

Enhancement of positron binding energy in molecules containing π bondsJ. R. Danielson ^{*}, S. Ghosh , and C. M. Surko *Physics Department, University of California, San Diego, La Jolla, California 92093, USA* (Received 8 August 2022; accepted 7 September 2022; published 23 September 2022)

Observation of vibrational Feshbach resonances in the annihilation spectra of positrons on molecules provides a direct measurement of the positron-molecule binding energy ϵ_B . Annihilation measurements are presented for ring hydrocarbons with different numbers of π bonds, for which it is observed that the presence of π bonds generally increases the positron binding energies. These molecules were chosen because other global molecular parameters (e.g., polarizability, dipole moment, and geometry) are approximately constant, so the observed differences in ϵ_B can be related to changes in the nature of the bonds. The molecular ionization potential E_i is an exception: for these molecules, the inclusion of π bonds tends to decrease E_i , and the number of π bonds also exhibits a correlation with ϵ_B . Comparison with other molecules with π bonds indicates that the changes in ϵ_B are better correlated with the changing electronic structure of the bonds rather than with a direct dependence of ϵ_B on E_i . The relationship between the dependence of ϵ_B on the number of π bonds and electron-positron correlation effects (such as virtual positronium formation) is discussed.

DOI: [10.1103/PhysRevA.106.032811](https://doi.org/10.1103/PhysRevA.106.032811)**I. INTRODUCTION**

To date, positron-molecule binding energies ϵ_B have been measured for over 90 molecules [1–5]. The data show that ϵ_B depends sensitively upon molecular composition and structure. However, accurate theoretical predictions of ϵ_B continue to represent a major challenge. One significant issue is that the correlation potential can be much larger than the lowest-order electrostatic terms. This includes not only the polarization terms but also the effects of virtual positronium, which is unique to positron-matter interactions [6–13]. It is often hard to obtain reliable results from simple calculations; on the other hand, even for moderate-size polyatomics, the computational cost for more sophisticated calculations can become quite high [9,12–17]. Thus, further experimental studies of selected sets of molecules can be of value as a guide to theory.

This paper describes studies of the dependence ϵ_B on the specific types of chemical bonds with a focus on π -bonded molecules. Molecules were chosen such that the electronic structure of the bonds can be changed while keeping the polarizability α , permanent dipole moment μ , and molecular geometry approximately fixed. Considered here are two remaining global parameters, the molecular ionization potential E_i and the number of π bonds in the molecule N_π .

Measurements are presented for hydrocarbon ring molecules with different numbers of π (i.e., “double”) bonds. The addition of each π bond, with the removal of two hydrogen atoms, results in only a slight change in the global α . In contrast, the change in the electronic structure associated with the π bond is significant; for example, it often results in relatively large changes to E_i . Adding a π bond will also make the ring asymmetric, and this leads to a small permanent

dipole moment. However, for all molecules considered, the change in μ is <0.5 D, and in previous studies, this resulted in only a small change in ϵ_B , if any [1,3,18].

Since all of the molecules in the current study are rings, the geometrical location of the atom cores is approximately the same, while the number of π bonds is changed. Thus, it is argued here that the changes observed in the binding energies are due to the changing electronic structure of the bonds. These ring molecules are also compared with the results for other chemical species to elucidate the generality of the results. Although changes to E_i seem to be an indicator of changes in ϵ_B within a particular chemical series, the absolute value of E_i does not appear to be a useful parameter in predicting ϵ_B . Instead, it appears that *changes in E_i* are correlated with *changes in the number of π bonds N_π* , and both correlate with changes in ϵ_B .

The remainder of this paper is organized as follows. Section II briefly describes the experiments. Although the focus of this paper is on ϵ_B , the annihilation spectra are presented and briefly discussed. The ϵ_B results are discussed in Sec. III, where they are placed in context with data for other π -bonded molecules. Further, the results are related to other parametric studies [1,4,19] and to a recent many-body calculation [13]. Section IV presents a summary and concluding remarks.

II. SPECTRAL MEASUREMENTS

Low-energy positron annihilation spectra for molecules often exhibit distinct peaks that are identified as vibrational Feshbach resonances (VFRs) and are associated with IR active vibrational modes (i.e., mediated by electric-dipole coupling) [22–24]. These resonances, located at energy ϵ_ν , are downshifted from the vibrational mode energy $\hbar\omega_\nu$ by the

