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Energy-resolved positron annihilation rates for molecules

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The development of high resolution positron beams has enabled measurements of annihilation rates for molecules as a function of incident positron energy. Vibrational Feshbach resonances in these spectra provide evidence for the existence of positron-molecule bound states. In this paper we present further studies of this phenomenon. Evidence is presented for positronically excited bound states (i.e., in addition to the ground state) in $C_{12}H_{26}$ and $C_{14}H_{30}$. Measurements of the annihilation spectra of the halomethanes, CH_3F, CH_3Cl, and CH_3Br, exhibit strong resonances that vary significantly with the substituted halogen. Annihilation spectra for linear alkanes and ring molecules are compared. Annihilation spectra and infrared absorption spectra are compared for a number of molecules. Finally, annihilation rate measurements are presented for a variety of molecules at energies $\geqslant$0.5 eV (i.e., above the vibrational resonances). These provide a measure of the annihilation rates in the absence of vibrational resonances.

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I. INTRODUCTION

As antimatter has become more widely available in the laboratory, it is increasingly important to understand in detail the interactions between antiparticles and ordinary matter. Obtaining such an understanding presents significant challenges to modern atomic and molecular physics. The presence of the light electron and positron, absent the exchange interaction, can lead to strong electron-positron correlations difficult to model using the quantum chemical techniques so successful in conventional electron systems. In particular, the positronium channel, whether open or closed, is essential for many processes of interest but difficult to incorporate into theoretical calculations.

Early measurements of positron-on-molecule annihilation using thermal positrons revealed a number of unusual phenomena. One of the most important observations was that annihilation rates for some molecules exceed the free electron annihilation rate by many orders of magnitude [1–3]. The dimensionless parameter Z_{eff} is a quantitative measure of this enhancement. This quantity is defined by normalizing the measured annihilation rate by the rate of annihilation of positrons in a free electron gas of the same number density [4], namely:

$$Z_{\mathrm{eff}} = \frac{\Gamma}{\pi r_0^2 c n_m}. \tag{1}$$

In this expression, Γ is the annihilation rate, r_0 is the classical electron radius, c is the speed of light, and n_m is the molecular number density. The parameter Z_{eff} has been crudely interpreted as the *effective* number of electrons per molecule which contribute to annihilation, assuming that the positron and electron motions are not correlated. However, for molecular species such as hydrocarbons, Z_{eff} is found to be so much larger than Z, the number of electrons in the molecule, that interpretation of Z_{eff} as an effective number of electrons clearly fails. In fact, in the alkanes (C_nH_{2n+2}), this rate grows exponentially with the number of electrons [5,6]. As we discuss below, this is due to highly correlated states in which the positrons form long-lived resonances with target molecules.

The development of the Penning-Malmberg buffer-gas trap has led to a new class of experiments by transforming the standard warm, continuously moderated positron beam into a colder (25 meV FWHM), pulsed positron beam [8]. The unusual annihilation effects observed when thermal positrons interact with hydrocarbons can now be resolved as a function of positron energy. Experiments of this type [6,7] revealed remarkable new features, such as those illustrated in Fig. 1. This figure shows the normalized annihilation rate, Z_{eff}, as a function of positron energy for propane and hexane. In propane, for example, the annihilation is enhanced near the energies of vibrational modes. The most prominent peak is associated with the C-H stretch vibrational mode at 370 meV, but similar effects are observed throughout the region of energies of the other vibrational modes. In larger alkane molecules, such as hexane, the C-H peak is significantly larger and much further shifted below the C-H stretch mode energy.

These observations are qualitatively consistent with a model involving vibrational Feshbach resonances (VFR), proposed by a number of authors [3,9], and developed in detail by Gribakin [10]. The VFR enhancement of annihilation rates requires the existence of a bound state of the positron and the target molecule. At specific incident positron energies, the ground state molecule plus an unbound positron is nearly degenerate with the vibrationally excited molecule with a bound positron, namely

$$E_{v=0} + \epsilon_k = E_{v=1} - \epsilon_b, \tag{2}$$

where $E_{v=0}$ and $E_{v=1}$ are the ground and vibrationally excited energies of the molecule, ϵ_k is the kinetic energy of the positron, and ϵ_b is the binding energy of the positron to the molecule. In this resonant state, the overlap between the positron and electron wave functions is greatly enhanced, which in turn greatly enhances the probability of annihilation.

As shown in Fig. 1, this effect is manifested in the measured annihilation spectra by large resonant enhancements associated with the molecular vibrational modes. Due to the

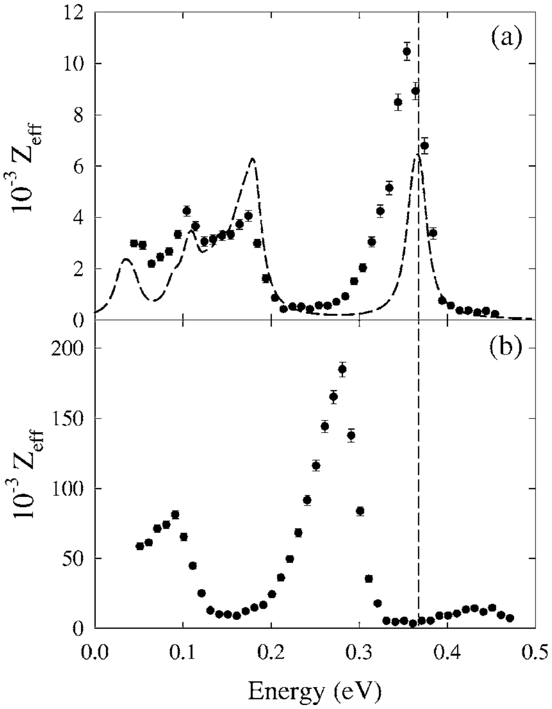

FIG. 1. The energy-resolved Z_{eff} spectra (●) for (a) propane (C_3H_8); and (b) hexane (C_6H_{14}), both scaled by a factor of 10^{-3} [6,7]. Also shown in (a) is the vibrational mode spectrum for propane (---), arbitrarily scaled in amplitude and broadened by a Lorentzian line shape with a width of 10 meV. The vertical dashed line indicates the position of the C-H stretch mode in these molecules.

binding of the positron and molecule, these resonant features occur at an energy lower than that of the vibrational mode by the positron-molecule binding energy, ϵ_b, which ranges from a few tens of meV for smaller alkane molecules (e. g., propane and butane) to more than 200 meV for large molecules (e. g., $C_{12}H_{26}$). In the alkanes, the binding increases linearly with molecular size, while the annihilation rate, Z_{eff}, grows exponentially with molecular size, reaching $\sim 10^7$ for $C_{12}H_{26}$ [6].

