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LETTER TO THE EDITOR

Three-body effects in positron annihilation on molecules

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Abstract

Detailed studies of the behaviour of positrons in selected room temperature molecular gases at densities below 1 amagat ($\equiv 2.69 \times 10^{25}$ molecules m^{-3}) have allowed the isolation of two- and three-body effects upon the rate of annihilation. Investigations of gas mixtures have helped in removing ambiguities in the interpretation of the data noted in the first study of this phenomenon [1].

Though positron, e^+, annihilation in gases has been studied for more than 50 years, recent experimental developments have shed new light on the complex nature of the interactions of the positron leading to annihilation; see e.g. [2]. Particular cases of interest are species of molecular gas in which $\langle Z_{\rm eff}\rangle$, the ensemble-averaged effective number of electrons available for annihilation as seen by the positron, is much greater than the actual number of molecular electrons, Z. This effect was observed in seminal work by Paul and St. Pierre [3] and received further attention over the years [4] using traditional positron lifetime techniques; see e.g. [5] for a discussion of these methods. In such experiments positrons emitted from a radioactive source slow down directly in the gas under study. In the case of the molecular species studied here, those positrons which do not form positronium annihilate after reaching thermal equilibrium with the gas molecules.

More recently, the study of positron scattering and annihilation using positron traps, and associated beams, has been exploited by Surko and co-workers [2]. Here trapped positrons can interact with molecular gases under single-molecule collision conditions. The number of molecular species for which annihilation parameters were studied has been considerably extended using the trap technique, with instances of $\langle Z_{\rm eff}\rangle/Z$ as high as 10^5 reported [6, 7]. Furthermore, using a narrow energy width beam extracted from a trap [8], energy-resolved $Z_{\rm eff}$ measurements have been presented for the first time [9, 10] for a number of molecular species of interest here. Considerable structure was found in the energy dependences of $Z_{\rm eff}$, which was related to the vibrational modes of the respective molecule. This has provided a detailed insight into the nature of the temporary positron–molecule bound states, which in

many instances precede annihilation. From that work it is clear that annihilation can occur in positron–molecule (M) collisions via the two-body process,

$$e^+ + M \rightarrow \{e^+M\}^* \rightarrow 2\gamma + M^+, \tag{1}$$

where $\{e^+M\}^*$ is the temporary positron–molecule complex, with the 'star' denoting some internal excitation, since the kinetic energy of the positron must be momentarily distributed internally within the complex. Reaction (1) competes with break up of the complex into the positron-plus-molecule state, with the size of $\langle Z_{\rm eff}\rangle$ influenced by the lifetime of the intermediate state.

The importance of the role of virtual states and particularly vibrational Feshbach resonances in the annihilation process for high $\langle Z_{\rm eff}\rangle$ molecules has been enunciated by Gribakin and co-workers [11–13]. Informed by the prominence of single mode features in the measured energy dependence of $Z_{\rm eff}$ [9, 10], it is now thought that initial capture proceeds via the so-called vibrational doorway states [12]. However, due to the high vibrational density of states available in the molecule, a multi-mode vibration of the $\{e^+M\}^*$ state ensues.

A different interpretation of the high values of $\langle Z_{\rm eff}\rangle$ has been suggested by Nishimura and Gianturco [14] who have modelled positron collisions with small hydrocarbons. They found that transient deformations of the C–H bonds can result in low-energy virtual states shifting to negative energy bound states during the collision. This effect may result in longer lived compound states leading to enhancements in $\langle Z_{\rm eff}\rangle$. A brief review of the more general topic of positron annihilation in the vicinity of inelastic thresholds has been given recently [15].

In this work we report further on the phenomenon of three-body influences on positron annihilation in molecules where $\langle Z_{\rm eff}\rangle \gg Z$. This effect, which occurs in a gas density, ρ, range only accessible using traditional positron lifetime apparatus, was unambiguously identified recently [1] in the e^+-C_2H_4 system. There it was pointed out that data presented schematically in earlier works [4] suggested that the effect was not confined to that molecule. By reinterpreting the earlier data [4], three-body annihilation coefficients were extracted for the gases CCl_2F_2, C_2H_6, C_3H_8 and n-C_4H_{10} [1]. Here we report the results of detailed measurements of the annihilation rate, $\langle\lambda_f\rangle$ of positrons in these gases and in CHF_3. We have also repeated the earlier study on C_2H_4. Our purpose is to firmly establish both the $\langle Z_{\rm eff}\rangle$ and the three-body coefficients of these gases, particularly where the results were previously gleaned from data over 20 years old. Gas mixture experiments have also been performed in which both atomic and molecular species with $\langle Z_{\rm eff}\rangle \approx Z$ were added to a high $\langle Z_{\rm eff}\rangle$ molecule in an effort to gain insight into the mechanism underlying the three-body effect.