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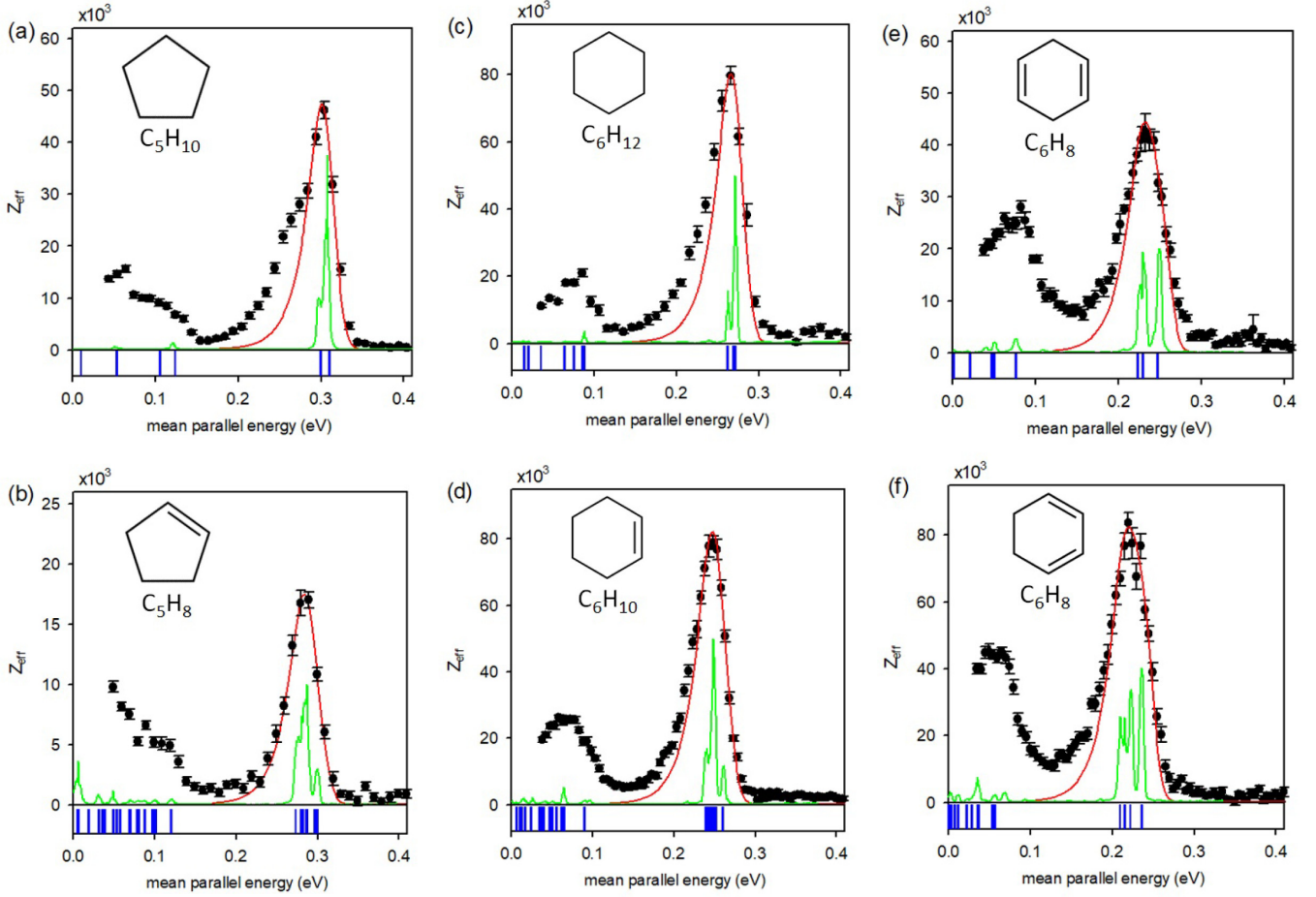


FIG. 1. Z_{eff} data plotted versus beam energy for (a) cyclopentane ($\epsilon_B = 49$ meV), (b) cyclopentene ($\epsilon_B = 70$ meV), (c) cyclohexane ($\epsilon_B = 82$ meV), (d) cyclohexene ($\epsilon_B = 105$ meV), (e) 1,4-cyclohexadiene ($\epsilon_B = 116$ meV), and (f) 1,3-cyclohexadiene ($\epsilon_B = 132$ meV). Error bars are statistical. The solid red line is the VFR fit to the high-energy CH modes. Vertical lines show the locations of the downshifted IR-active fundamental vibrational modes. The solid green line is the arbitrarily scaled, downshifted infrared spectrum [20].

positron-molecule binding energy ϵ_B ,

$$\epsilon_V = \hbar\omega_V - \epsilon_B. \quad (1)$$

Thus, if the vibrational mode energies are known, the locations of the resonances provide a direct measurement of the positron-molecule binding energy ϵ_B .

