equation (5) for HCN and formaldehyde (H_2CO) agree to within a factor of two with the calculations. The

Table 3. Values of $Z_{\mathrm{eff}}^{\mathrm{th}}/Z$ for aromatic and oxygen-containing molecules and the predictions of equation (5) for their binding energies are compared for molecules where $|\epsilon_b|$ has not been measured. Also given are values of Z, α, μ and E_i [31–33]. Data for $Z_{\mathrm{eff}}^{\mathrm{th}}$ from [24, 25]; see the text for details. As in table 1, values in parentheses are lower bounds for molecules that lack known values for μ. Note that for all the aromatics (including benzene), the N_π term is included in equation (5).

Molecule name	Formula	Equation (5) (meV)	Z	$Z_{\mathrm{eff}}^{\mathrm{th}}$	$Z_{\mathrm{eff}}^{\mathrm{th}}/Z$	α (Å^3)	μ (D)	E_i (eV)
Oxygen-containing molecules								
Acetic acid	$C_2H_4O_2$	30	32	5,880	180	5.3	1.7	10.4
Acetone	C_3H_6O	66	32	98 400	3,100	6.3	2.9	9.7
Propionic acid	$C_3H_6O_2$	53	40	27 200	680	7.1	1.8	10.2
1-Propanol	C_3H_8O	50	34	19 900	590	7.0	1.7	10.2
Glycerol	$C_3H_8O_3$	88	50	1,470 000	29 000	8.4	2.7	–
Dimethyl Sebacate	$C_{12}H_{22}O_4$	(233)	126	7,560 000	60 000	24.4	–	–
Perfluorinated aromatics								
Hexafl.benzene	C_6F_6	141	90	1,200	90	9.8	0	9.9
Octafl.toluene	$C_6F_5CF_3$	(165)	114	1,240	114	11.7	–	9.9
Octafl.naphth.	$C_{10}F_8$	272	132	3,080	132	15.5	0	8.9
Substituted benzenes								
Fluorobenzene	C_6H_5F	176	50	45 100	900	10.0	1.6	9.2
1,2-difl.benzene	$C_6H_4F_2$	189	58	32 800	570	9.8	2.4	9.3
1,3-difl.benzene	$C_6H_4F_2$	173	58	13 100	225	9.8	1.6	9.4
1,4-difl.benzene	$C_6H_4F_2$	141	58	13 500	230	9.8	0	9.2
Chlorobenzene	C_6H_5Cl	204	58	72 300	1,250	12.1	1.6	9.1
Bromobenzene	C_6H_5Br	215	76	172 000	2,300	13.0	1.7	9.0
Toluene	$C_6H_5CH_3$	179	50	190 000	3,800	12.3	0.4	8.8
1,2-dimeth.benzene	$C_6H_4(CH_3)_2$	208	58	180 000	3,100	14.1	0.6	8.6
1,3-dimeth.benzene	$C_8H_4(CH_3)_2$	201	58	210 000	3,600	14.1	0.3	8.6
1,4-dimeth.benzene	$C_8H_4(CH_3)_2$	195	58	200 000	3,400	14.1	0	8.5
Aniline	$C_6H_5NH_2$	192	50	400 000	8 000	11.5	1.5	7.7
Nitrobenzene	$C_6H_5NO_2$	254	64	430 000	6,700	12.1	4.2	9.9
Other aromatics								
Pyridine	C_5H_5N	181	42	85 400	2 000	9.5	2.2	9.3
Anthracene	$C_{14}H_{10}$	422	94	4,330 000	46 000	22.8	0	7.5

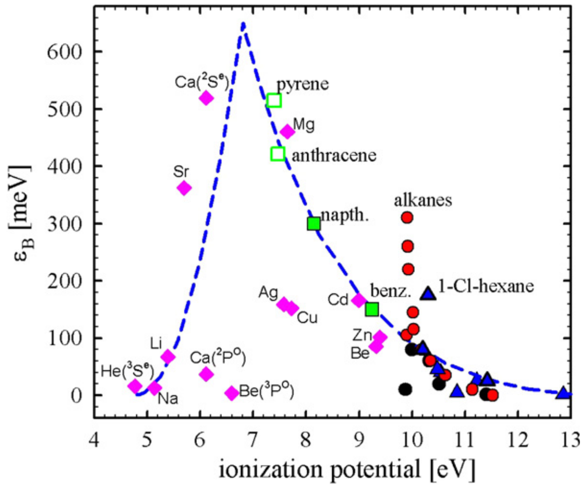

Figure 3. Positron binding to atoms and molecules as a function of ionization potential: (dashed line) model alkali atom [5] and (diamonds) calculated binding energies for atoms; also shown are binding energies for molecules: (circles) alkanes and alkane related; (triangles) molecules with permanent dipole moments; (squares) aromatic molecules; and (open squares) the predictions of equation (5) for anthracene and pyrene.

predictions from equation (5) for urea [$(NH_2)_2CO$] and acetone (C_3H_6O) are considerably larger than the theoretical values given in [14]. This is consistent with the view expressed in [13] that the predictions in [14] for ϵ_b for urea and acetone might be expected to underestimate ϵ_b for these species.