The mechanism for exponential growth of Z_{eff} is still open to debate. However, it is believed that in the case of alkane molecules with more than two carbon atoms, vibrational energy redistribution is responsible [3,10,11]. According to this model, the positron is captured into a "doorway state," usually by exciting a fundamental vibrational mode of the molecule. This vibrational energy is then rapidly redistributed into one of the many degenerate combination modes, greatly enhancing the number of available resonant states and hence the overall annihilation rate. If the total density of vibrational states is included, the estimated growth of Z_{eff} is too large [11]. One way to moderate this is to include fewer modes or to allow for inelastic detrapping. In the latter case, a component vibration with energy greater than positron binding de-excites, ejecting the positron before annihilation can occur.

In this paper, the results of studies of the energy-resolved annihilation spectra for a range of molecules are presented with the goal of gaining further insight into this phenomenon of enhanced annihilation rates in molecules. A primary focus of the present study is understanding the effect of structural variations beyond those observed in previous studies of alkane molecules. It will be shown that small changes frequently affect not only the local mode strengths and positions but also global features such as binding energies and the overall magnitudes of Z_{eff}.

Data are presented for the largest alkane molecules studied to date, $C_{12}H_{26}$ and $C_{14}H_{30}$, that provide evidence for a second positron bound state (i.e., a *positronically excited* bound state). Since large molecules are expected to be more difficult to treat theoretically, the results of additional studies of small molecules are presented, namely data for the halogenated methanes CH_3F, CH_3Cl, and CH_3Br. These molecules exhibit large resonant enhancements with positions and strengths that depend on the particular halogen. To test the dependence of the observed VFR on molecular conformation, the spectra of three-carbon and six-carbon alkanes are compared with the analogous ring-shaped molecules (including benzene in the six-carbon case).

For further insight into the positron capture process, annihilation rate spectra are compared to infrared absorption spectra. The infrared data provide a quantitative measure of the long-range dipole coupling to vibrational modes. Continuing this theme, measurements of the infrared absorption spectra for hexane, 1-fluorohexane, nonane and 1-fluorononane were made and compared with previously published Z_{eff} data. While the addition of a fluorine atom to these molecules produces a large effect on the annihilation peak associated with the C-H vibrational mode, very little change is observed in the corresponding infrared spectra.

Finally, the annihilation spectra were measured for a number of molecules in the region of energies above that of the vibrational modes but below the positronium formation threshold. These spectra, which are approximately constant in this region of energies, provide a measure of the direct annihilation rate, absent vibrational resonance effects. The paper ends with a brief set of conclusions and suggestions for future work on problems of interest.

II. EXPERIMENT

The experimental arrangement used to measure Z_{eff} is described in detail elsewhere [6,7]. Positrons from a radioactive ^{22}Na source are slowed by a solid neon reflection moderator and magnetically guided into a three-stage Penning-Malmberg buffer-gas trap. A 1.5 kG magnetic field confines the positrons in the radial direction. Positrons are trapped in a potential well in the axial direction using an N_2 buffer gas. The trapped positrons cool to the temperature of the electrodes in the third stage of the trap by collisions with N_2 and CF_4 molecules. They are then forced out of the trap by raising the electrostatic potential in the third trapping stage and are magnetically guided through a gas cell filled with a low pressure (e.g., $\sim 10^{-4}$ Torr) of the gas to be studied. As the positrons pass through this gas cell, annihilation events are recorded by detecting the resulting 511 keV annihilation radiation. The annihilation rate is calculated from the number of annihilation events, the number of positrons transiting the gas cell, the length of the cell, the pressure of the test gas, and the energy of the positrons in the gas cell. It should be noted that in all plots of Z_{eff}, there is an estimated overall uncertainty of ~10%, due largely to uncertainties in the test-gas pressure.

Some of the infrared (ir) absorption spectra presented in this paper were taken using a Fourier-transform infrared spectrometer. The samples were diluted to 0.2 molar concentration in a carbon disulfide solvent. Since the exact path length in the sample cell was not known, the absolute molar absorptivities could not be determined. However, since the same cell geometry was used for all molecules studied in this way, the *relative* magnitudes are reliable. The background due to the solvent was measured and subtracted to obtain the reported ir spectra. In addition to these spectra, where indicated, ir spectra for other species were taken from the NIST chemistry webbook database [12]. These NIST data have arbitrary absorptivity scales that are independent of each other.

Finally, for other molecules, computations of oscillator strengths for dipole-allowed infrared transitions were performed using the GAMESS quantum computational package [13] using a 6-31G(*d*) basis set both for optimizing the geometry and computing the Hessian matrix.

III. EVIDENCE FOR A SECOND POSITRON BOUND STATE

A. Dodecane

It is plausible that, as the attraction between the positron and a target molecule increases with increasing molecular size, the resulting attractive potential well might become deep enough to support a second bound state. In this case, new resonances might be expected to appear in larger alkanes just below the energies of the molecular vibrational modes. These resonances would correspond to the first (positronically) excited states of the vibrationally excited positron-molecule complex. As the size of the molecule is increased, these resonances would be expected to move to lower energy (i.e., corresponding to increased binding).

Pursuing this hypothesis, we examined the Z_{eff} spectrum for dodecane ($C_{12}H_{26}$), shown in Fig. 2. This spectrum exhibits a large peak associated with the C-H stretch mode at an incident positron energy ~150 meV, downshifted by about 220 meV from the C-H stretch energy and consistent with the trend for other alkanes studied [6]. It also has a second peak at 360 meV, much smaller in amplitude than the peak associated with the positronic ground state. As there are no fundamental modes above the C-H stretch mode, this would appear to be the excited state postulated above. To rule out possible interactions with multiple target particles, the annihilation rate Z_{eff} in this energy range was measured for several test-gas pressures. These measurements confirmed that the peak is a two-body effect (involving a positron and a single molecule). While it cannot be entirely ruled out, there are reasons to believe that this second peak is not simply a combination mode. In particular, no other combination modes have been observed in alkanes to date, and the energy of the peak does not correspond to a simple, two-mode combination.

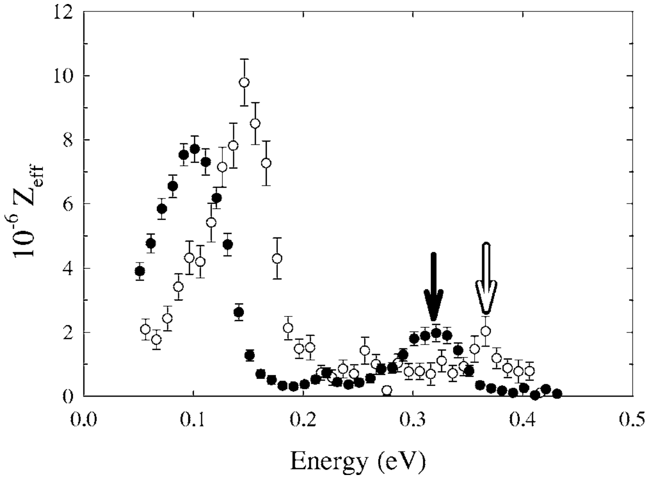

FIG. 2. The energy-resolved Z_{eff} spectrum for (○) dodecane ($C_{12}H_{26}$); and (●) tetradecane ($C_{14}H_{30}$), with the former scaled by a factor of 10^{-6} and the latter scaled arbitrarily. Arrows indicate the locations of the second peaks interpreted here as evidence for positronically excited bound states. See text for details.

