

## Three-body effects in the annihilation of positrons on molecules

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A detailed investigation of positron annihilation in ethylene gas at room temperature and at densities  $\rho$  below 1 amagat ( $\equiv 2.69 \times 10^{25}$  molecules  $\text{m}^{-3}$ ) has revealed that the mean free positron annihilation rate  $\langle \lambda_f \rangle$  displays a density dependence of the form  $\langle \lambda_f \rangle = a\rho^2 + b\rho$ , with  $a$  and  $b$  constants. This implies that positrons can annihilate in the gas as a result of three-body interactions and is an unambiguous observation of this effect. The physical interpretation of this result is discussed, particularly in the light of related work on positron annihilation on single molecules. It is shown that earlier work on positron annihilation on molecular gases has displayed effects similar to those described here, but their significance has not previously been appreciated.

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The annihilation of positrons in gases has been studied for nearly five decades. These investigations have been of interest to atomic and molecular scientists, since the quantity  $Z_{\text{eff}}$  that parametrizes the increase in the positron annihilation cross section over that predicted by the Dirac free electron gas theory is a sensitive test of approximate wave functions used in scattering calculations. Most experiments have been performed using positrons from a radioactive source stopping directly in the gas under study before annihilation. Thus, gas densities typically greater than 1 amagat have been used.

Recently a positron-beam-based technique was developed by Surko and co-workers [1] for the study of positron-molecule interactions. Here slow positrons are cooled to room temperature by collisions with molecular nitrogen buffer gas and confined in a Penning-Malmberg trap [2]. Their interaction with small quantities of added gas can then be studied such that positron-single-molecule collision conditions are assured. A central outcome of this work [3–5] has been the confirmation that, for some molecules  $\langle Z_{\text{eff}} \rangle$  (where the angular brackets denote an average over the positron energy distribution upon annihilation) is much greater than the actual number of electrons in the molecule,  $Z$ , as discovered in early positron lifetime investigations [6,7]. Importantly, the number of species studied was considerably extended using the trap technique, with some molecules reported having  $\langle Z_{\text{eff}} \rangle$  as high as  $10^6$ – $10^7$  ( $\langle Z_{\text{eff}} \rangle / Z$  up to  $10^5$ ) [3,5].

The physical origin (see [3] for a recent discussion and an accompanying theoretical paper by Gribakin [8]) of the high  $\langle Z_{\text{eff}} \rangle$ 's is a subject of topical research. Surko and co-workers favored a picture in which in some cases the positron is able to form a temporary complex with the molecule, from which it has an enhanced probability of annihilation. In this model, which is similar to one used to explain the attachment of electrons to molecular species [9], the excess positron energy is shared (temporarily) among vibrational excitation modes of the molecule. In addition to this “resonant” process, positrons are able to annihilate as a result of direct collisions with the molecule. The cross section for this mechanism is enhanced if the scattering cross section is large; this may be

as a result of low lying virtual or weakly bound states. Gribakin [8] argued from the unitary limit that  $\langle Z_{\text{eff}} \rangle$  may rise to a maximum of  $\sim 10^3$  by this mechanism. The direct and resonant processes are not mutually exclusive so that positrons may annihilate with a particular molecule by either mechanism. The role of vibrational processes in annihilation has been confirmed by the recent observation of a resonant-like feature just below the excitation threshold of  $\text{C}_4\text{H}_{10}$  and  $\text{C}_4\text{D}_{10}$  in the first energy-resolved measurements of  $\langle Z_{\text{eff}} \rangle$  [10].