As shown in table 4, there is a large discrepancy between the prediction of equation (5) and calculations of ϵ_b for LiH (i.e. $\sim$ an order of magnitude) [15, 41, 42]. This is also the case for the other alkali hydrides, for which calculations predict binding energies $\sim$ 1 eV [43]. This discrepancy is due to the fact that the ionization potential of LiH (and the other alkali hydrides) is close to the binding of a positronium atom (e.g. $E_i - 6.8\ \mathrm{eV} = 1.1\ \mathrm{eV}$ for LiH). Thus, the relevant physical picture more closely resembles that of a PsH complex in the attractive potential of the positively charged metal ion [42]. Thus, it is not surprising that there is a discrepancy between the predictions of equation (5) and calculations of ϵ_b for LiH.

As a final note, as indicated in figure 3, the binding energies of the aromatics studied to date, benzene and napthelene, follow closely the model alkali atom curve. As is also shown, the predictions of equation (5) indicate that the next larger aromatics, anthracene and pyrene are expected to behave similarly. The reason for this close correspondence of the aromatics with the model alkali curve is not presently understood.

Another goal of this analysis is to identify candidate molecules for further theoretical and experimental study. For theoretical analysis, it is helpful if the molecule has a small number of atoms, each with relatively small atomic number

Table 4. Comparisons of theoretical predictions for positron–molecule binding energies (in units of meV) with those of equation (5).

Name	Formula	α (Å^3)	μ (D)	ϵ_b, equation (5) (meV)	ϵ_b, th (meV)
Cyanide	HCN	2.5	3.0	21	35[a]
Formaldehyde	H_2CO	2.8	2.3	11	18[b]
Urea	$(NH_2)_2CO$	9.7	4.6	140	13[c]
Acetone	$(CH_3)_2CO$	6.4	2.9	67	4[c]
Lith. hydride	LiH	3.8	5.9	95	1000[d]

[a] Reference [44].
[b] Reference [13].
[c] Reference [14].
[d] References [15, 41, 42, 45].

and hence a simple electronic structure. For experimental study, they should have appreciable vapour pressures (e.g. molecular number densities $\geqslant 10^{-8}$ amagat) at not too high temperatures ($T \leqslant 500$ C), be stable at the relevant ambient temperature and not be deleterious to the vacuum system. One such molecule is carbon disulfide, CS_2 ($\alpha = 8.8$, $\mu = 0$), with a predicted binding energy from equation (5) of 40 meV. This molecule has π bonds which may further increase ϵ_b. Nevertheless, 40 meV is a substantial binding energy (e.g. comparable to butane) and thus likely to be amenable to both theoretical and experimental investigation. We plan to measure the annihilation spectrum for this molecule in the near future.

For the species studied to date, the largest binding energies for a given number of atoms are seen in the aromatic molecules. Thus, the study of larger species (i.e. polycyclic aromatic hydrocarbon (PAH) molecules), such as the three- and four-ring variants, anthracene and pyrene, would be of interest.

It will also be of interest to investigate the interaction of low-energy positrons with cage-like carbon structures such as C_{60}. It has been predicted that they will exhibit a positive energy, positron-in-cage resonance at an incident energy of approximately 3 eV [46]. Application of equation (5) to C_{60} ($\alpha = 76$; $E_i = 7.6$ eV) predicts a positron binding energy of 880 meV. However, due to the relatively small ionization potential of C_{60}, it is likely the bound state of a positron to C_{60} will be more akin to a Ps atom moving in the field of a C_{60}^+ ion (e.g. similar to LiH), and hence is outside of the range of validity of the analysis. Thus, C_{60} might provide the opportunity to investigate this qualitatively different kind of positron binding mechanism experimentally.

Finally, as shown in table 2, $Z_{\mathrm{eff}}^{\mathrm{th}}$ and $Z_{\mathrm{eff}}^{\mathrm{th}}/Z$ for perfluoroalkane molecules are much smaller than those for alkanes. However, equation (5) predicts that perfluorocarbons other than perfluoromethane and perfluoroethane do bind positrons. Examples of strong positron binding to the perfluorocarbons are (cf table 2) perfluorohexane ($\epsilon_b = 88$ meV) and perfluorooctane ($\epsilon_b = 135$ meV). This warrants further investigation (e.g. by measurement of the $Z_{\mathrm{eff}}(\epsilon)$ spectra for these molecules).

6. Concluding remarks

In this paper a regression analysis is described that is intended to elucidate the dependence of positron–molecule binding energy on molecular parameters. A useful parameterization (equation (5)) was obtained using a linear combination of the molecular dipole polarizability, α, the permanent dipole moment, μ, and the number of π bonds in aromatic molecules. The predictions of equation (5) are consistent with most available data. A number of predictions are made in tables 2 and 3 for molecules where $Z_{\mathrm{eff}}^{\mathrm{th}}$ has been measured, but not the binding energy. Regarding a possible benchmark comparison between theory and experiment for ϵ_b, it is suggested that CS_2 might be a good candidate.

It is expected that the expression for positron–molecule binding energies in equation (5) will be useful in identifying interesting species (e.g. the perfluoroalkanes) for future study. It could also be useful in predicting the behavior of low-energy positrons in a wide range of chemical environments including biological systems (e.g. in PET analysis) and in materials science in conjunction with studies of insulators using techniques such as ACAR and PALS.

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