B. Tetradecane

Intrigued by the dodecane result, we measured the spectrum for tetradecane ($C_{14}H_{30}$). It is also shown in Fig. 2. In this case, the tetradecane pressure is uncertain due to the extremely low pressure required for this high Z_{eff} material. Since an absolute normalization of Z_{eff} cannot be determined without knowledge of this pressure, the spectrum in Fig. 2 has been scaled arbitrarily for comparison with the dodecane spectrum. In the tetradecane spectrum, both the higher and lower energy resonances are clearly visible (i.e., corresponding to the positron ground state and first excited state). As shown in Fig. 3, the binding energy corresponding to the primary C-H stretch peak in tetradecane is consistent with the trend reported for the other alkanes [6], namely a linear relationship between binding and molecular size. The higher lying, excited-state peak also shifts a similar amount, appearing to maintain a fixed energy above the first peak.

These observations led Gribakin and Lee to study this effect in the alkanes using a zero-range potential model [14].

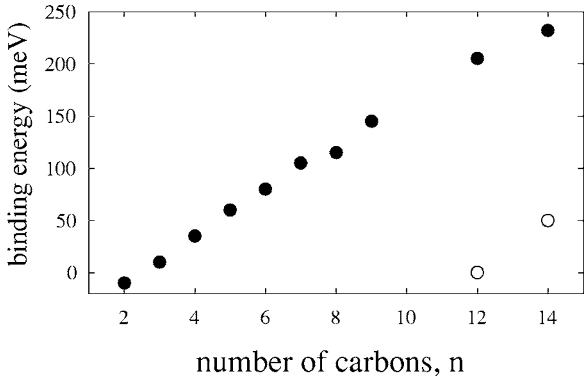

FIG. 3. Binding energy as a function of the number of carbons in alkane molecules (●). The binding energies of two positronically excited bound states (○) are also shown.

In particular, they extended a model used previously to describe krypton dimers [15] and represented the CH_2 and CH_3 groups in alkanes by zero-range potentials with identical scattering lengths. The binding energy could then be determined from the total scattering length of the composite molecule. Using this approach, they calculated positron binding energies as a function of the number of carbons, with the monomer scattering length chosen such that propane would be very weakly bound.

Their predicted binding energies agree within a factor of 2 with those observed experimentally. They also found that a second bound state solution first appears in the 10 carbon alkane, which is slightly smaller than the onset number of carbons observed in experiment. Essentially, increasing the number of carbon potentials increases the binding of all positronic states until the next excited state solution is drawn below the continuum to become a true bound state. Considering the simplifications made in the model, this degree of agreement is encouraging.

The resonance associated with the positron-molecule ground state is much larger than the excited state resonance, even though both are mediated by the same C-H vibrational mode. This effect occurs naturally in the VFR model if the positron kinetic energy is quickly redistributed among the vibrational modes of the molecule and detrapping is allowed [10]. The deeper the binding, the less likely it is that a vibration (or a nonlinearly coupled combination of vibrations) will have sufficient energy to eject the positron. Hence Z_{eff} is enhanced. In addition, deeper binding results in a larger positron density in the vicinity of the molecule, which can also enhance Z_{eff}.

IV. ANNIHILATION ON HALOGENATED METHANES

While VFR effects are very large and well documented in large molecules, the size of these molecules virtually precludes any first-principles theoretical description in the foreseeable future. Hence, we were motivated to study smaller molecules that exhibit resonances in Z_{eff} (i.e., molecules with considerably fewer vibrational modes). The halogenated methanes fit this description well and provide an opportunity to examine further the local and global factors that affect Z_{eff} spectra. By substituting various halogen atoms for a hydrogen, one can change the physical properties of the molecule and alter its mode frequencies. Like deuterium substitution, this can help in the identification of particular modes responsible for the VFR.

The Z_{eff} spectra of CH_4, CH_3F, CH_3Cl, and CH_3Br are shown in Fig. 4. The methane molecule, CH_4, is relatively featureless, likely due to its high degree of symmetry, which results in weak infrared activity and no dipole moment. A featureless spectrum is also observed for CF_4, probably for similar reasons [6]. This featureless spectrum is *not*, however, shared by the rest of the halomethanes studied here. It should be noted that they all have dipole moments exceeding the critical value, $D_{cr}=1.625$ D, required for dipole-bound states [16,17].

When methane's symmetry is broken by the substitution of a fluorine atom to form CH_3F, a peak is observed at

