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Resonant Annihilation and Positron Bound States in Benzene

S. Ghosh,[*] J. R. Danielson,[†] and C. M. Surko[‡]
Physics Department, University of California San Diego, La Jolla, California 92093, USA

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Positrons attach to molecules in vibrationally resonant two-body collisions that result in greatly enhanced annihilation rates. Measurements of annihilation as a function of positron energy are presented for benzene using a cryogenic, trap-based beam. They establish a positron binding energy of 132 ± 3 meV to test state-of-the-art theoretical calculations, and they exhibit many unexpected resonances, likely due to combination and overtone vibrational modes. The relationship of these results to the unique π-bonded structure of benzene is discussed.

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Positron interactions with matter are of interest in numerous contexts including positron emission tomography, materials studies, the formation and study of antihydrogen, and understanding astrophysical phenomena [1–10]. While some aspects of these interactions are well understood, there are a number of important outstanding questions. One fundamental question is the extent to which electron-positron correlations, including virtual positronium formation, contribute to positron interactions with and binding to atoms, molecules, and condensed matter systems. While such effects are believed to be an important, if not a dominant, component of positron binding to nonpolar materials, they have proven difficult to treat theoretically.

Positrons are predicted to bind to various types of ordinary matter; however the only available experimental data are for molecules where the positron can couple to the target via vibrational Feshbach resonances (VFR) [9]. Thus the studies reported here are expected to provide fundamental insights into positron interactions with matter relevant not only to molecules but to the atomic and condensed matter systems as well.

This Letter focuses on the annihilation spectrum of benzene, C_6H_6. It has a high degree of symmetry including a unique π-bonded structure. It plays an important role in a number of fields ranging from chemistry and chemical physics to the composition of the interstellar medium [8,11]. Earlier measurements indicated that the positron-benzene binding energy E_b was unexpectedly large [12] as compared, for example, to the arguably analogous ring molecule cyclohexane. In addition, the benzene annihilation spectrum was found to be qualitatively different (with significantly broader features) than that observed in alkane and cycloalkane molecules, to the extent that there were questions as to whether the mode identification and binding energy were correct. The Letter presented here focuses on these issues.

Presented here are new, high-resolution measurements for the annihilation spectra of benzene and four deuterated isotopologues as a function of positron energy made with a cryogenic, trap-based positron beam. The increased energy resolution permits precise measurements of E_b for all molecules studied, and the inclusion of partially deuterated molecules facilitates a more certain mode identification. Taken together, the protonated and deuterated molecules have the same binding energy, 132 meV, to within ±3 meV. These measurements test theoretical predictions [13–15] and place stringent limits on the extent to which deuteration changes E_b.

While the largest peaks in the benzene and deuterated benzene spectra are the C-H/C-D vibrational stretch-mode resonances, a broad spectrum of resonances is observed at lower energies in all molecules studied. The term "broad spectrum" is used here to denote a region of enhanced annihilation where, although there is some structure, identification of individual resonances is not possible with current techniques. Previous annihilation measurements were unable to resolve these features from the C-H stretch resonances. This spectrum is unusual given that these resonances appear in a region of energies lacking fundamental vibrational modes. The spectral weight of these features in benzene contributes 70% of the total, thus providing evidence of another, potentially new and different paradigm for resonant positron annihilation in molecules.

The results presented here for both E_b and the annihilation spectrum as a function of incident positron energy are discussed in the context of the unique π-bonded structure of benzene and recent theoretical predictions.

In the case of dipole-allowed excitation of fundamental vibrational modes, a theory of positron attachment successfully predicts the annihilation rate as a function of incident positron energy (henceforth the annihilation spectrum) for small molecules [16]. The resonance condition is

$$E_r = \hbar\omega_\nu - E_b \tag{1}$$

where E_b is the positron-molecule binding energy, $\hbar\omega_\nu$ is the energy of the vibrational mode, and E_r is the incident positron energy at the resonance. Thus if the $\hbar\omega_\nu$ are known, the downshifts in the resonances are a direct measure of the binding energy.

For larger molecules, greater enhancements are observed that are believed to be due to intramolecular vibrational energy redistribution (IVR) on the VFR [9]. Discrete resonances due to other than fundamental vibrational modes (e.g., combinations and overtones) have also been observed, albeit infrequently [17]. A large experimental data base has been assembled for annihilation VFR and IVR-enhanced VFR, particularly for the case of hydrocarbon molecules [18]. These data have motivated numerous theoretical studies [13,14,19–27]. They have also established chemical trends in the annihilation spectra and binding energies, including the dependence on molecular structure, isomerization, and chemical substitution [18,28–31].