The experimental techniques to study these resonances were described in detail previously [2,23,25]. Slow positrons (\sim eV) are provided by a ^{22}Na radioisotope source and a solid neon moderator. They are magnetically guided into a three-stage buffer-gas trap [26]. The positrons are accumulated in a Penning-Malmberg trap and cooled to \sim 300 K by collisions with N_2 and CF_4 [27]. After cooling to the ambient temperature, the positrons are gently ejected from the trap by pulsing the confining electrodes to form a nearly monoenergetic positron beam [25], with a mean beam-transport energy of 0.7 eV and with a total energy spread \leq 40 meV, FWHM. The typical number of positrons per pulse is \sim 20 000, but this can be varied depending upon the experiment.

The beam is magnetically guided into a gas cell where an electrode is electrically biased to set the mean parallel energy of the beam (i.e., the energy associated with the motion of the positrons in the direction of the magnetic field). The test gas

is injected into the gas cell through a leak valve. The pressure range is maintained in the range 1–30 μ Torr (depending on the molecule and annihilation signal strength), as measured with a manometer. Single-annihilation γ rays are measured while the beam interacts with the test gas. The beam energy distribution is measured using a retarding potential analyzer (RPA) [2,25,28]. The count rate vs positron energy is converted into a normalized annihilation rate Z_{eff} [23] using the known number of positrons per pulse, the gas pressure, and the detector calibration.

Shown in Fig. 1 are the annihilation spectra for cyclopentane (C_5H_{10}), cyclopentene (C_5H_8), cyclohexane (C_6H_{12}), cyclohexene (C_6H_{10}), 1,4-cyclohexadiene (C_6H_8), and 1,3-cyclohexadiene (C_6H_8) as a function of the mean parallel energy of the positron beam. In the work presented here, mean parallel energy is used since it can be measured directly using the RPA. The spectrum for benzene (C_6H_6) is presented in Fig. 2. The error bars for Z_{eff} are statistical based on the overall annihilation count rate. The energy scale is believed to be good to ± 2 meV based on the reproducibility of measurements (e.g., separated by several months) and measurement of the time-of-flight of the positrons through the gas cell. Recently, we published high-resolution spectra for both

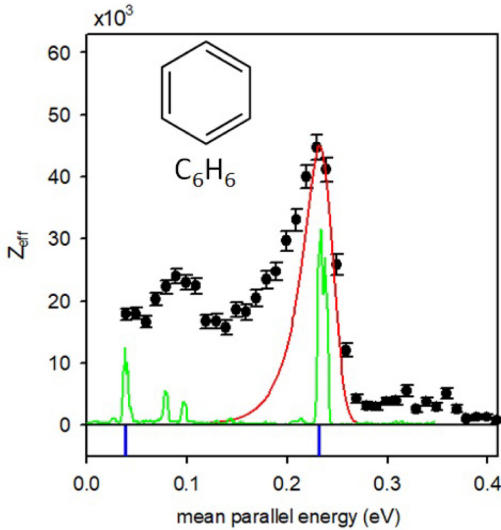


FIG. 2. Z_{eff} data plotted versus beam energy for benzene ($\epsilon_B = 133$ meV). Error bars are statistical. The solid red line is the VFR fit to the high-energy CH mode. Vertical lines show the locations of the downshifted IR-active fundamental vibrational modes. The solid green line is the arbitrarily scaled, downshifted infrared spectrum [20]. This measurement updates the results presented in Ref. [21].

cyclopentane [29] and benzene [30] using a cryotrap-based beam (50K), and the measured values of ϵ_B are the same to within ± 1 meV. However, to maintain consistency with the other measurements, only data using the 300 K beam are reported here.

The spectra in Fig. 1 all show distinct resonant structures with the most prominent peak in the energy range 0.2–0.3 eV. These resonances are associated with the high-energy, dipole-allowed C-H stretch vibrational modes. The specific vibrational mode energies change depending on the types of bonds in each molecule. For example, the C-H stretch modes associated with carbons that participate in a double bond are typically higher in energy than the normal C-H stretch vibrations associated with methylene (CH_2) groups. The current 300 K beam resolution (FWHM ~ 36 meV) is not sufficient to separate these peaks. Thus, the total width of the resonance will depend on the spacing of the vibrational modes, and this leads to a broader resonant peak in molecules that exhibit a larger spread in mode energies. This needs to be accounted for in order to get the best fits to the resonances.

To fit to the measured C-H stretch peak, the resonances associated with the IR-active fundamental modes are treated as δ functions. They are convolved with the beam energy distribution and then summed to yield a single resonance peak. The total width of the resonance is a combination of the beam parameters and the spread of the vibrational modes. The binding energy and peak magnitude are independently scanned to obtain the best fit to the data, which then determines the experimental ϵ_B . The result is shown as the solid red line in each plot. For this study, only the IR-active CH stretch modes have been used to obtain ϵ_B . No attempt has been made to fit the entire spectrum, although this could be investigated in the future. The downshifted locations of the IR-active vibrational

modes used in the fit are shown in Fig. 1 (from [31–36]). The downshifted IR spectra (from Ref. [20], arbitrary amplitude scale) are also shown to indicate the contribution that the spread of mode energies may make to the resonance widths.