The experiments were performed using standard positron lifetime spectroscopy methods [5, 16]. The gas cell and related technology are similar to that described elsewhere, except that our gas chamber is limited to pressures of around 1.5 bar and currently only has room temperature capabilities. The lifetime spectra were obtained and stored using commercially available equipment and were analysed offline using standard routines to obtain $\langle\lambda_f\rangle$ [4]. Gas samples were commercially available and were used without further treatment. Note that at the temperatures and pressures used in this study all gases are essentially ideal, with deviations always below 1%. Figure 1 shows the measured annihilation rates at various gas densities for three of the six species studied here. The lines shown indicate fits to the functional form,

$$\langle\lambda_f\rangle = a\rho + b\rho^2, \tag{2}$$

which encompasses annihilation by both two- and three-body processes. The fit to (2) is good in each case, with the exception of C_4H_{10} for which b has a large statistical uncertainty. Attempts to fit a cubic term resulted in a third coefficient consistent with zero in all cases.

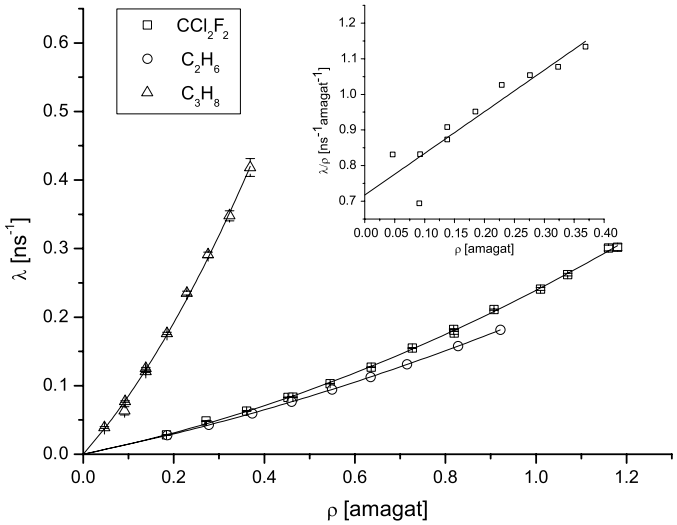

Figure 1. Behaviour of $\langle\lambda_f\rangle$ versus gas density for ethane, propane and freon. The lines shown are the respective quadratic fits. The data for propane are replotted as $\langle\lambda_f\rangle/\rho$ in the inset, with the linear fit according to (4) shown.

Table 1. Annihilation parameters for some of the molecular species amenable to traditional lifetime studies and for which $\langle Z_{\rm eff}\rangle \gg Z$. To convert the three-body coefficients, b, into units of cm^6 s^{-1}, a numerical conversion factor of 1.38×10^{-33} should be applied.

Gas	$\langle Z_{\rm eff}(0)\rangle$	b/ω (amagat^{-1})	$b/(\omega\langle Z_{\rm eff}(0)\rangle)$(amagat^{-1})
C_2H_4	1153 ± 75	668 ± 105	0.58 ± 0.10
C_2H_6	674 ± 21	332 ± 28	0.49 ± 0.05
C_3H_8	3660 ± 60	5754 ± 323	1.58 ± 0.10
C_4H_{10}	$15\,149 \pm 856$	$14\,308 \pm 11476$	1.1 ± 0.9
CCl_2F_2	698 ± 3	481 ± 6	0.69 ± 0.03
CHF_3	267 ± 7	33 ± 6	0.12 ± 0.02