The experimental apparatus and procedures have been described in detail elsewhere [9,32]. Positrons from a ^{22}Na radioactive source are moderated to electron-volt energies using a solid Ne moderator at 8 K. They are magnetically guided into a Penning-Malmberg-style buffer gas trap at 293 K, where they thermalize to the ambient via inelastic collisions with N_2 and CF_4 molecules. Positrons with mean parallel energy (i.e., energy in motion parallel to the guiding magnetic field) ~0.65 eV are then magnetically guided into a separate cryogenically cooled trap at 50 K, where they thermalize to 50 K via collisions with CO molecules [32].

Pulses of positrons are then guided into the test-gas cell at a 1 Hz rate. The mean parallel energy ranges from 25 meV to hundreds of meV, set by the voltage on the gas cell [33]. The parallel energy distribution is approximately Gaussian with a width $\sigma_\parallel$ [32]. The positron temperature T in the cryotrap determines the energy spread in the plane perpendicular to the magnetic field. For the data presented here, $T = 5 \pm 0.5$ meV, and $\sigma_\parallel = 8.5 \pm 0.5$ meV.

The test-gas pressure is adjusted from 10 to 30 μtorr to keep back scattering to $\leq 10\%$ and minimize the uncertainty in the number of positrons per pulse. Single γ rays are detected using a CsI detector during an 8.5 μs time interval in which the positrons make one round trip through the gas cell. The signal from the CsI detector is integrated over the pulse. In the absence of the target gas, the cell is used as a retarding potential analyzer (RPA) to measure the parallel energy distribution of the positron beam, and adiabatic invariance of the positron orbits is exploited to measure T [33,34]. The annihilation signal is converted to the conventional normalized annihilation rate $Z_{\rm eff}$ [9] using the number of positrons per pulse, the gas pressure, and the path length in the gas cell viewed by the detector. Noise in the data is statistical, and systematic errors are < 15%.

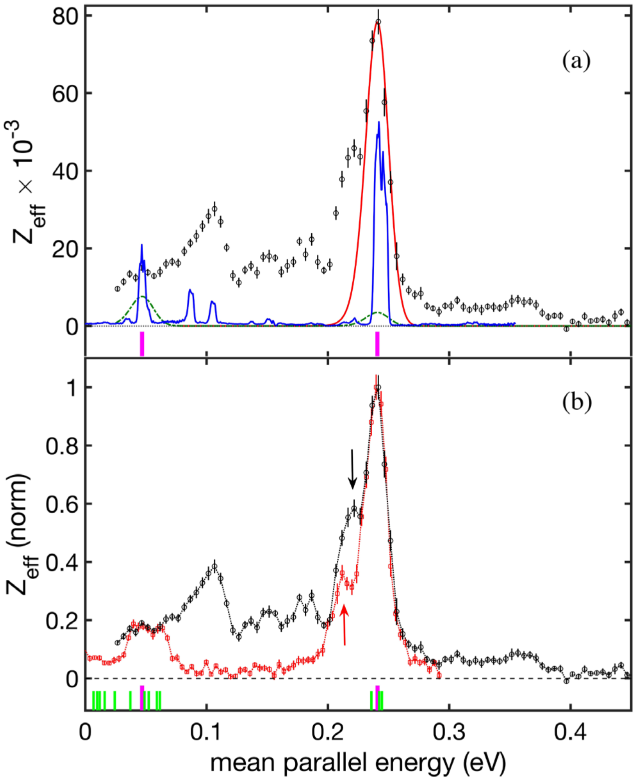

FIG. 1. (a) The positron annihilation spectrum of benzene (open circles) as a function of the mean parallel energy of the positron beam. Vertical magenta bars indicate the locations of the downshifted dipole-allowed vibrational modes. The red curve is the convolution of the beam energy distribution with a delta function at the DA mode position [35,36], downshifted to fit the experimental peak, to yield $E_b = 133 \pm 3$ meV. The blue line is the downshifted infrared absorption spectrum (in arbitrary units) from Ref. [37]. The green dashed-dot line is the prediction of the VFR theory [16] using the dipole coupling strengths from the IR spectrum [38]. (b) The normalized annihilation spectrum for benzene (black circles; magenta bars for DA modes) compared with that for cyclohexane (open red squares; green bars for DA modes), $E_b = 78$ meV. The amplitudes of the large C-H peaks have been normalized, and the cyclohexane data and bars shifted so that the peaks coincide. The peak value for cyclohexane is $Z_{\rm eff} = 1.24 \times 10^5$, a factor of 1.6 larger than benzene.