This fitting process was repeated for each molecule (solid red line), and the results are listed in Table I along with relevant global molecular parameters. As expected, the data show that the six-carbon molecules (with larger α) have larger ϵ_B values than the five-carbon molecules. However, there is a distinct increase in ϵ_B for the molecules with π bonds. This increase in ϵ_B is also correlated with a decrease in E_i . The last two columns show that, for all the molecules except benzene, there is a strong correlation between the number of π bonds, N_π , and E_i . The question then becomes whether it is the changing electronic structure of the bonds or the changing ionization energy that is responsible for the increased ϵ_B .

As shown in Figs. 1 and 2, the fits provide a good description of the peaks in most molecules. However, some of the molecules exhibit a slight excess broadening on the low-energy side of the C-H peak. The most extreme examples are cyclopentane in Fig. 1(a) and benzene in Fig. 2, although it is also apparent in cyclohexane [Fig. 1(c)]. These features are discussed in more detail below. In all cases, the analyses shown by the red curves in Figs. 1 and 2 were used since the high-energy sides of the resonances are well fit. With the exception of cyclohexane and benzene, both sides of the peaks are reasonably well fit, and the binding energy is tightly constrained (i.e., with a total uncertainty of ± 3 –5 meV).

III. DISCUSSION

The values of ϵ_B from Figs. 1 and 2 and other relevant parameters are summarized in Table I. The global molecular parameters (α , μ , E_i , N_π) are used to group ϵ_B for the different molecules, and trends in the data are used to clarify the important factors determining ϵ_B . The goal is not to find a new empirical fit (e.g., with different and/or more fit parameters), but rather to better understand the role of π bonds in determining ϵ_B .

Data for a set of comparison molecules are given in Table II. This group includes chain alkanes [18,21], ethylene [23], chlorosubstituted methanes [4,38], and chlorosubstituted ethylenes [4,39]. The ethylenes all have a single C-C associated π bond, so they form a good set to compare to the current measurements. In contrast to the ring molecules, the chlorosubstituted molecules often have a significant permanent dipole moment unless it happens to be zero by symmetry. Thus, the chloromethanes are included as a control group since they lack a double bond but otherwise have α and μ comparable to those of the chloroethylenes. Recently, there was a combined theoretical and experimental study of chlorosubstituted molecules, including the molecules considered here [4]. Generally, the modeling showed good agreement with the measurements except for the chloroethylenes (discussed below).

The measured ϵ_B for the comparison molecules and the associated molecular parameters are shown in Table II. These molecules are compared to the current measurements in Figs. 3(a)–3(d) as a function of polarizability α , dipole moment μ , ionization potential E_i , and number of π bonds N_π ,

TABLE I. Fit results and molecular parameters for ring hydrocarbons with different numbers of π bonds. All data were taken with a room-temperature positron beam, $\sigma_{\parallel} \approx 10$ meV, $\sigma_{\perp} \approx 20$ meV. Values for α , μ , and E_i are from [37]. ε_{pk} is the energy for the peak of the resonance, and $Z_{\text{eff}}(\varepsilon_{\text{pk}})$ is the value of Z_{eff} at the peak. Symbols identify the number of carbons, with solid symbols indicating one of more π bonds, and open symbols indicating zero π bonds. A superscript A indicates that the π bonds are aromatic.

| Molecule | Formula | Symbol | ε_B (meV) | ε_{pk} (eV) | $Z_{\text{eff}}(\varepsilon_{\text{pk}})$ | α (10^{-30} m ³) | μ (D) | E_i (eV) | N_{π} |
|--------------------|--------------------------------|--------|-----------------------|--------------------------------|---|--|-----------|------------|----------------|
| Cyclopentane | C ₅ H ₁₀ | □ | 49 ± 3 | 0.303 | 46 200 | 9.1 | 0 | 10.3 | 0 |
| Cyclopentene | C ₅ H ₈ | ■ | 70 ± 3 | 0.284 | 18 000 | 8.9 | 0.2 | 9.0 | 1 |
| Cyclohexane | C ₆ H ₁₂ | ◇ | 82 ± 5 | 0.265 | 80 200 | 11.0 | 0 | 9.9 | 0 |
| Cyclohexene | C ₆ H ₁₀ | ◆ | 105 ± 3 | 0.247 | 81 600 | 10.7 | 0.33 | 9.0 | 1 |
| 1,4-Cyclohexadiene | C ₆ H ₈ | ◆ | 116 ± 4 | 0.233 | 44 000 | 11.0 | 0 | 8.8 | 2 |
| 1,3-Cyclohexadiene | C ₆ H ₈ | ◆ | 132 ± 3 | 0.222 | 81 800 | 10.6 | 0.44 | 8.3 | 2 |
| Benzene (aromatic) | C ₆ H ₆ | ◆ | 133 ± 5 | 0.230 | 44 700 | 10.4 | 0 | 9.3 | 3 ^A |

respectively. In Fig. 3, all of the solid data symbols indicate one or more π bonds, whereas the open symbols indicate there are none.