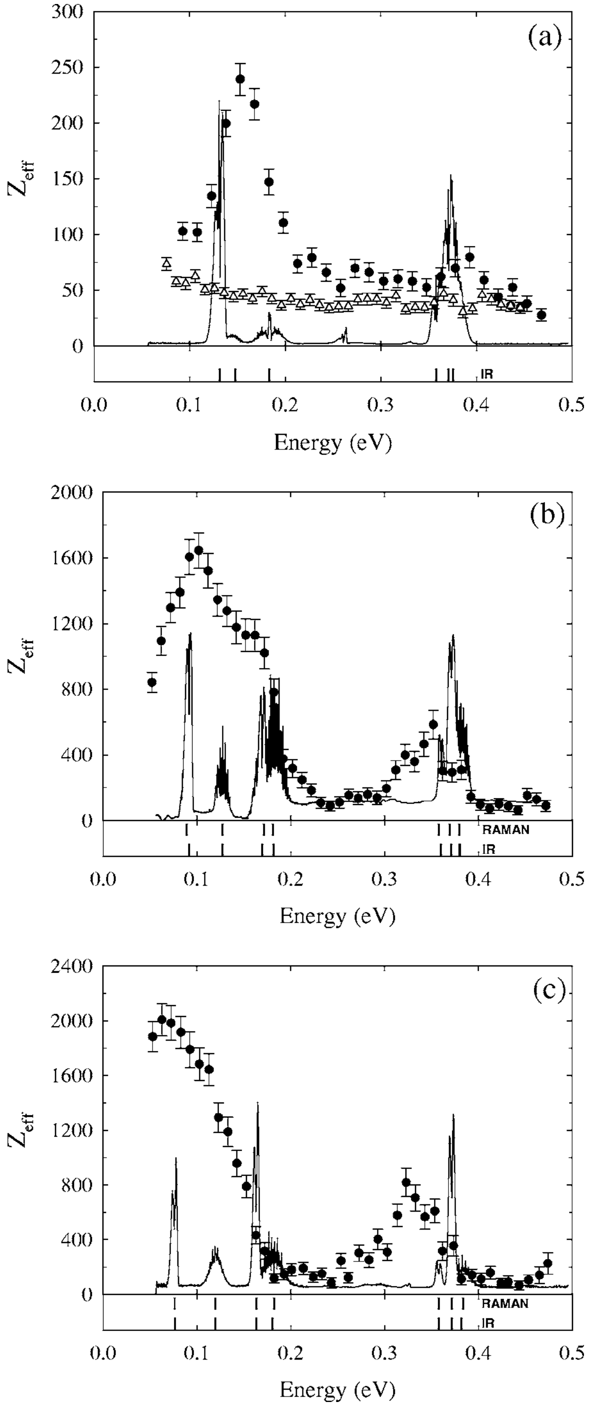

FIG. 4. Energy-resolved Z_{eff} spectra for (a) CH_4 (△) and CH_3F (●); (b) CH_3Cl (●); and (c) CH_3Br (●). The lines (—) represent the respective experimental ir absorption spectra from the NIST data base (normalized arbitrarily and collected under different conditions). The bottom panel in each plot indicates the experimentally determined energies of infrared- and Raman-active vibrational modes [12]. Note that the ir modes and spectra in (a) correspond to CH_3F, whose Raman modes are unavailable.

~150 meV and a second, much weaker, peak at ~395 meV. The first is likely due to either the C-H bend mode or the C-F stretch and bend modes, which are too close to resolve. The second is about 20 meV *above* the C-H stretch, which is the highest energy fundamental mode. This is an exceptional result in that, to date, no other molecule has exhibited such a positive energy shift. This peak position would seem incompatible with VFR theory, which requires a positive binding energy for the existence of a resonance. This inconsistency could, in principle, be resolved if the energy of the molecular vibrations were sufficiently increased by the presence of a positron.

As the size of the halogen is increased, a number of new trends can be seen. The C-H stretch peak shifts systematically to lower energies: 395 meV for CH_3F, 352 meV for CH_3Cl and 323 meV for CH_3Br. This indicates increased binding. In addition, both the high- and low-energy peaks grow dramatically. The peak around 150 meV grows nearly an order of magnitude from CH_3F to CH_3Cl and becomes significantly wider. In contrast with results for the alkanes, this study of the halogenated methanes provides insight into the importance of other parameters besides the number or type of vibrational modes in determining the magnitude and the energy spectrum of Z_{eff}. In the case of the halogenated methanes, their large molecular dipole moments and the halogen atom polarizabilities are likely relevant and potentially important parameters. It is hoped that these data could be used to benchmark theoretical calculations of the Z_{eff} spectra for relatively small molecules.

The Z_{eff} spectrum of CH_3Cl shows three distinct peaks. The high energy peak is due to one or more of the C-H stretch modes. The remaining two low energy peaks, which nearly overlap, are likely due to the C-Cl modes and C-H bend modes, respectively. The low energy modes spread apart between CH_3F and CH_3Cl which may explain why the two peaks can be resolved in CH_3Cl and not CH_3F. The spectrum of CH_3Br is more difficult to evaluate as its lowest energy peak occurs near the lower end of our measurement range, at ~50 meV. With this in mind, the second low energy peak still appears to be missing if a uniform shift due to binding is assumed.

The ir absorption spectra in Fig. 4 do not appear to be strong indicators of the Z_{eff} peak heights. Nevertheless, each peak can still be associated with a particular ir-active mode. The data shown in Fig. 4 motivated a calculation of Z_{eff} for CH_3Cl and CH_3Br assuming the positrons are captured by infrared-active modes [18]. It indicates that all modes contribute nearly equally to Z_{eff} and estimates binding energies of 8.5 and 12 meV, respectively.

V. EFFECT OF STRUCTURAL CHANGES—RINGS VS CHAINS

A. Three carbon chains and rings

The molecules propane (C_3H_8) and cyclopropane (C_3H_6) provide a comparison of a relatively small linear alkane molecule with the analogous ring molecule. The cyclopropane ring is formed by eliminating the terminal methyl groups on the alkane chain, so that the end carbons can be joined. These two molecules have similar C-C and C-H stretch and bend modes, albeit cyclopropane has fewer of them. Their Z_{eff} annihilation and infrared spectra are shown in Fig. 5. These data potentially provide insight into the importance of terminal CH_3 groups and carbon backbone motion.

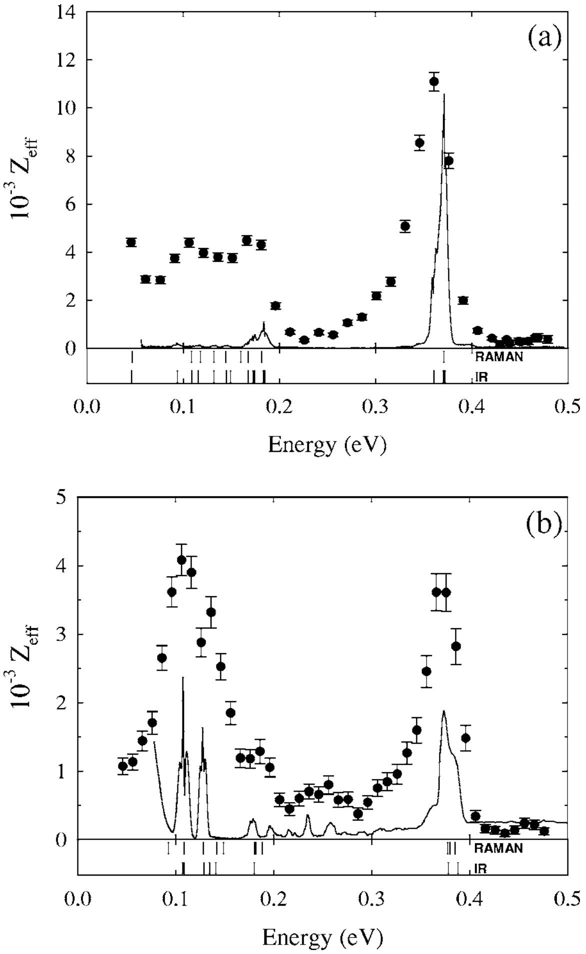

FIG. 5. The energy-resolved Z_{eff} spectra (●) for (a) propane (C_3H_8); and (b) cyclopropane (C_3H_6), both scaled by a factor of 10^{-3}. The lines (—) represent the experimental ir absorption spectra, arbitrarily normalized. The lower panels indicate the energies of ir and Raman active vibrational modes [12].