Ethylene ( $\text{C}_2\text{H}_4$ ) is a simple example of a molecule for which  $\langle Z_{\text{eff}} \rangle \gg Z$  (trap measurements have found  $\langle Z_{\text{eff}} \rangle \approx 1200$  [5]). A recently corrected calculation [11–13] obtained a thermally averaged value of  $\langle Z_{\text{eff}} \rangle$  at room temperature more than an order of magnitude below this result. This calculation included only electronic configurations in the basis set describing the positron-ethylene interaction so that the effects connected to vibrational excitation would be expected to be poorly represented. One motivation for our investigation was to provide an independent measurement, at room temperature, of the value of  $\langle Z_{\text{eff}} \rangle$  for this molecule using the traditional lifetime technique for comparison with the trap measurement. However, the most significant aspect of the work reported here is the observed density dependence of the positron annihilation rate  $\langle \lambda_f \rangle$ .

The experiment was conducted using standard positron lifetime spectroscopy techniques. The gas cell and related technology have been adequately described elsewhere [14]. The lifetime spectra were obtained and stored using commercially available units. Offline analyses to obtain  $\langle \lambda_f \rangle$ , and hence  $\langle Z_{\text{eff}} \rangle$ , were performed using standard techniques [7,15].

Figure 1 shows the measured annihilation rates at various  $\rho$  in the approximate density range 0.1–1.0 amagat. The line shown is the fit to the functional form  $\langle \lambda_f \rangle = a\rho^2 + b\rho$ . The fitting parameters were  $a = 245 \pm 8$  ( $\mu\text{s amagat}^2$ ) $^{-1}$  and  $b = 139 \pm 6$  ( $\mu\text{s amagat}$ ) $^{-1}$ . (A fit was also attempted including a cubic term. The values of  $a$  and  $b$  extracted from this agreed with the values above, though with larger uncertainties; the cubic coefficient was consistent with zero.) As a

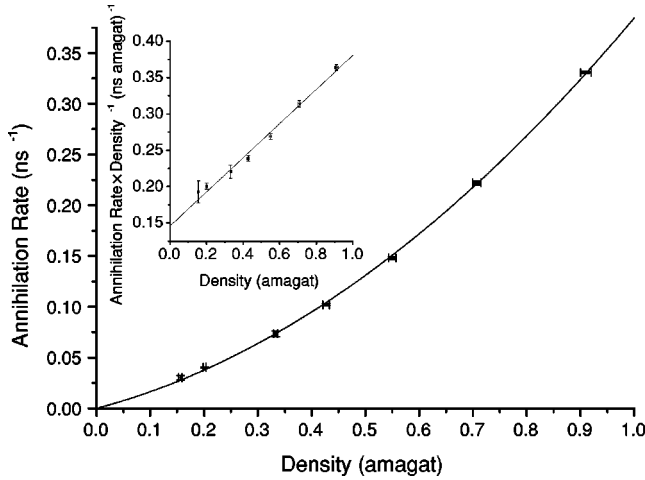


FIG. 1. The behavior of the free positron annihilation rate  $\langle \lambda_f \rangle$  versus gas density  $\rho$  for ethylene. The line shown is the quadratic fit to the data. The same data are replotted as  $\langle \lambda_f \rangle / \rho$  in the inset with the corresponding linear fit.

further check on the functional form of  $\langle \lambda_f \rangle$ , the data were replotted, as shown in the inset of Fig. 1, in the form  $\langle \lambda_f \rangle / \rho = a\rho + b$ . The values of  $a$  and  $b$  extracted from a straight line fit to this plot were  $235 \pm 10$  ( $\mu\text{s amagat}^2$ )<sup>-1</sup> and  $146 \pm 6$  ( $\mu\text{s amagat}$ )<sup>-1</sup> respectively. We take a weighted average of these two fits to obtain final values, together with the largest uncertainty in each case; thus  $a = 241 \pm 10$  ( $\mu\text{s amagat}^2$ )<sup>-1</sup> and  $b = 142 \pm 6$  ( $\mu\text{s amagat}$ )<sup>-1</sup>.