Shown in Fig. 1(a) is the annihilation spectrum of benzene as a function of the mean parallel energy of the positron beam (i.e., parallel energy is used, since it can be measured directly with the RPA). The energies of the two dipole-allowed (DA) transitions, taken from Ref. [35], are marked with magenta bars. Also shown is the infrared absorption spectrum of benzene downshifted to match the peak due to the C-H stretch mode located at 240 meV in the figure. Using the fit (red curve) and Eq. (1), the binding energy is 133 ± 3 meV. This uncertainty of ± 3 meV includes the energy scale and the resonance fit and is valid for all E_b values in this Letter. The other dipole-allowed mode, located at 50 meV, is either absent or is obscured by the broad spectrum of annihilation at that location.

In Fig. 1(b), the benzene spectrum is compared to that of cyclohexane, the ring-alkane molecule with the same number of carbon atoms. Cyclohexane, as with most molecules studied, exhibits large resonances due to positron coupling to DA fundamental modes, with little or no other structure. In contrast, benzene exhibits a much broader spectrum of annihilation from the C-H peak down to where the measurements stop at 25 meV. A similar, but less intense broad spectrum is observed *above* the C-H stretch peak. Both broad features occur in regions in which DA fundamental modes are absent. Such broad features, extending over ≥ 100 meV in energy, have not been observed in other molecules studied to date.

Defining the annihilation spectral weight in an energy interval (E_1, E_2) as $S(E_1, E_2) = \int_{E_1}^{E_2} Z_{\mathrm{eff}} dE$, the weight in the C-H stretch peak [i.e., under the red curve in Fig. 1(a)] is 31%, the lower plateau contributes 65%, and the upper plateau is 3% of the total spectral weight in benzene. Thus almost 70% of the spectral weight in benzene is due to positron coupling to other than DA fundamental modes. The contrast between benzene and cyclohexane (i.e., representative of molecules studied previously) is illustrated in Fig. 1(b) in the interval of energies 0.1–0.18 eV.

While the most promising candidates for these novel and broad spectral features are unresolved multimode resonances, there is no direct evidence that this is the case. Assuming they are distinct resonances, we have no information as to the number and spacing these resonances, due to limited resolution. These spectral features appear to be different than another spectral feature, statistical multimode resonant annihilation, which includes multimode resonances at all orders and increases continuously from much higher energies as energy is decreased [39].

The benzene annihilation spectrum in Fig. 1 exhibits other noteworthy features. There is a peak approximately 25 meV below the C-H stretch resonance [black arrow in Fig. 1(b)]. While this feature has been observed in alkanes and cycloalkanes [e.g., red arrow, Fig. 1(b)] [17], it is larger in amplitude relative to the C-H peak in benzene. Another notable feature is a broader peak in annihilation at approximately 100 meV in mean parallel energy which may be associated with the combination bands seen in the IR spectrum.

In cyclohexane and other ring alkanes and alkanes, there are typically two sharp rises in the spectrum as positron energy is decreased, unless the binding energy becomes so large as to obscure the lower one. They are associated with DA fundamental vibrations and can be used with Eq. (1) to determine the positron binding energy. However, in benzene, only the high-energy C-H stretch peak is available for this purpose. In the previous benzene measurements, this peak was found to be unusually broad which made it difficult to determine E_b. The use of the cryobeam data better resolves the C-H peak [cf. Fig 1(a)], thus providing a more precise measurement of E_b. Benzene deuteration studies were also conducted to confirm the mode identification and verify this binding energy measurement.