The C-H stretch annihilation peaks in propane and cyclopropane occur at similar locations, as do their vibrational mode energies. The small downshifts that are observed indicate that these molecules have similar, small positron binding energies. As discussed in the next section, the similar binding energies of propane and cyclopropane are consistent with results for hexane and cyclohexane.

The C-H stretch annihilation peak in cyclopropane is only about one-third the height of the analogous peak in propane. Forming a ring from propane involves reducing the number of C-H stretch modes by 25%. Considering the measurements and models for alkanes in which the Z_{eff} peak height grows exponentially with the number of C-H stretch modes, one might expect the peak height to decrease faster than the number of modes. Alternatively, this difference between propane and cyclopropane could indicate the importance of the C-H modes associated with terminal methyl groups in determining the C-H peak height.

An unusual feature in the cyclopropane spectrum, as compared to propane, is the peak at ~100 meV which is the same magnitude in Z_{eff} as the broad plateau at ~100 meV in propane. Rather than exhibiting a decrease in magnitude with decreasing mode density, this feature, presumably due to the C-H bend modes is much narrower in cyclohexane, more closely approximating the ir spectrum of this molecule (i.e., as compared to propane). As discussed below, this behavior is qualitatively different than that observed in cyclohexane, where the amplitude of the entire spectrum is proportionately lower than that in hexane at all vibrational energies. Perhaps propane is at a critical size where the mode density is low and individual modes become more important. Thus, resonances in the spectrum might be switched off as certain modes disappear, as is the case when the ring molecule is formed.

The infrared spectra of propane and cyclopropane are also shown in Fig. 5. The ir and Z_{eff} spectra of cyclopropane are relatively similar. However this is not true for propane. The ir spectrum of propane has a C-H peak that dominates the rest of the spectrum by more than an order of magnitude in amplitude, with virtually no ir activity below 180 meV. In contrast, the Z_{eff} spectrum has more evenly weighted peaks throughout the energy range of the vibrational modes. This is another example where there is seemingly little connection between the ir magnitudes and Z_{eff} magnitudes.

B. Six carbon chains and rings

Continuing the comparison of chain and ring hydrocarbons, the annihilation spectra of hexane (C_6H_{14}), cyclohexane (C_6H_{12}), and benzene (C_6H_6) are shown in Fig. 6. Cyclohexane, like cyclopropane is formed by connecting the terminal carbons of the alkane. It has nearly the same number of C-H stretch modes as hexane (12, compared with 14 for hexane) and, as can be seen in Fig. 7, the modes are predicted to be similarly infrared active. Note that these ir spectra are computer generated (rather than measurement based) in order to ensure a common normalization. Benzene has the same number of carbons as cyclohexane, but fewer hydrogen atoms by a factor of 2, resulting in double bonds shared among the carbon atoms. This does not significantly affect the energy of its C-H stretch modes but does reduce their number. This is reflected in a significantly weaker ir absorption.

In comparison with hexane, both benzene and cyclohexane have significantly smaller Z_{eff} than the linear molecule. For cyclohexane, this effect cannot be attributed to a decrease in mode number or ir strength. On the other hand, it is an additional indication that the terminal methyl (CH_3) groups may be important in the VFR enhancement of Z_{eff}. Another important issue is the location of the C-H stretch peaks in the Z_{eff} spectra. While the large peaks for hexane and cyclohexane are at approximately the same energy, the largest peak in benzene is significantly lower in energy. If these are all C-H stretch peaks, in the context of the vibrational Feshbach resonance model, this would indicate that positrons bind more strongly to benzene than to the other two molecules. In this interpretation, the binding energy for benzene is ~130 meV as compared to ~80 meV for hexane and cyclohexane.

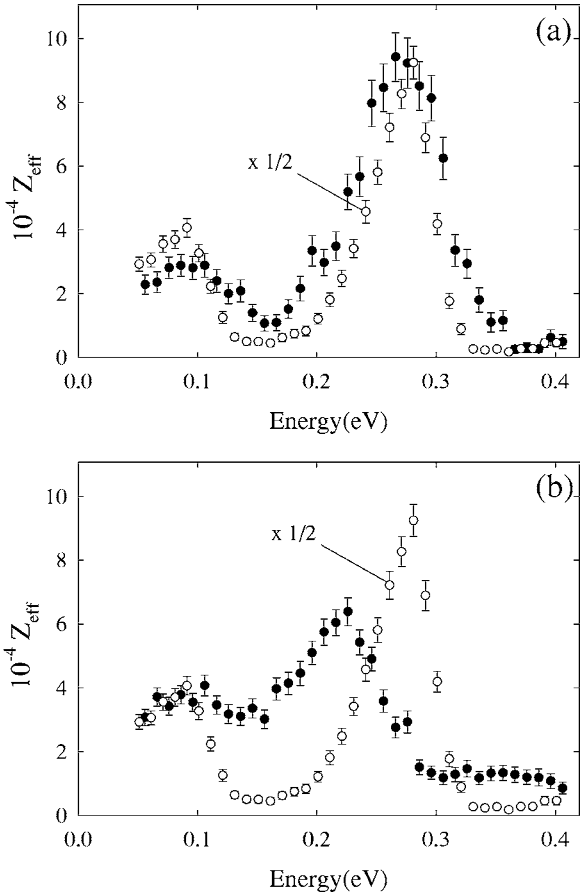

FIG. 6. The energy-resolved Z_{eff} spectra (●) for (a) cyclohexane (C_6H_{12}) and (b) benzene (C_6H_6), both scaled by 10^{-4}. In both figures, the open circles (○) are the data for hexane (C_6H_{14}), scaled by 0.5 for ease of comparison. For reference, the thermal Z_{eff}'s of hexane, cyclohexane, and benzene are 120 000; 20 000; and 15 000, respectively [19].

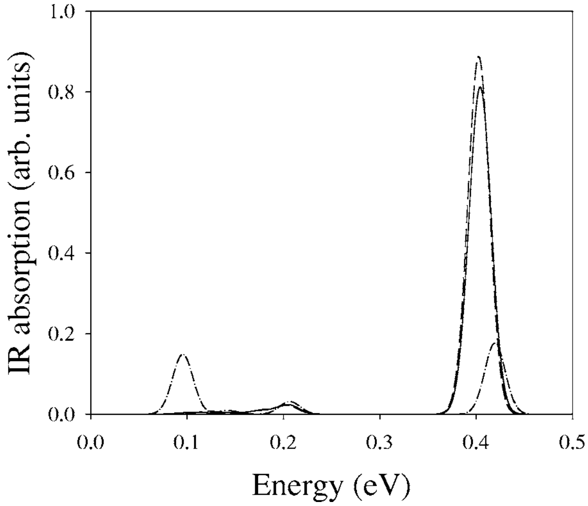

FIG. 7. The infrared absorption spectrum for hexane (—), cyclohexane (--) and benzene (-·-) as computed using the GAMESS quantum computational package [13] using a 6-31Gd basis set.