Thus, the data in Fig. 1 are consistent with positrons annihilating while interacting *both with one ethylene molecule, and with two simultaneously*; i.e., as a result of both two-body and three-body collisions. An early measurement [16] reported such an effect in nitric oxide, but later work [17] attributed the observed effect to the formation of dimers by impurity nitrogen dioxide molecules. It is interesting to note the density at which the two-body and three-body contributions to the annihilation rate are equal. This occurs when  $\rho = b/a$ , i.e., at around 0.6 amagat. The three-body contribution is 10% of  $\langle \lambda_f \rangle$  at a density as low as 0.07 amagat.

It is readily seen that a three-body effect is plausible by comparing the de Broglie wavelength  $\lambda_{\text{dB}}$  of a thermal positron with the mean molecular separation of the molecules in the (ideal) gas  $\langle r_{\text{sep}} \rangle$ . The latter is related to the gas density according to  $\langle r_{\text{sep}} \rangle = 2(3/4\pi\rho)^{1/3} \approx (40 \text{ \AA})/\rho^{1/3}$  with  $\rho$  in units of amagat. At room temperature,  $\lambda_{\text{dB}} \approx 60 \text{ \AA}$ , such that  $\lambda_{\text{dB}} = \langle r_{\text{sep}} \rangle$  when  $\rho \approx 0.3$  amagat. This lies within the density range in which the three-body effects are observed. It is also pertinent to compare  $\langle r_{\text{sep}} \rangle$  with the  $e^+ - \text{C}_2\text{H}_4$  scattering length, which from the work of da Silva *et al.* [11] is  $\sim 10 \text{ \AA}$ . This suggests that three-body effects should occur in the few amagat range—not wildly out of line with our observations.

The parameter  $b$  can be used to derive  $\langle Z_{\text{eff}}(0) \rangle$  (the “zero density” value; see below) for  $\text{C}_2\text{H}_4$  to compare with previous experiment and theory. Using standard relationships [7] a value of  $710 \pm 30$  is found; much lower than the result of 1200 derived from the trap measurements [5], and outside the combined uncertainties of the two experiments [18]. The

TABLE I. Annihilation parameters for five gases which have been investigated at moderate densities and for which  $\langle Z_{\text{eff}}(0) \rangle \gg Z$ . Values of  $\langle Z_{\text{eff}}(0) \rangle$  and  $a/\omega$  for gases other than  $\text{C}_2\text{H}_4$  are taken from [7]; no uncertainties can be provided on these quantities.

Gas	$\langle Z_{\text{eff}}(0) \rangle$	$a/\omega$ (amagat <sup>-1</sup> )	$a/[\omega\langle Z_{\text{eff}}(0) \rangle]$ (amagat <sup>-1</sup> )
$\text{CCl}_2\text{F}_2$	700	1000	1.4
$\text{C}_2\text{H}_6$	660	320	0.5
$\text{C}_3\text{H}_8$	3500	7250	2.1
$\text{C}_4\text{H}_{10}$	15000	25000	1.7
$\text{C}_2\text{H}_4$	$710 \pm 30$	$1190 \pm 50$	$1.64 \pm 0.10$

origin of this discrepancy is not known. However, both experiments are in serious discord with theory [11–13].

Our observation of the quadratic dependence of  $\langle \lambda_f \rangle$  on  $\rho$  for  $\text{C}_2\text{H}_4$  has prompted a search for similar effects in data published previously for other gases. Complex dependencies of  $\langle \lambda_f \rangle$  on both gas density and temperature have been reported for a variety of species (see, e.g., [14,19,20] for summaries); however, the most detailed collation of data at room temperature and moderate density for gases with  $\langle Z_{\text{eff}}(0) \rangle \gg Z$  was provided by Heyland *et al.* [7]. Although only schematic line graphs were given, it is apparent that their lower density data exhibit a linear increase of  $\langle Z_{\text{eff}} \rangle$  with  $\rho$ ;  $\langle Z_{\text{eff}}(\rho) \rangle \propto \langle \lambda_f \rangle / \rho = a\rho + b = a\rho + \omega\langle Z_{\text{eff}}(0) \rangle$ . However, Heyland *et al.* [7] failed to comment on the functional form of their data. We have used the slopes of their graphs to deduce the parameter  $a$  for four gases, which are presented in Table I as values of  $a/\omega$ , where  $\omega \approx 0.2$  ( $\mu\text{s amagat}$ )<sup>-1</sup> is the Dirac annihilation parameter [7], along with  $a/\omega$  for ethylene.

