Dipole Enhancement of Positron Binding to Molecules

J. R. Danielson, J. J. Gosselin, and C. M. Surko
Department of Physics, University of California at San Diego, La Jolla, California 92093, USA

(Received 27 April 2010; published 9 June 2010)

Measurements of positron-molecule binding energies are made for molecules with large permanent dipole moments (>2.7 D), by studying vibrational-Feshbach-mediated annihilation resonances as a function of incident positron energy. The binding energies are relatively large (e.g., ≥ 90 meV) as compared to those for similar sized molecules studied previously and analogous weakly bound electron-molecule (negative ion) states. Comparisons with existing theoretical predictions are discussed.

DOI: 10.1103/PhysRevLett.104.233201 PACS numbers: 34.80.Uv, 34.80.Lx, 71.60.+z, 78.70.Bj

While the interaction of positrons with ordinary matter is important in many areas including medicine, materials science, and astrophysics, many basic phenomena are poorly understood. One such process is the binding of positrons to matter, where factors such as electron-positron correlations and the role of virtual positronium formation have proven difficult to treat theoretically [1], and the transient nature of the positron-matter complexes makes them difficult to study experimentally [2].

There is theoretical evidence that positrons can bind to atoms [1], however, existing calculations for molecules are much less precise [3–8]. On the experimental front, there have been no measurements of positron binding to atoms, primarily due to the difficulty in forming positron-atom bound states in two-body collisions. In contrast, positrons have been found to attach to molecules via Feshbach-resonances in which a vibrational mode absorbs the excess energy. These resonances result in large enhancements in the annihilation rate [9,10]. This process has been employed to measure positron binding energies ϵ_b using the relation

$$\epsilon_\nu = \omega_\nu - \epsilon_b, \tag{1}$$

where ϵ_ν is the energy of the annihilation resonance due to vibrational mode ν with energy ω_ν. Using this technique, values of ϵ_b have been measured for more than 30 molecular species [11].

Theoretical work has focused on small molecules with relatively large permanent dipole moments μ (e.g., 2.3–6 D) [3–8], while the measurements to date have been done on larger molecules that are either nonpolar, or have dipole moments <2 D. Binding to these molecules is largely due to the dipole polarizability α of the molecule, with only a relatively small enhancement from μ [12]. Presented here are measurements of ϵ_b for four relatively simple molecules, acetaldehyde $(CH_3)HCO$, acetone $(CH_3)_2CO$, acetonitrile $(CH_3)CN$ and carbon disulfide. All except CS_2 have large dipole moments (i.e., ≥ 2.7 D). The latter molecule is a comparison case of a small (i.e., triatomic) molecule with $\mu = 0$ but with a relatively large dipole polarizability.

The binding energies reported here range from 75 meV for CS_2 to 180 meV for acetonitrile. They are large compared to those expected on the basis of previous measurements for similarly sized molecules [12], and those predicted theoretically (e.g., for acetone [8]). They are also quite large compared to those measured for analogous weakly bound electron-molecule (i.e., negative ion) states [13]. Contrasting with previous measurements, the new data highlight the importance of large dipole moments, e.g., (~2.7–4 D) in producing enhanced binding. New calculations for these molecules are in progress [14], and a very recent result for acetonitrile predicts a value within 30% of the measurement reported here [15]. This ability to compare theory and experiment represents a significant step in understanding positron binding to matter.