A. Polarizability and dipole moment

The molecular polarizability is dominated by the carbon and halogen atoms [40], with the change in the number of hydrogen atoms making only a small difference. This is best seen by comparing cyclohexane and benzene, where the loss of the six hydrogen atoms reduces α by only $\sim 5\%$, so the nonsaturated and saturated rings have about the same α values. Further, exchanging a carbon for a chlorine atom also keeps α approximately unchanged. For example, chloroform with one carbon and three chlorines has about the same α as dichloroethylene with two carbons and two chlorines. Thus, the plot of ε_B vs α shown in Fig. 3(a) results in groups of approximately constant α .

The most general statement is that typically, ε_B increases with α . This is best exemplified in Fig. 3(a) by the approximately linear increase of the chain alkanes (open triangles) with α [18,23]. This roughly holds for the other molecules as well, although there is a significant spread. The ring molecules (squares and diamonds) all show increased ε_B relative to the alkane line. In contrast, the chlorosubstituted molecules are observed to spread both above and below this line.

TABLE II. Binding energy data and molecular parameters for comparison molecules. Values for α , μ , and E_i are from [37]. Chloromolecule measurements are from [4]. The ε_B values for ethane and ethylene are older measurements [23] and have larger error bars. Solid symbols indicate one or more π bonds; open symbols indicate there are no π bonds.

| Molecule | Formula | Symbol | ε_B (meV) | α (Å ³) | μ (D) | E_i (eV) | N_{π} |
|-------------------------------------|---|--------|-----------------------|----------------------------|-----------|------------|-----------|
| Chloromethane | CH ₃ Cl | ○ | 26 ± 6 | 4.4 | 1.9 | 11.2 | 0 |
| Dichloromethane | CH ₂ Cl ₂ | ○ | 32 ± 4 | 6.5 | 1.6 | 11.3 | 0 |
| Chloroform | CHCl ₃ | ○ | 37 ± 3 | 8.4 | 1.0 | 11.4 | 0 |
| Carbon tetrachloride | CCl ₄ | ○ | 55 ± 8 | 10.5 | 0.0 | 11.5 | 0 |
| 1,2- <i>trans</i> -dichloroethylene | C ₂ H ₂ Cl ₂ | ● | 14 ± 3 | 8.2 | 0.0 | 9.6 | 1 |
| 1,2- <i>cis</i> -dichloroethylene | C ₂ H ₂ Cl ₂ | ● | 66 ± 8 | 8.0 | 1.9 | 9.7 | 1 |
| 1,1-dichloroethylene | C ₂ H ₂ Cl ₂ | ● | 30 ± 5 | 8.1 | 1.3 | 9.8 | 1 |
| Trichloroethylene | C ₂ HCl ₃ | ● | 50 ± 6 | 10.0 | 0.8 | 9.5 | 1 |
| Tetrachloroethylene | C ₂ Cl ₄ | ● | 57 ± 6 | 12.0 | 0.0 | 9.3 | 1 |
| Ethane | C ₂ H ₆ | ▽ | 2 ± 5 | 4.4 | 0.0 | 11.5 | 0 |
| Ethylene | C ₂ H ₄ | ▼ | 20 ± 8 | 4.2 | 0.0 | 10.5 | 1 |

For both the ring molecules and the alkane chains considered here, the dipole moment is either zero or very small (<0.5 D). As noted above, the addition of the π bonds does not add a significant dipole moment. In contrast, the chloro-substituted molecules have dipole moments typically between 1 and 2 D, except for those that are zero by symmetry. Typically, larger dipole moments tend to enhance the binding energy. However, for those cases the overall geometry of the molecule is also important (e.g., see [4,5,18]), and thus, there appears to be no simple predictive relationship using just these parameters.

B. Ionization potential and number of π bonds

The ionization potential of the molecule is set by the energy of the highest occupied molecular orbital (HOMO). For positron interactions, this also determines the positronium (Ps) formation threshold, $E_i - 6.8$ eV, where 6.8 eV is the binding energy of the ground state of Ps [41]. It is expected that the effect of “virtual positronium” can increase the strength of the attractive part of the correlation energy and lead to larger binding energies for targets with low E_i . This is similar to what has been calculated for positron-atom binding [8]. Early attempts to do this for molecules were inconclusive [1]. However, recently, a machine-learning study was published that appeared to identify such a dependence of ε_B on E_i [19].