The results for  $a/\omega$  for the five gases exhibit a range extending over almost two orders of magnitude, reminiscent of the range of  $\langle Z_{\text{eff}}(0) \rangle$  for these species. The final column of Table I presents  $a/[\omega\langle Z_{\text{eff}}(0) \rangle]$  ( $= a/b$ ), which represents an attempt to factor out the basic annihilation parameter of each molecule. It is apparent that the values of  $a/[\omega\langle Z_{\text{eff}}(0) \rangle]$  are close to one another (within a factor of approximately 4, including that for  $\text{C}_2\text{H}_6$  which is slightly lower than the others). This observation implies that there is a common mechanism (or mechanisms) that causes  $\langle Z_{\text{eff}}(0) \rangle \gg Z$  for these species. Furthermore, the fact that  $\langle Z_{\text{eff}}(0) \rangle$  can be used to scale the three-body coefficient strongly suggests that the same mechanisms underlie both the two- and three-body annihilation processes.

It is instructive to compare the behavior of the molecular gases considered so far with those for which  $\langle Z_{\text{eff}}(0) \rangle \approx Z$ . In the latter cases values of  $a/[\omega\langle Z_{\text{eff}}(0) \rangle]$  at room temperature can again be extracted from the work of Heyland *et al.* [7] but now the values are around two orders of magnitude smaller, and may even be negative. Thus, not only  $\langle Z_{\text{eff}}(0) \rangle$ , but also the size of  $a/[\omega\langle Z_{\text{eff}}(0) \rangle]$ , reflects the enhanced annihilation probability of the positron with certain molecules. The fact that annihilation can occur as a result of positron interactions both with one or with two molecules and that, in one sense, these decay modes are in competition, also suggests that the positron need not be localized around a particular molecule. If it is, the complex must be very

weakly bound such that its wave function is still extended in nature. This observation is similar to one of the conclusions drawn from studies of the  $\gamma$ -ray energy spectra for positrons annihilating from molecules [21], namely, that there appears to be an equal probability of the positron annihilating with any of the valence electrons. As such the positron “density” seems to be distributed about the molecule, rather than localized at a particular (atomic) site. Our work suggests that this argument can be extended beyond the single molecule picture. We are not aware of any other similar observation in low energy positron and electron physics.

An alternative hypothesis to a straightforward three-body interaction to form a temporary positron–double-molecule complex may be that the positron can attach temporarily to one molecule and a second can then, by collision, stabilize the complex leading to annihilation [20]. The rate of such a process is governed by the collision cross section for the extra molecule with the positron-molecule complex, and the positron attachment time. Simple considerations suggest that, for the molecules studied here, the collisional stabilization mechanism is unlikely. Furthermore, the near constancy of the parameter  $a/[\omega\langle Z_{\text{eff}}(0)\rangle]$  (Table I) points against this hypothesis.

In conclusion, detailed measurements at gas densities below 1 amagat have revealed a quadratic form for the free positron annihilation rate in ethylene. Similar behavior has been inferred for four other gases which have been investigated in a similar density range and for which  $\langle Z_{\text{eff}}(0)\rangle \gg Z$ . The parabolic coefficient for all five gases has been found to scale with  $\langle Z_{\text{eff}}(0)\rangle$ . This implies that the same mechanisms operate for all of these gases and are responsible for both the two- and three-body annihilation modes. It is suggested that the positron wave function is extended in nature and that it can form a temporary complex with either one or two molecules. The value of  $\langle Z_{\text{eff}}(0)\rangle$  derived from the current measurement does not agree with that obtained recently from a positron trap measurement [5,3], and is in marked discord with theory [11–13].

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