The experimental procedures to measure molecular annihilation rates as a function of incident positron energy in a room-temperature gas are discussed in detail in Ref. [11]. Positrons from a 15 mCi ^{22}Na source and neon moderator are accumulated and cooled to 300 K in a three-stage, Penning-Malmberg, buffer-gas trap. Energy-tunable positron pulses, formed at a 3 Hz rate, are magnetically guided through a cylindrical electrode filled with the test gas. The kinetic energies of the incident positrons are adjusted by varying the bias voltage on the gas cell. The beam energy distribution is the convolution of a Maxwellian of width 25 meV (FWHM) to account for the gyromotion in the plane perpendicular to the magnetic field with a Gaussian with the same width to account for the motion parallel to the field [11]. This results in an asymmetric distribution in total positron energy and a 12 meV downshift of the resonant peaks relative to the peaks in positron parallel energy [11,16]. The data here are plotted as a function of total positron energy taken to be 12 meV larger than the mean parallel energy. Binding energies are obtained by identifying the vibrational resonances in the annihilation spectra and using Eq. (1).

2Γ annihilation events are detected using a single CsI detector. Positron pulses are kept in flight and pass through the gas cell 2 or 3 times within the time window in which annihilation events are recorded. Absolute values of $Z_{\rm eff}$

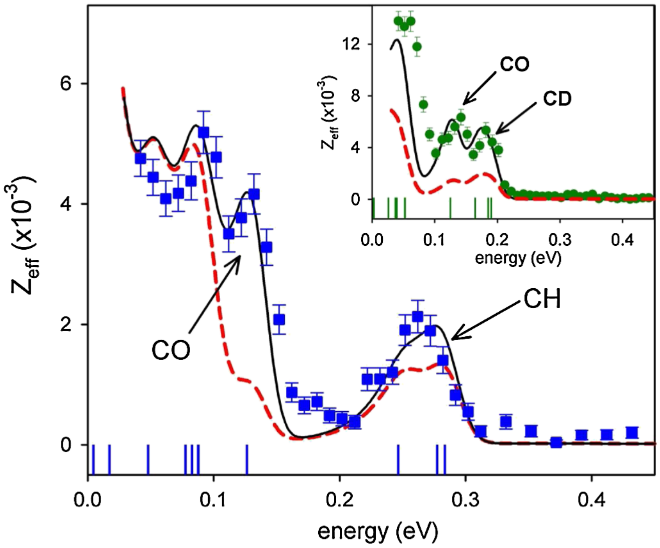

FIG. 1 (color online). Annihilation-rate spectrum of acetaldehyde ($(CH_3)HCO$) as a function of incident positron energy. Error bars are statistical. The dashed line is the prediction of the single-mode theory of Ref. [16], with $\epsilon_b = 90$ meV. The solid line is a fit to the spectrum using a 90 meV binding energy, with the magnitudes of the modes (i.e., in this case principally the CO mode) adjusted for best fit. Vertical lines show positions of the IR-active vibrational modes downshifted by 90 meV. The inset shows results for the deuterated analog $(CD_3)DCO$. Mode energies are from Ref. [27].

for test species are obtained from measurements of the incident positron energy, the positron pulse strength, the path length in view of the detector, and the test-gas pressure. Uncertainties in the test-gas pressure (measured with a manometer) and other parameters are estimated to result in a $\pm 20\%$ uncertainty in Z_{eff}. Time-of-flight measurements of the beam pulses indicate an electrical-potential uniformity of approximately ± 10 meV in the gas cell. Drifts of the beam energy over data runs are kept to $\leq$ 5–10 meV. Because of uncertainties from scattering at small positron energies, only data for incident positron energies of ≥ 50 meV are shown.

Shown in Figs. 1–4 are annihilation-rate spectra resolved as a function of total positron energy for acetaldehyde, acetone, acetonitrile and CS_2, respectively. The annihilation rates are given in terms of the quantity Z_{eff}, where $Z_{\mathrm{eff}} = \lambda/(\pi r_0^2 c n_m)$, and λ, r_0, c, n_m, are the measured annihilation rate, the classical electron radius, the speed of light, and the density of the molecular gas, respectively. The value $Z_{\mathrm{eff}} = Z$ is the rate expected for a positron in a free electron gas of density $n = Z n_m$, where Z is the number of electrons on the molecule [17]. Because of vibrational Feshbach resonances (VFR), all four molecules exhibit resonant peaks and large annihilation-rate enhancements above the free-electron-gas value, i.e., $Z_{\mathrm{eff}} \gg Z$ (where $Z = 24, 32, 22$, and 38, for Figs. 1–4, respectively). Vertical lines at the bottom of each figure show the locations of the IR-active vibration modes (downshifted by the binding energy). The positions of the peaks are readily associated with the molecular vibrations. Prominent IR-active stretch modes are labeled in the figures.