While this would appear to break the trend of stronger binding leading to larger Z_{eff}, the combination of fewer C-H

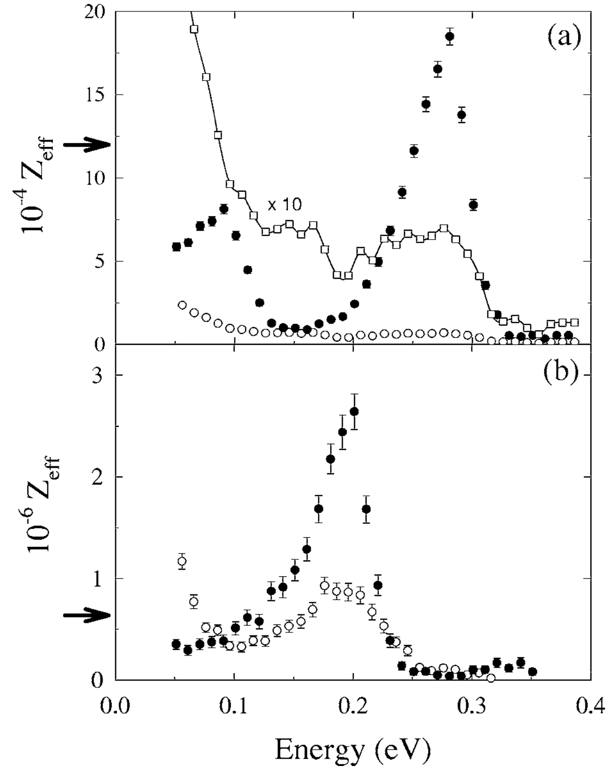

FIG. 8. Energy-resolved Z_{eff} spectra for (a) 1-fluorohexane ($C_6H_{13}F$) (○) compared with hexane (C_6H_{14}) (●) scaled by 10^{-4}; and (b) 1-fluorononane ($C_9H_{19}F$) (○), compared with nonane (C_9H_{20}) (●) scaled by 10^{-6}. In (a), the data for 1-fluorohexane are also plotted multiplied by a factor of 10 (□). The arrows on the ordinate indicate the value of Z_{eff} for the fully hydrogenated species in a 300 K thermal distribution of positrons. The thermal Z_{eff} of 1-fluorohexane is 269 000, which is off the scale of the plot. The thermal Z_{eff} of 1-fluorononane has not been measured.

modes *and* the lack of terminal methyl groups in benzene may suppress any enhancements in Z_{eff} gained from deeper binding. However, one must bear in mind that benzene is not a small change from cyclohexane. The shape of the ir and Z_{eff} spectra in benzene is quite different, and so other factors may be relevant. Nevertheless, alternative explanations for the location of the main Z_{eff} peak in the benzene spectrum are even less compelling. In particular, it is difficult to associate the largest Z_{eff} peak in benzene with any mode other than the C-H stretch and still get positive binding. The second strongest mode in the ir spectrum, for example, is a ring stretch at ~200 meV, which is about 30 meV below the main peak in the Z_{eff} spectrum.

VI. COMPARISON OF Z_{eff} AND INFRARED SPECTRA FOR FLUOROALKANES

Substitution of a fluorine atom for a hydrogen in alkane molecules has been shown to produce very large effects on annihilation rates and annihilation spectra. Figure 8 shows Z_{eff} spectra for 1-fluorohexane ($C_6H_{13}F$) and 1-fluorononane ($C_9H_{19}F$) [6]. These molecules differ from the alkanes, hexane (C_6H_{14}) and nonane (C_9H_{20}), by the substitution of a fluorine atom for one of the hydrogen atoms in either of the two methyl (CH_3) groups at an end of the molecule. The effect of this substitution on Z_{eff} is dramatic. In both of these fluorinated molecules, there is a large reduction in the magnitude of the peak associated with the C-H stretch vibrational mode. In 1-fluorohexane, the amplitude of the peak is reduced by more than a factor of 20, while in 1-fluorononane the peak is reduced by ~2.5. In both cases, the position of C-H stretch peak is not significantly different from that in the nonfluorinated (fully hydrogenated) species. In the context of the VFR model, this means the positron-molecule binding energy is unchanged by fluorination.

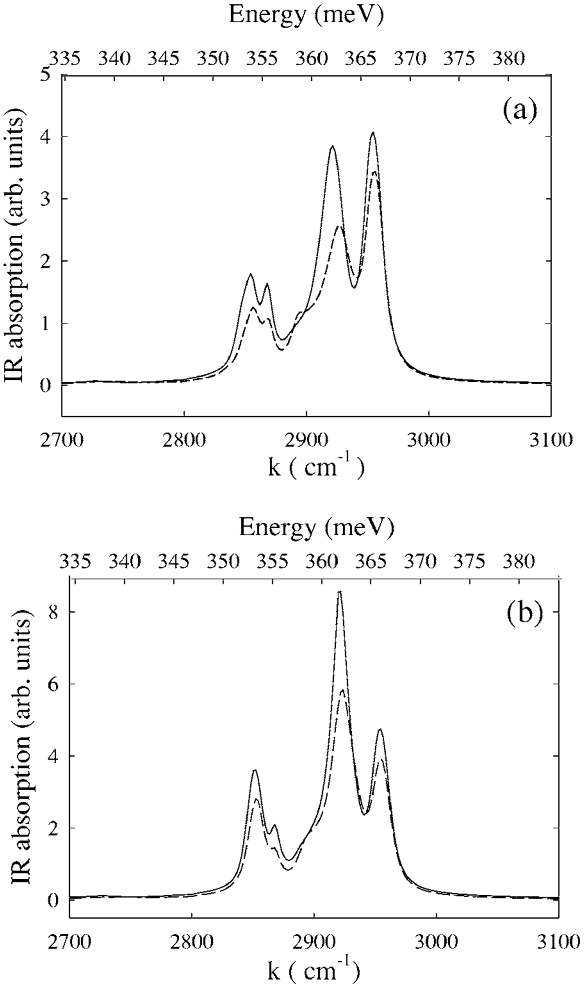

FIG. 9. (a) Infrared (ir) absorption for hexane (—) and 1-fluorohexane (---) over the range of the C-H stretch vibrational energies; (b) ir absorption for nonane (—) and 1-fluorononane (---). The units of absorbtivity are arbitrary, but are the same for all four molecules. See text for details.