The parameter a is related to the quantity $\langle Z_{\rm eff}(0)\rangle$, the 'zero density' value of $\langle Z_{\rm eff}\rangle$, as deduced from the trap experiments, by $a = \omega\langle Z_{\rm eff}(0)\rangle$ where $\omega \approx 0.2$ (μs-amagat)$^{-1}$ is the Dirac annihilation parameter for a free electron gas (see e.g. [4]). Thus (2) can be rewritten (with $\langle\lambda_f\rangle$ in units of μs^{-1}) as

$$\langle\lambda_f\rangle = 0.2\langle Z_{\rm eff}(0)\rangle\rho + b\rho^2, \tag{3}$$

or

$$\langle\lambda_f\rangle/\rho = 0.2\langle Z_{\rm eff}(0)\rangle + b\rho. \tag{4}$$

A plot of $\langle\lambda_f\rangle/\rho$ versus ρ for propane is included as an inset in figure 1 for illustrative purposes. Table 1 provides a summary of the values of $\langle Z_{\rm eff}(0)\rangle$, b/ω and $b/\omega\langle Z_{\rm eff}(0)\rangle$ derived from the quadratic fits for all species.

The argument was made in [1] that the presence of three-body effects in $\langle\lambda_f\rangle$ was plausible when the positron thermal de Broglie wavelength is compared both to the mean molecular separation of the molecules, and the relevant positron–molecule scattering length (from theory, [17]). However, in that work it was noted that an alternative explanation may

involve stabilization of the temporary positron–molecule bound state $\{e^+M\}^*$, formed as a precursor to annihilation, by collision with another molecule. The latter would constitute the third body. It was argued in [1], on the basis of assumed collision cross sections and the trend of $b/(\omega\langle Z_{\rm eff}(0)\rangle)$ (as measured for C_2H_4, and derived from [4] for the other gases), that the stabilization mechanism was unlikely. However, the two possible three-body reaction mechanisms for the positron may be summarized as follows:

$$e^+ + M + M \rightarrow \{e^+MM\}^* \rightarrow 2\gamma + M^+ + M \tag{5}$$

in which the $\{e^+MM\}^*$ complex is the three-body analogue of the two-body state in equation (1), and

$$\begin{aligned} e^+ + M + M^\dagger(A) &\rightarrow \{e^+M\}^* + M^\dagger(A) \rightarrow \{e^+M\} + M^{\dagger *}(A^*) \\ &\rightarrow 2\gamma + M^+ + M^{\dagger *}(A^*). \end{aligned} \tag{6}$$

Reaction (6) may also be expected to occur for a collision with any molecule or atom (hence the designations $M^\dagger$ and A) since removal of excess internal energy can be achieved by internal excitation of $M^\dagger$, and via momentum transfer with either $M^\dagger$ or A. Reaction (5) might be termed the direct three-body process, with reaction (6) being that due to collisional stabilization.

In the present experiment we have attempted to eliminate one or other of these mechanisms by performing experiments on gas mixtures. Specifically, mixtures of the $\langle Z_{\rm eff}\rangle \gg Z$ molecule C_2H_6 were made with the three $\langle Z_{\rm eff}\rangle \approx Z$ species argon, nitrogen and carbon dioxide. The rationale here is that the contribution to $\langle\lambda_f\rangle$ from direct two-body annihilation on the added species would be negligible in comparison to the effect of the high $\langle Z_{\rm eff}\rangle$ gas. Furthermore, the density of the high $\langle Z_{\rm eff}\rangle$ gas was chosen such that the effect of the three-body process was evident in $\langle\lambda_f\rangle$. Mixtures were made with an ethane density of about 0.46 amagat, and with the density of the added gas of around 0.28 amagat. At 0.46 amagat the three-body process accounts for around 23% of $\langle\lambda_f\rangle$ in C_2H_6, rising to 37% at the combined density of 0.74 amagat in the pure gas alone.

For all added species the measured value of $\langle\lambda_f\rangle$ was consistent with that expected of the mixture, within the experimental uncertainties. The latter included a few per cent effect due to the long time lags encountered in preparing fully mixed gas samples at the densities used. Thus, we infer that reaction (6) does not proceed efficiently with added species $M^\dagger$ and A, and that it is most likely that the three-body mechanism is that of reaction (5) in which a positron interacts simultaneously with two high $\langle Z_{\rm eff}\rangle$ molecules, resulting in an increased probability of annihilation. Thus, the positron wavefunction must be distributed over both molecules, as postulated in [1]. Evidence was found from a trap study of the γ energy spectra from positrons annihilating on high $\langle Z_{\rm eff}\rangle$ molecules [18] that the annihilation was equally likely with any of the valence electrons. This work, together with [1], suggests that this is also true for two molecules simultaneously for the weakly bound positrons involved in such annihilations. Our contribution here is to show that this conclusion applies generally for high $\langle Z_{\rm eff}\rangle$ molecules on the basis of our new measurements.