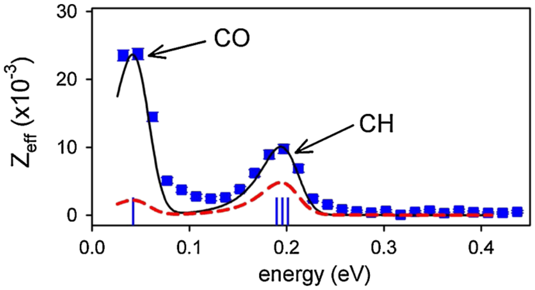

FIG. 2 (color online). Energy-resolved annihilation-rate spectrum of acetone $(CH_3)_2CO$. Notation is as in Fig. 1. The solid and dashed curves correspond to $\epsilon_b = 173$ meV. Mode energies are from Ref. [28].

To ascertain that the CH mode identification is correct, we also measured the spectra for the fully deuterated analogs of these molecules. An example is shown in the inset to Fig. 1, where the measured annihilation spectrum of acetaldehyde-d4, $(CD_3)DCO$, is shown. The vertical lines show the locations of the IR-active vibrational modes shifted by the same 90 meV binding energy. It can be seen that the CO mode peak stays fixed near 0.13 eV for both data sets, but the peak near 0.28 eV is shifted down to 0.18 eV in the deuterated data, as expected for the change from the CH to CD modes. Similar shifts (not shown) are observed for acetone-d6 and acetonitrile-d4, verifying the identification of the highest-energy peak as due to the CH stretch mode [9,11]. Based on the shifts of these peaks, the measured binding energies are 90, 173, 180, and 75 meV, for acetaldehyde, acetone, acetonitrile, and CS_2, respectively, with estimated systematic uncertainties of ± 10 meV.

A theory by Gribakin and Lee describes the spectrum of annihilation resonances due to vibrational modes (possibly including combination or overtone modes), given the value of ϵ_b [16]. The dashed curves in Figs. 1–4 are the predictions of this theory, broadened by the experimental positron energy distribution, including only fundamental IR-

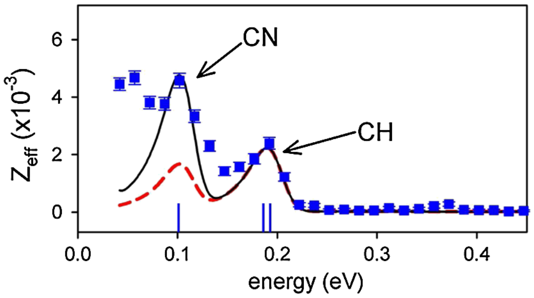

FIG. 3 (color online). Energy-resolved annihilation-rate spectrum of acetonitrile $(CH_3)CN$. Notation is as in Fig. 1. The solid and dashed curves correspond to $\epsilon_b = 180$ meV. Mode energies are from Ref. [29].