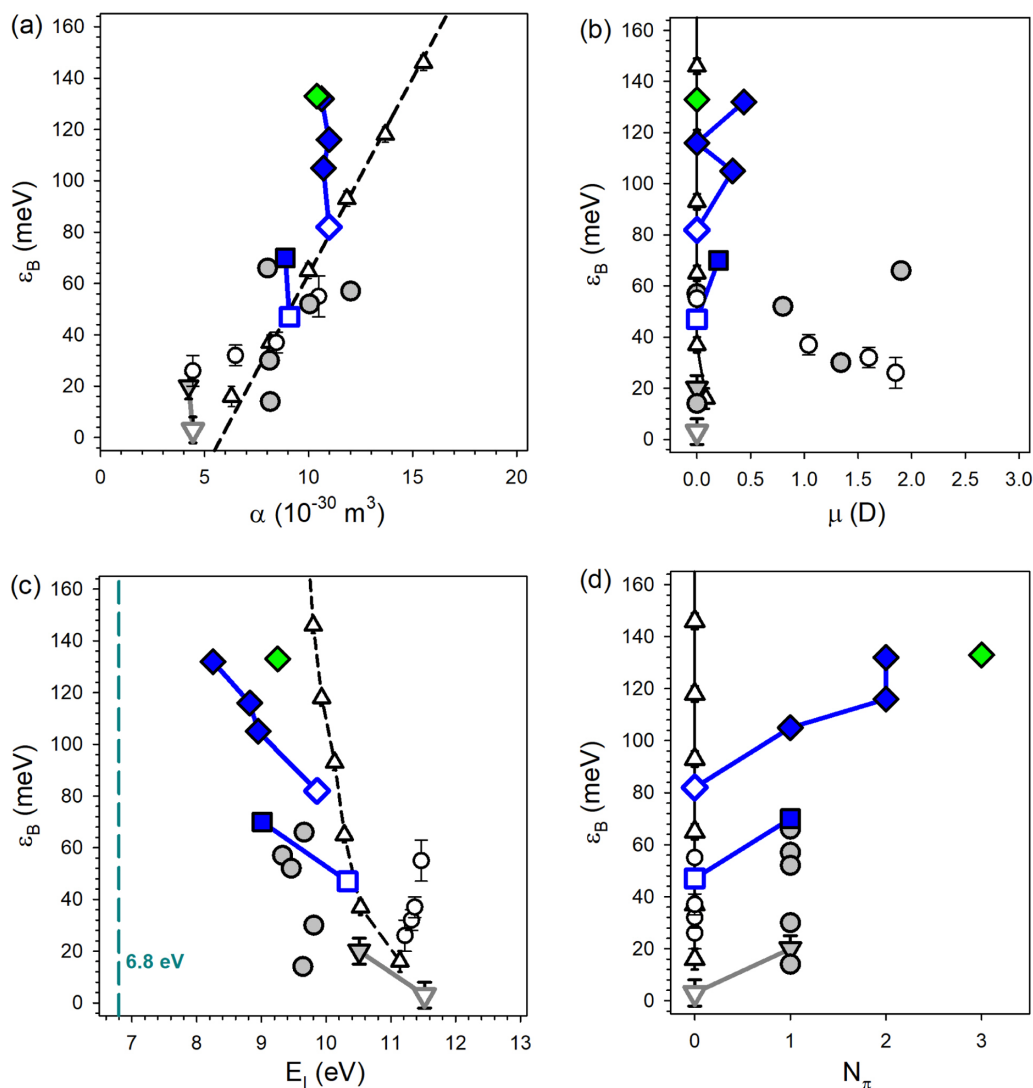


FIG. 3. Measured positron binding energy ε_B vs molecular parameters (a) α , (b) μ , (c) E_i , and (d) N_π . Upward triangles are chain alkanes, squares are five-carbon rings, diamonds are six-carbon rings, downward triangles are ethane and ethylene, circles are chlorosubstituted methanes and ethylenes. Solid symbols indicate one or more π bonds; open symbols indicate there are zero π bonds. Dashed lines show the trend for the chain alkanes. Solid lines are guides to the eye that connect molecules with the same number of carbon atoms. For other details, see Tables I and II.

The ring molecules for which data are shown in Figs. 1 and 2 provide a good opportunity to explore this effect further. As noted above, the addition of π bonds does not change α or μ appreciably, and thus, the observed changes can be assumed to be due to the different electronic structures of the bonds. One global parameter that does change appreciably is E_i ; namely, as shown in Table I, the addition of π bonds almost always lowers E_i . This also correlates with larger ε_B relative to the rings with no π bonds [i.e., open square and diamond in Fig. 3(c)].

The key question is whether it is E_i or some other property of the π bonds that leads to the enhanced values of ε_B . Figure 3(d) shows a plot of ε_B as a function of N_π . It is striking that this plot is roughly a mirror image of Fig. 3(c), which plots ε_B vs E_i . Thus, it appears that the number of π bonds is also a relevant parameter. This was used in an early parametrization of the ε_B data [1], where it was seen that, in order to fit the aromatic

molecules benzene and naphthalene, a term linear in N_π was required.