The values for b/ω (and hence $b/\omega\langle Z_{\rm eff}(0)\rangle$) for C_2H_4 from the present study differ from those measured in [1]. There is also a discrepancy between the current value for $\langle Z_{\rm eff}(0)\rangle$ and that of Charlton *et al* [1]. This is discussed below; however we consider that the values presented here supercede those in [1]. There are no other values of the three-body coefficient to compare to our work, other than those derived in [1] from the earlier studies of Heyland *et al* [4]. There is tolerable accord with these data, given the uncertainties in the present study (particularly for C_4H_{10}) and the fact that no uncertainties were quoted in the earlier work.

Surveying the values of $b/\omega\langle Z_{\rm eff}(0)\rangle$ from table 1 we tentatively conclude that there is a trend, with the coefficient for lower $\langle Z_{\rm eff}(0)\rangle$ molecules being lower than those that have

higher values of $\langle Z_{\rm eff}\rangle/Z$. There is a suggestive correlation with $\langle Z_{\rm eff}(0)\rangle$, notwithstanding the large uncertainty on $b/\omega\langle Z_{\rm eff}(0)\rangle$ for butane.

The values for $\langle Z_{\rm eff}(0)\rangle$ for the species investigated are given in table 1. Where appropriate, there is good accord between these values and those given in [4]. The values of this parameter from trap experiments for ethane, propane and butane are 1280, 2350 and 11 300 respectively [6, 7]. Thus, the significant discord in $\langle Z_{\rm eff}(0)\rangle$ for these species between trap and high density lifetime experiments remains. The value of $\langle Z_{\rm eff}(0)\rangle$ for CHF_3 from the present measurements is in excellent accord with the trap measurement of 247 [6]. To our knowledge, this gas has not previously been studied by the traditional positron lifetime method.

The present result for $\langle Z_{\rm eff}(0)\rangle$ for C_2H_4 is in good accord with the trap result of 1200 [7]. However, there is notable discord with the value of 710 ± 30 given by Charlton *et al* [1] in their first report of the three-body effect. In the course of this study we have performed experiments on different samples of C_2H_4 and have always found values consistent with [7]. The origin of the discrepancy with the earlier experiment [1] is unknown, but it may involve the use of an impure gas sample. Unfortunately, it was not possible to repeat the study, as that gas sample was not available to us. In any case, the room temperature value of $\langle Z_{\rm eff}(0)\rangle$ for C_2H_4 is now firmly established, and this may aid future theoretical investigations of positron–molecule interactions. It is notable that the current theory [17], as corrected [19], is in disagreement with experiment. In future studies it would be useful to extend the density range to search for deviations from equation (3), and for the effects of the saturation of the annihilation rate as the positron lifetime approaches the $\approx$500 ps spin-averaged vacuum lifetime of ground state positronium (see e.g. [20–22]). Extending the study across a systematic family of halogenated hydrocarbons (e.g. $C_2H_nF_{6-n}$) may also be useful in illuminating systematic trends, particularly with respect to the behaviour of the three-body coefficients.

Varying the temperature of the gas may also provide another way to access information about the positron–molecule states. Studies of the positron temperature dependence of $\langle Z_{\rm eff}\rangle$ were reported using the trap technique [6]. Here the positron temperature was raised by exciting the motion of the trapped particles. The results of that study showed a monatonic decline in $\langle Z_{\rm eff}\rangle$, at least up to an energy of about 0.05 eV. The main difference between that experiment and a temperature study using the traditional lifetime method would be that in the latter both the positron and gas temperature would be changed. Theoretical guidance on the potential utility of such studies would be of value, as would a comprehensive investigation of annihilation for simple molecules for which $\langle Z_{\rm eff}\rangle \gg Z$ [23, 24]. Such challenging studies will hopefully be undertaken in the not-too-distant future [24].

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