As discussed above, a potentially important mechanism for producing vibrational excitation and the observed resonances is long-range dipole coupling, which can be measured using infrared absorption. The infrared spectra for the molecules studied in Fig. 8 were measured to investigate the degree to which the observed reductions in Z_{eff} with fluorination can be attributed to changes in these dipole oscillator strengths. Figure 9 shows the infrared absorption spectra for 1-fluorohexane, hexane, 1-fluorononane and nonane. The infrared absorption spectra in the region of the C-H stretch modes are largely unchanged with single-fluorine substitution. The slight reduction in coupling magnitude for the fluorinated molecules can be attributed to the reduction by one in the *number* of C-H stretch modes. The conclusion is that factors other than changes in dipole coupling (as reflected in changes in the ir spectra) are required to explain the large changes in magnitude of the C-H stretch peaks shown in Fig. 9. These fluorination results reinforce the idea that seemingly small changes in molecular structure (e.g., those that barely affect the vibrational mode energies and ir absorption spectra) can produce very large changes in the Z_{eff} spectra.

The other major effect of single fluorination substitution in large hydrocarbon molecules is an increase in Z_{eff} at lower energies (i.e., $\leqslant 100$ meV). This is immediately apparent in Fig. 8(b), where the Z_{eff} of 1-fluorononane rises more rapidly than the Z_{eff} of nonane as the positron energy is decreased. This trend is not apparent in the spectrum of 1-fluorohexane shown in Fig. 8(a). However, the Z_{eff} value for 1-fluorohexane for a thermal distribution of positrons is 269 000, which is significantly larger than in any of the structure observed at higher energies [19]. More importantly, it is larger than the thermal Z_{eff} of hexane. The physical origin of this effect is unclear. If this large Z_{eff} value is to be attributed to low-lying Feshbach resonances, it remains to be explained why the resonances at low energies are enhanced while the resonances at higher energies are suppressed.

Regarding these large values of Z_{eff} at small positron energies, one may be tempted by the proposition that Z_{eff} could be enhanced at low energies by the presence of a low-lying positron-molecule resonance or bound state [10,20]. This model appears to have merit in the case of heavier noble gas atoms and small molecules. However, in large molecules, the magnitude of the observed enhancements are much larger than can be explained by this mechanism.

VII. NONRESONANT Z_{eff} IN MOLECULES

It is of interest to consider the annihilation rates of molecules in the substantial range of energies between that of the vibrational modes (i.e., where vibrational Feshbach resonances are observed) and the thresholds for positronium formation. Our measurements of a number of molecules in this range of energies show that Z_{eff} depends only weakly on positron energy. This is in agreement with the energy dependence seen in previous theoretical calculations and models of Z_{eff} in noble gases and polyatomic molecules [10,21–25]. In this range of energies, the interaction of the positron with the molecule is relatively independent of the details of the molecular vibrational structure. An example of our data for butane is shown in Fig. 10.

Although a more detailed study of Z_{eff} would be useful, we present here only a single, average value of Z_{eff} in the plateau region of each target. These values, which we refer to as $Z_{\mathrm{eff}}^{(d)}$, are summarized in Table I. In each case, the average annihilation rate was calculated over the range of energies, $\Delta\epsilon$, indicated in the table. The errors given in the table represent the standard deviations of the measurements made in this energy range. Typically, these errors are large since other scattering processes require that test-gas pressure be kept low to avoid multiple scattering. This in turn reduces the achievable signal to noise.

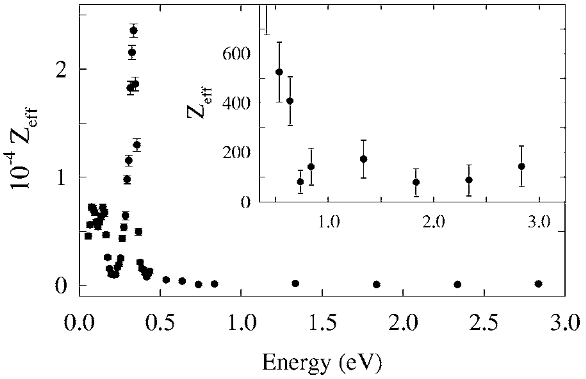

FIG. 10. Energy-resolved Z_{eff} spectrum for butane (C_4H_{10}), scaled by 10^{-4}, illustrating the relatively small values of Z_{eff} above the energy range of the molecular vibrations. The value for $Z_{\mathrm{eff}}^{(d)}$ for butane in Table I is the average of all data at energies greater than 0.7 eV and less than 3.0 eV. The inset is a close up of Z_{eff} in this energy range.

As shown in Table I and Fig. 11, large molecules tend to have large values of $Z_{\mathrm{eff}}^{(d)}$. These molecules typically also have large values of Z_{eff} for thermal positrons, $Z_{\mathrm{eff}}^{\mathrm{th}}$, which are also given in Table I. The results in Table I indicate that $Z_{\mathrm{eff}}^{(d)}$ increases faster than linearly with molecular size, at least for the alkanes. With regard to the historical association of Z_{eff} with the total number of target electrons, Z, we note the relatively poor correlation of $Z_{\mathrm{eff}}^{(d)}$ with Z. This is not surprising since inner shell electrons contribute little to the annihilation for positrons with energies less than a few electron volts [26].

It is important to note that unlike Z_{eff} measured at lower energies, where VFR phenomena are important, $Z_{\mathrm{eff}}^{(d)}$ may be more amenable to calculation (e.g., using simplified models in which the nuclei are fixed). Fixed-nuclei calculations are available for at least three of the molecules listed in Table I: $Z_{\mathrm{eff}}^{(d)}$ values for CH_4, CF_4, and NH_3 were predicted to be 28, 90, and 18, respectively, as compared with measured values of 21, 11, and 47 [22]. It is hoped that these data for $Z_{\mathrm{eff}}^{(d)}$ will stimulate further theoretical calculations of Z_{eff}.

VIII. CONCLUDING REMARKS

At this point, there is considerable evidence that positrons bind to a wide variety of molecules via vibrational Feshbach resonances, particularly in alkanes containing more than two carbon atoms. However, the factors that determine the magnitude of Z_{eff} for each vibrational mode and the magnitudes of the positron binding energies are still largely unknown. To some degree, this is due to a lack of energy resolution to identify specific modes. But it is also due to a paucity of energy-resolved experimental Z_{eff} spectra beyond the alkanes and a few other targets. This paper attempts to address the latter issue.

In the case of the largest alkanes studied thus far, dodecane and tetradecane, a resonant feature was observed above

TABLE I. Average “direct” annihilation rates, $Z_{\mathrm{eff}}^{(d)}$, for positrons in the indicated energy range, $\Delta\epsilon$, below the threshold for positronium formation. Also shown are the total number of target electrons, Z, and where available, the values of Z_{eff} for thermal positrons, $Z_{\mathrm{eff}}^{\mathrm{th}}$.