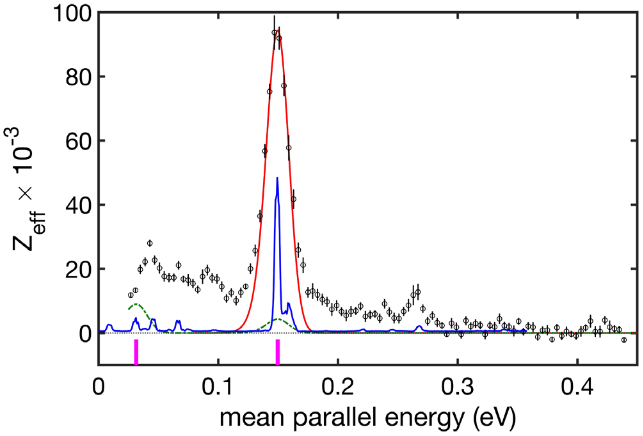

FIG. 2. The annihilation spectrum for benzene-d6. Magenta bars indicate the downshifted DA fundamental modes. The red curve is the convolution of the positron beam with a delta function at the downshifted C-D mode position to yield $E_b = 130 \pm 3$ meV. The blue line is the downshifted infrared absorption spectrum (in arbitrary units) [37]. The green dashed-dot line is the prediction of the VFR theory [16] using the dipole coupling strengths from the IR spectrum [38].

Shown in Fig. 2 is the spectrum of benzene-d6. The DA C-D modes, taken from Ref. [35], and the IR spectrum have been downshifted to coincide with the annihilation spectrum. Using the fit (red curve) and Eq. (1), this corresponds to a binding energy of 130 ± 3 meV. The broad spectra of annihilation above and below the C-D peak are qualitatively similar to those in benzene. The measurements do not extend to sufficiently low energies to determine whether there is a peak at the location of the lower energy DA mode. A peak tens of meV below the C-D stretch mode, similar to that below the C-H peak in benzene, is not evident in benzene-d6.

Shown in Fig. 3 are the spectra for three partially deuterated benzenes, benzene-d1, -d3 and -d5. The high-energy plateau above the C-H stretch peak appears to be less prominent in the partially deuterated benzene molecules, and very small in benzene-d5. A peak near 100 meV is evident in all spectra measured, but less prominent in benzene-d5. The magnitudes of Z_{eff} at the dominant C-H/C-D stretch peaks are ordered according to the number of the DA fundamental C-H/C-D modes [35]: one in benzene and benzene-d6, one C-H and one C-D in benzene-d3, 1 C-D and 5 C-H in benzene-d1, and 5 C-D and 1 C-H in benzene-d5.

The E_b values were determined from Eq. (1) and the shifts in the mode frequencies required to match the C-H and C-D peaks. All DA modes were used to fit benzene-d3. However the multiple DA C-H (C-D) modes in benzene-d1 (benzene-d5) [35,40] led to an ambiguity, and so only the C-D (C-H) mode was used for those molecules (red curves

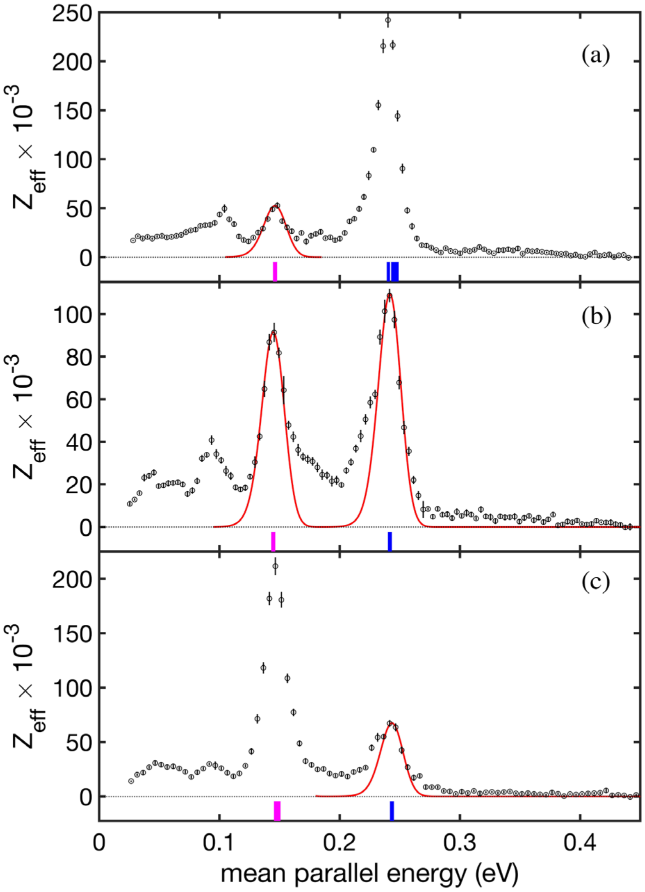

FIG. 3. The annihilation spectrum for (a) benzene-d1, (b) benzene-d3, and (c) benzene-d5. Magenta and blue bars are downshifted DA C-D and C-H modes [35]. The red curve is the convolution of the positron beam with delta functions at the downshifted DA mode positions, yielding (a) $E_b = 132$, (b) 134, and (c) 132 meV.