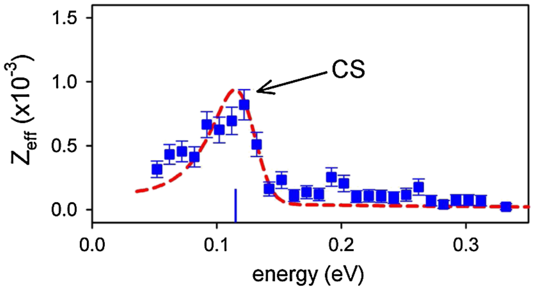

FIG. 4 (color online). Energy-resolved annihilation-rate spectrum of carbon disulfide CS_2. Notation is as in Fig. 1. From the best fit, the positron binding energy is 75 meV. Mode energies are from Ref. [30].

active modes assumed to contribute maximally, with no adjustable parameters beyond ϵ_b. The theory does a good job of representing the high-energy CH stretch peak in acetonitrile and the CS vibration in CS_2. Similar agreement is obtained for the CH peak in acetaldehyde if a sixth, nominally IR-inactive, mode is included. However, the entire spectrum for acetone and the low-energy spectra of both acetaldehyde and acetonitrile show clear differences. This is likely due to enhancements to the annihilation rate due to intramolecular vibrational redistribution (IVR) [11,18]. The solid lines in Figs. 1–3 show fits to the respective spectra, using the measured positron beam energy distribution and fitting both the value of ϵ_b and the resonance amplitudes for the CO mode in acetaldehyde, all modes in acetaldehyde-d4, the CN mode in acetonitrile, and all modes in acetone.

In all of the hydrocarbon molecules, the lower-frequency modes match better to a slightly smaller binding energy (e.g., $\Delta\epsilon \sim 10$ meV) than that obtained from the high-energy CH stretch peak. This same effect is observed in the comparison of the CH and CD stretch peaks in acetaldehyde. It is independent of gas pressure and thus does not appear to be due to elastic scattering. This effect is not understood and warrants further study.

The positron binding energies measured to date are relatively small on the atomic scale (i.e., $\epsilon_b \ll 1$ eV), and so the positron wave function is expected to be diffuse compared to that for the electrons. There are two classes of negative ions (i.e., electron-molecule complexes). In the first, the extra electron is accommodated in a spatially compact valence orbital. In this case, the electron affinity depends on the orbital energy, ranging from unbound to deeply bound (e.g., open shell orbitals). The second class of negative ions has a large and diffuse electron cloud which is only weakly bound to the molecule, and attributed to electron coupling to μ and α [13]. This type of anion is analogous to the one we focus on here.

In Table I, the four molecules studied are compared with molecules for which positron and electron binding energies have been calculated and/or measured. Included is the very recent configuration-interaction calculation for acetonitrile that predicts $\epsilon_b = 135$ meV [15], which is within 30% of that reported here. An improved calculation for acetone, using the same technique, is in progress. The negative ions in Table I are restricted to those with closed valence shells. Several trends are apparent. Generally, larger values of μ and α produce larger binding energies. Where comparisons are available, the values of ϵ_b for positrons are considerably larger than those for electrons. This is consistent with a trend noticed earlier comparing electron binding to CO_2 clusters [25] to positron binding to (similarly nonpolar) alkane molecules. The effect of large μ on ϵ_b in the positron case appears to be particularly strong.

TABLE I. Measured and predicted positron- and electron-molecule binding energies ϵ_b (meV), permanent dipole moments μ (D) and dipole polarizabilities α (Å^3) for selected molecules. Data for μ and α taken from Ref. [19]. Data from Figs. 1–4 in bold.

Molecule	Formula	μ (D)	α (Å^3)	ϵ_b (meV) Positrons Meas.	Positrons Pred.	Electrons[g] Meas.	Electrons[g] Pred.
Carbon disulf.	CS_2	0	8.7	**75**		0.7	
Butane	C_4H_{10}	0	8.2	40[a]			
Methanol	CH_3OH	1.7	3.3	2[a]			
Meth.-chloride	CH_3Cl	1.9	5.4	25[a]			
Formaldehyde	H_2CO	2.3	2.8		19[b]		0.02
Acetaldehyde	C_2H_4O	2.8	4.6	**90**		0.6	0.95
Acetone	C_3H_6O	2.9	6.4	**173**	4[c]	2.6	1.6
Propanal	C_3H_6O	2.7	6.5			1.0	0.6
Hydr. cyanide	HCN	3.0	2.5		35[d]	4	3.3
Acetonitrile	CH_3CN	3.9	4.4	**180**	135[e]	19	15.5
Lith. hydride	LiH	5.9	3.8		1000[f]	342	330

[a]Ref. [11]. [b]Ref. [5]. [c]Ref. [8]. [d]Refs. [6,7]. [e]Ref. [15]. [f]Ref. [3]. [g]Meas. from Refs. [20–23], pred. from Refs. [20,24].