Target	Z	$Z_{\mathrm{eff}}^{(d)}$	$\Delta\epsilon$ (eV)	$Z_{\mathrm{eff}}^{(\mathrm{th})}$	$Z_{\mathrm{eff}}^{(d)}/Z$
Argon	18	13.4±0.6	0.7–2.6	33.8	0.74
Xenon	54	54±6	0.6–3.6	401	1.0
Methane (CH_4)	10	21±3	0.6–3.6	142	2.1
CF_4	42	11±2	0.7–1.1	54.4	0.26
CH_3F	18	22±2	0.6–2.0	1390	1.2
CHF_3	34	28±5	0.5–3.6	247	0.82
Ethane	18	32±4	1.3–2.3	660	1.8
Propane	26	55±43	1.8–2.8	3500	2.1
Butane (C_4H_{10})	34	118±37	0.7–2.8	11300	3.5
d-butane (C_4D_{10})	34	132±56	0.8–2.8		3.9
Pentane (C_5H_{12})	42	246±56	1.0–2.0	37800	5.9
Ammonia	10	47±8	0.5–2.3	1600	4.7

the principal C-H stretch resonance. We interpret this as evidence of a second, positronically excited bound state mediated by excitation of the C-H stretch vibrational mode.

The effect of small structural alterations on the Z_{eff} spectra was investigated for several molecules. Methane exhibits both local and global changes in Z_{eff} spectra as a result of halogen substitution. Data presented for three halomethanes, CH_3F, CH_3Cl, CH_3Br reveal striking changes as the size of the halogen is increased. The binding energy increases nearly linearly with electron shell number, and the resonant peak heights increase nonlinearly by over an order of magnitude. In contrast with similar trends in the alkane series, trends in the halomethanes cannot be attributed to changes in the number of vibrational modes. Of particular interest are the data for CH_3Cl, where the vibrational modes are sufficiently well separated that resonances of three distinct mode symmetries can be observed. It is hoped that these halomethane Z_{eff} spectra can be used to motivate and benchmark theoretical calculations, since they are likely more amenable to first-principles theoretical calculations as compared with spectra for larger molecules.

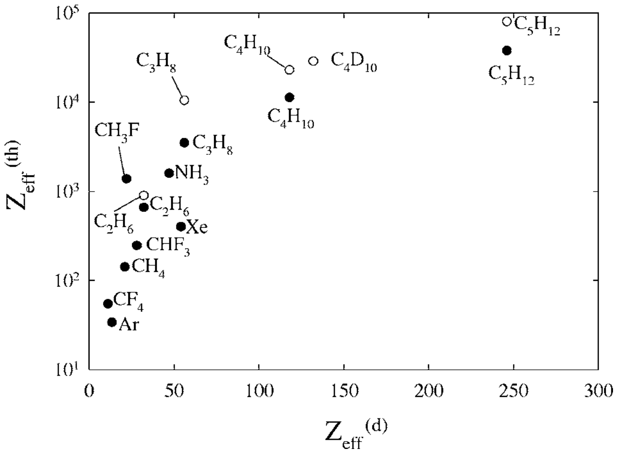

FIG. 11. $Z_{\mathrm{eff}}^{\mathrm{th}}$ as a function of $Z_{\mathrm{eff}}{}^{d}$ (●) for the molecules listed in Table I. The open circles (○), where shown, represent the values at the C-H stretch peak for the given molecule.

A second study of changes in Z_{eff} spectra with changes in molecular structure compared linear alkane molecules with ring hydrocarbons containing the same number of carbons. In the case of propane and cyclopropane, ring creation actually eliminates some low energy resonances rather than reducing their magnitude. This is perhaps an indication of an underlying selection rule. It is interesting to note that these resonant modes appear to “switch on” with a Z_{eff} of a few thousand. Similarly, the halogenated methanes, which have relatively few modes, have Z_{eff} values that do not exceed a few thousand. Perhaps this indicates that there is a maximum Z_{eff} which can be produced in a relatively small molecule by a single mode. Further study of “borderline” small molecules similar to cyclopropane may help to test this idea.

Studies of the six-carbon molecules, hexane, cyclohexane and benzene, provided further insight. The Z_{eff} value of cyclohexane is half that of hexane at all energies in spite of the fact that both molecules have similar numbers of vibrational modes. The Z_{eff} value of benzene is smaller still. However, in addition to having no terminal methyl groups, benzene has fewer vibrational modes.

The benzene Z_{eff} spectrum is quite unusual in that the main annihilation peak is downshifted from the C-H stretch mode by 130 meV as compared with 80 meV for hexane and cyclohexane. Assuming this peak is due to the C-H stretch mode, this indicates increased binding in benzene. In the alkanes, increased binding energy is strongly correlated with larger Z_{eff} values. The fact that benzene has a smaller Z_{eff} than both cyclohexane and hexane appears to contradict this trend. Study of a molecule such as 1-3-5 hexatriene, another six-carbon planar molecule with C-C bonding similar to benzene but without the ring shape, may shed light on this behavior.

A systematic comparison was made between the infrared absorption spectra and the Z_{eff} spectra of a number of molecules. Infrared absorption provides a quantitative measure of electric dipole coupling to the vibrational modes and, presumably, VFR. While one cannot rule out the possibility that Z_{eff} peaks are associated with ir-active modes, there is little evidence that dipole coupling alone is responsible for the observed VFR. In the alkanes, the replacement of a single hydrogen with a fluorine on a terminal methyl group decreases Z_{eff} dramatically. Such substitutions in hexane and nonane did not result in commensurate reductions in ir absorption. This lack of correlation between the ir and Z_{eff} magnitudes was also seen in hexane, cyclohexane, propane, and cyclopropane. It is clear that ir coupling strengths alone are not consistent predictors of Z_{eff} spectra—other factors are clearly important.

The final topic addressed in this paper is the magnitude and spectrum of annihilation in molecules above the energy range of the vibrational modes, but below the threshold for positronium formation. Studies of a number of molecules indicate that Z_{eff} is approximately constant in this range of energies. The values of Z_{eff} are much smaller than those observed in the VFR region. It would be interesting to compare these "nonresonant" values of Z_{eff} with the predictions of fixed-nuclei calculations, rather than with values measured at lower positron energies where VFR are typically important and often dominant.

In this paper we have presented studies of positron annihilation spectra, positron-induced VFR, and positron binding to molecules. We believe that these phenomena merit further theoretical and experimental exploration. In the case of large molecules, while the experimental signatures of positron VFR are fairly clear, consistent quantitative agreement between theoretical predictions and experimental measurements has yet to be achieved. In the case of small molecules, many open questions remain, including in many cases, the underlying mechanism or mechanisms responsible for observed large values of Z_{eff}.

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