in Fig. 3). The result is $E_b = 132 \pm 3$, 134 ± 3, and 132 ± 3 meV, respectively, for benzene-d1, -d3, and -d5. Taken together, the partially deuterated benzene measurements and those for benzene and benzene-d6 yield an average value of the benzene binding energy of 132 ± 3 meV. If one were to postulate a dependence of E_b on deuteration, as has been observed in electron attachment to molecules [41], the measurements presented here indicate that it is small (i.e., within the error bars of the measurements).

The binding energy for benzene is much larger, for example, than that for cyclohexane (i.e., 133 meV vs 78 meV). This raises an important question as to the mechanisms of positron binding in benzene. There have been a number of predictions for the binding energy of benzene using various calculational techniques and other predictions using global parameters and extrapolations from test sets of molecules. Theoretical calculations have found the prediction of positron binding to nonpolar molecules (including benzene) to be particularly challenging [15,25,26]. Since benzene is unique in terms of molecular structure, scaling estimates using global parameters are difficult. Nevertheless, with benzene as a motivating example, a global-parameter scaling model was proposed that included the number of molecular π bonds (three in benzene) as an additional term in the binding energy [22, 24].

A recent *ab initio* many-body theory provides important insights into positron-molecule binding, particularly relevant to nonpolar molecules such as benzene [15]. This theory indicates that the virtual positronium formation and positron-hole contributions to the correlation energy are crucial to accurate predictions of positron-molecule binding energies and that π bonds, when present in a molecule, make a particularly important contribution to the binding energy.

It is well known that the π-bond electron density peaks above and below the plane of the benzene molecule. According to the theory of Ref. [15], the calculated positron density in the benzene bound state also appears to peak in these spatial regions. Qualitatively, this can be expected to enhance the binding energy by providing electron density away from the repulsive atomic cores. The prediction of Ref. [15] for E_b in benzene is 116 meV, which is within 15% of the measured value. Generally, the addition of π bonds appears to increase binding energies. Virtual positronium formation and the electron-geometry effect associated with the π bonds appear to be important contributions to this effect.

Annihilation spectra have been studied in more than 80 molecules. While multimode annihilation resonances and those due to electric quadrupole coupling to fundamental modes have been observed in selected molecules, in the majority of molecules, the most prominent features are associated with DA fundamental modes. The spectrum of benzene is a notable exception. Because of symmetry, there are just two fundamental DA modes in benzene and benzene-d6 in the region of energies studied, and the measurements show that one of them, if present, makes only a small contribution. The majority of the spectral weight in the annihilation spectrum appears to be due to other than fundamental modes. While benzene has an unusually high degree of symmetry and a unique electronic structure, it is unclear at present whether this might be the origin of these contributions to the annihilation spectrum.

In summary, the annihilation spectra of benzene and deuterated and partially deuterated benzene molecules have been studied using a cryogenic, high-resolution positron beam. Exploiting the ability to average the measurements of the five benzene molecules studied, the positron-benzene binding energy was determined to be 132 ± 3 meV. Recent theory indicates that a major contribution to the relatively large value of E_b is due to electron-positron correlations. These effects, which can be studied in detail in molecules, are likely to be relevant to positron interactions with atoms and condensed matter systems as well.

Finally, the benzene annihilation spectrum exhibits unusually large components of (likely) multimode vibrational resonances. Although the IR spectra have features associated with combination and overtone modes in this region, it is unclear whether they can provide sufficient coupling to explain the observed enhancements in annihilation. Beyond dipole coupling, it is also possible that some other positron-molecule coupling mechanism is responsible for these features, and so further theoretical work is encouraged. Study of these features in the partially deuterated molecules could also give further insight into specific mode combinations that might be responsible for the observed enhancements.

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[*]soumen@physics.ucsd.edu
[†]jrdanielson@ucsd.edu
[‡]csurko@ucsd.edu

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