Beyond the current data for ring molecules, there are. Comparing ethane to ethylene (downward triangles), there is a similar drop in E_i and an increase in ε_B for the molecule with the π bond (ethylene). As can be seen in both plots, the increase $\Delta\varepsilon_B \sim 20$ meV from ethane to ethylene is approximately the same as the increase from cyclopentane to cyclopentene and from cyclohexane to cyclohexene. However, it is clear that the *absolute values* of E_i are quite different for these molecules, so this argues against a direct dependence of ε_B on E_i .

A more extreme example is the comparison of the chloromethanes (open circles) to the chloroethylenes (solid circles) in Figs. 3(c) and 3(d). Unlike the rings, the geometric shape of these molecules does change considerably from one group to the other. This leads to significant variation in the resulting dipole moments, making the comparison more diffi-

cult than for the case of the rings. However, both groups have the same types of atoms (carbon, hydrogen, and chlorine), the molecules are comparable in size (five vs six total atoms), and they have comparable spreads in α and μ [Figs. 3(a) and 3(b)]. Thus, although it would not be appropriate to compare individual molecules, it is reasonable to compare members (or subsets) of the respective groups. Looking at Fig. 3(c), a grouping vs E_i is apparent, where the chloroethylenes, each with a single π bond, have lower E_i by ~ 2 eV relative to the chloromethanes. Even with this large gap, the two sets of molecules exhibit about the same spread in ϵ_B . So, for this case, the addition of π bonds does not appear to increase ϵ_B . Similarly, the smaller *absolute value of E_i* appears to make no significant change in ϵ_B .

The data for benzene [i.e., green diamond in Fig. 3(c)] is an exception. With three π bonds, it would normally be expected to lower E_i even further. However, as is well known, benzene is aromatic, where the π bonds form a more stable, lower-energy electronic structure, and thus, the ionization energy actually rises slightly. If there were a direct dependence on E_i , one might then expect ϵ_B to drop. However, as seen in the data, ϵ_B is still larger than that of 1,4-cyclohexadiene and comparable to that of 1,3-cyclohexadiene. Here again, it appears that the absolute value of E_i alone cannot explain the enhancement of ϵ_B .

The dependence of ϵ_B on molecular composition and geometry was considered recently in a study of chlorine-substituted molecules, including those considered here [4]. In that work, a model correlation potential was used with the full molecular geometry in order to calculate ϵ_B . These calculations fit several parameters to one or more molecules in order to tune the model. Once tuned, the model can be used for a wide range of molecules with similar substitutions. This was shown to work quite well for the broad range of chlorine-substituted molecules, including the chloromethanes, chloropropanes, and other molecules with no π bonds. It was also tested with ethylene and the chloroethylenes. For ethylene, the model yielded a value of ϵ_B a factor of 4 *smaller* than that of the measurement.

For the chloroethylenes, the calculations were systematically *larger* by as much as a factor of 2. The model used the same parameters as for the other molecules, so the only difference was the presence of the π bond. Thus, something more would be needed to model these effects (i.e., similar to the conclusion of [1]). It is interesting to note that it would have to lead to a *decrease* in ϵ_B for chloroethylenes and an *increase* in ϵ_B for ethylene. This is in contrast to the ring hydrocarbons and ethylene, where the effect of the π bonds is always to increase ϵ_B . This effect can also be seen in Fig. 3(a), where several chloroethylenes are seen to be *below* the linear alkane curve.

As a summary statement, albeit approximate, there is a correlation, not between E_i and ϵ_B , but between *changes in E_i* and the *changes in ϵ_B* for similar molecules. A roughly equivalent (still approximate) parametrization can be made with the number of π bonds N_π .

Additional theoretical insights into the roles of E_i and N_π in determining ϵ_B come from the recent *ab initio* many-body calculations of Hofierka *et al.* [13]. They were able to include virtual positronium in a systematic manner in the correlation

potential and showed that it can lead to a factor of 2 or greater increase in ϵ_B . They also showed that increases in ϵ_B do not correlate with the absolute E_i ; rather, the increase is due to the sum of the interactions with many valence electronic orbitals. In fact, for several molecules, the HOMO (which determines E_i) actually contributes *less* than some of the more deeply bound electronic orbitals.

The prominent role of π bonds in positron-molecule attraction is likely due to the fact that the positrons are repelled by the positively charged atomic cores. Electrons that form σ (single) bonds are generally found between the nuclei, while the electrons in π bonds are located away from the line (or plane, as in ethylene or benzene) that contains the atomic cores. Thus, it is “easier” for positrons to access the electron-rich regions of the π bonds compared with the σ bonds. The electrons in π bonds effectively contribute more to the positron attraction than electrons in the σ bonds, while their other contributions (e.g., to the polarizability) are approximately the same.