A previous analysis, restricted to a data set for which $\mu \lesssim 2$ D showed that the positron binding energies ϵ_b (in meV) for nonaromatic molecules could be parameterized by the empirical relation [12]

$$\epsilon_b = 12.4\alpha + 19.8\mu - 69 \text{ [meV]}, \tag{2}$$

where μ and α are in the units indicated in Table I. With the possible exception of CS_2 (discussed below), the new measurements presented here do not follow this scaling, but exhibit a stronger dependence upon μ and α. Comparing acetaldehyde and acetonitrile, the coefficient of the μ term is larger by a factor $\sim$4, increasing to 78 meV/D. Increased sensitivity to α is also observed. Comparing acetone and acetaldehyde, the coefficient of the α term is also increased by a factor of $\sim$4 beyond that in Eq. (2) to 50 meV/Å^3. There are not enough data to discern an actual dependence upon parameters in this regime other than to establish that the simple scaling in Eq. (2) does not apply. Whether, in fact μ and α are appropriate variables in this case is unclear.

It is known that a static dipole can bind an electron or positron when $\mu \geq 1.625$ D [26]. In contrast, experimental studies of electron-molecule binding indicate that μ must be $\gtrsim 2.5$ D for binding energies of meV or greater [20]. As the binding becomes stronger, the dipole can potentially localize the positron on a portion of the molecule. In this case, one might expect ϵ_b to depend upon the *local*, rather than the total value of α.

In the case of CS_2 with $\mu = 0$, the measured value of ϵ_b is closer to that predicted by Eq. (2) with 40 meV predicted vs 75 meV measured. There is some evidence in small molecules that π bonds enhance the binding above that predicted by Eq. (2), and this could explain at least part of this discrepancy [12]. Carbon disulfide has a permanent quadrupole moment and this also might contribute to the binding energy [21].

Details of the spectra presented here show a number of interesting effects. For example, while CS_2 fits well the predictions of the single-mode theory of Ref. [16], the largest molecule studied, acetone, shows relatively strong IVR at all resonant peaks. Acetaldehyde and acetonitrile exhibit intermediate behavior, whereby the highest energy (CH stretch) peaks have amplitudes close to those predicted by the theory, while the lower energy modes (CO or CN) are enhanced due to IVR. This mixed behavior may provide some insight into the criterion (i.e., the threshold) for IVR.

In this Letter, we report new data for positron-molecule binding energies, exploring the regime of dipole moments $\mu > 2$ D. The binding energies for these species are found to be larger than those for similar sized molecules with smaller values of μ, and they also exhibit a much stronger dependence on μ and α. The relative simplicity of these molecules and their large binding energies make them good candidates for theoretical investigations, several of which are currently in progress. When compared with the electron binding energies for the analogous negative ions, the positron binding energies studied here are 10–100 times larger. These strikingly large differences are completely unexpected, for example, on the basis of simple coupling to a permanent dipole moment and are presently not understood. Whether they might be due to the absence of the exchange interaction or to electron-positron correlations is unclear. It is one of a number of topics in this area that warrant further study.

We wish to acknowledge helpful conversations with G. Gribakin, J. A. Young, and M. W. Bromley, and the expert technical assistance of E. A. Jerzewski. This work is supported by NSF grant PHY 07-55809.

[1] J. Mitroy, M. W. J. Bromley, and G. G. Ryzhikh, J. Phys. B **35**, R81 (2002).

[2] C. M. Surko, G. F. Gribakin, and S. J. Buckman, J. Phys. B **38**, R57 (2005).

[3] K. Strasburger, J. Chem. Phys. **114**, 615 (2001).

[4] R. J. Buenker, H. P. Liebermann, V. Melnikov, M. Tachikawa, L. Pichl, and M. Kimura, J. Phys. Chem. A **109**, 5956 (2005).

[5] K. Strasburger, Structural Chemistry **15**, 415 (2004).

[6] H. Chojnacki and K. Strasburger, Mol. Phys. **104**, 2273 (2006).

[7] Y. Kita, R. Maezono, M. Tachikawa, M. Towler, and R. J. Needs, J. Chem. Phys. **131**, 134310 (2009).

[8] M. Tachikawa, R. J. Buenker, and M. Kimura, J. Chem. Phys. **119**, 5005 (2003).

[9] S. J. Gilbert, L. D. Barnes, J. P. Sullivan, and C. M. Surko, Phys. Rev. Lett. **88**, 043201 (2002).

[10] G. Gribakin, J. A. Young, and C. M. Surko, Rev. Mod. Phys. (to be published).

[11] J. A. Young and C. M. Surko, Phys. Rev. A **77**, 052704 (2008); **78**, 032702 (2008).

[12] J. R. Danielson, J. A. Young, and C. M. Surko, J. Phys. B **42**, 235203 (2009).

[13] C. Desfrancois, H. Abdoul-Carime, N. Khelifa, and J. P. Schermann, Phys. Rev. Lett. **73**, 2436 (1994).

[14] D. Bressanini, R. J. Buenker, H. Chojnacki, M. Mella, K. Strasburger, and M. Tachikawa (private communication).

[15] M. Tachikawa, Y. Kita, and R. J. Buenker (private communication).

[16] G. F. Gribakin and C. M. R. Lee, Phys. Rev. Lett. **97**, 193201 (2006).

[17] M. Charlton and J. W. Humberston, *Positron Physics* (Cambridge University Press, Cambridge, England, 2001).

[18] G. F. Gribakin and C. M. R. Lee, Eur. Phys. J. D **51**, 51 (2009).

[19] *CRC Handbook of Chemistry and Physics*, edited by David R. Lide (CRC Press/Taylor and Francis, Boca Raton, FL, 2008/2009), 89th ed.

[20] H. Abdoul-Carime and C. Desfrancois, Eur. Phys. J. D **2**, 149 (1998).

[21] R. N. Compton, F. B. Dunning, and P. Nordlander, Chem. Phys. Lett. **253**, 8 (1996).

[22] N. I. Hammer, K. Diri, K. D. Jordan, C. Desfrancois, and R. N. Compton, J. Chem. Phys. **119**, 3650 (2003).

[23] H. W. Sarkas, J. H. Hendricks, S. T. Arnold, and K. H. Bowen, J. Chem. Phys. **100**, 1884 (1994).

[24] S. Bubin and L. Adamowicz, J. Chem. Phys. **121**, 6249 (2004).

[25] E. Leber, S. Barsotti, I. I. Fabrikant, J. M. Weber, M.-W. Ruf, and H. Hotop, Eur. Phys. J. D **12**, 125 (2000).

[26] J. E. Turner and K. Fox, Phys. Lett. **23**, 547 (1966).

[27] K. B. Wiberg, Y. Thiel, L. Goodman, and J. Leszczynski, J. Phys. Chem. **99**, 13 850 (1995).

[28] R. H. Mann and W. B. Dixon, J. Chem. Phys. **57**, 792 (1972).

[29] E. L. Pace and L. J. Noe, J. Chem. Phys. **49**, 5317 (1968).

[30] T. Shimanouchi, Tables of Molecular Vibrational Frequencies, Consolidated Volume 1, NSRDS NBS-39.