C. Other features of the annihilation spectra

There are additional features of the annihilation spectra shown in Figs. 1 and 2 that are worth noting. Returning to the feature observed on the low-energy side of the CH stretch peaks, the spectra of both cyclopentane [29] and benzene [30], studied with the higher-resolution cryogenic trap-based beam, begin to resolve small peaks at these locations. They may be related to combination vibrations near these locations that are visible in the IR spectrum.

The magnitudes of the Z_{eff} spectra also show interesting trends. Not surprisingly, the spectral magnitude for the five carbon rings (cyclopentane and cyclopentene) is smaller than that for the six carbon rings. This is consistent with the scaling with molecular size seen for other alkanes and similar hydrocarbons. However, cyclopentene is a factor of ~ 2 *smaller* than cyclopentane, even though cyclopentene nominally has more IR-active modes due to lower symmetry (C_{2v} vs D_{5h}). However, the integrated IR for cyclopentane is 50% larger, and since the symmetries are only approximate [42,43], the larger activity may lead to more resonances. In any case, the Z_{eff} values for these molecules are enhanced above simple expectations [2,24], so some level of intramolecular vibrational redistribution is likely occurring [44–46]. On the other hand, the infrared study of the CH modes of hydrocarbons by Stewart and McDonald found that the dilution factors for the two molecules were comparable (i.e., from which one would expect comparable levels of enhancement) [47]. Thus, the origin of the relative magnitudes of Z_{eff} for cyclopentane and cyclopentene remains an open question.

In contrast to cyclopentane and cyclopentene, the six-carbon molecules cyclohexane and cyclohexene have comparable annihilation magnitudes, and 1,3-cyclohexadiene is also about the same in magnitude. Although these molecules are structurally similar, given the different symmetries, it would be surprising if they had the same vibrational mode densities, so it is surprising that Z_{eff} is the same for all three. The last two six-carbon rings, 1,4-cyclohexadiene and benzene, are both about a factor of 2 smaller. The symmetries of the two are different, as are the number of IR-active modes, again

leading to a surprising result. However, making quantitative comparisons will require detailed calculations of the dipole coupling strengths and the density of vibrational states for the modes in these molecules.

IV. SUMMARY AND CONCLUDING REMARKS

Annihilation spectra for ring hydrocarbons with different numbers of π bonds were presented. The resulting measurements of ε_B were summarized in Table I, along with selected molecular parameters. Rings were chosen because the electronic structure of the bonds could be changed while leaving most global molecular parameters approximately fixed, thus allowing for a better separation of bond effects. A large effect of the π bonds is to decrease the molecular ionization potential, and there is also some correlation with positron-molecule binding energies with the types of molecular bonds. However, the measurements for benzene, which has a higher E_i and a large ε_B , and for the chloroethylenes, with lower E_i and smaller ε_B , suggest that the correlation is likely more related to the strength of the positron interaction with the bond electrons, rather than directly linked to the absolute E_i , although both effects could be occurring. One might speculate that the chlorine atoms perturb the π bonds such that the orbitals are different than in the rings, even though E_i is also reduced. It may also be that the larger core size of the chlorine atom results in pushing the positron wave function farther away, thus limiting the interaction with the bond and subsequently reducing ε_B . Both of these considerations would argue that it is the nature of the bond that matters most in the interaction with the positron.

These experimental data and the interpretation presented here were also discussed in the context of the results of the recent many-body theory of Hofierka *et al.* [13]. In particular their calculation included the important effect of virtual positronium in enhancing ε_B . Relevant to the current discussion, their calculations for molecules with π bonds demonstrated a strong dependence on the molecular orbitals and showed that the strongest interaction is often not necessarily with the orbital that sets E_i . Thus, absolute E_i will not necessarily be the parameter that sets ε_B . Rather, it is the structure of the electronic orbitals and how they interact with the positron that dominate the correlation interaction.

Evidence, from the experiments, model-potential calculations, and many-body theory, supports the idea that the nature of the bonds has an important contribution that goes beyond what is seen in the global parameters. This does not mean that simple relationships cannot be found among particular molecular series. It is clear these relationships do exist when the interactions are similar, the best example being saturated alkane chains. Instead, as with geometry, the electronic structure of the bond is another important parameter that needs to be considered, whose effects are not always proportional to the changes in global parameters. Due to these less direct relationships, a formula for molecules with one type of bond will not likely be transferable to molecules with different bonds, regardless of the similarity of other global molecular parameters.

ACKNOWLEDGMENTS

We would like to thank G. Gribakin, A. Swann, and D. Green for many helpful comments and suggestions related to the current work. This work was supported by the U.S. NSF, Grant No. PHY-2010699.

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