IOP PUBLISHING JOURNAL OF PHYSICS B: ATOMIC, MOLECULAR AND OPTICAL PHYSICS

J. Phys. B: At. Mol. Opt. Phys. **44** (2011) 175204 (5pp) doi:10.1088/0953-4075/44/17/175204

The temperature and density dependence of positron annihilation in CO_2 and SF_6

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Received 13 May 2011, in final form 17 July 2011
Published 12 August 2011
Online at stacks.iop.org/JPhysB/44/175204

Abstract

Positron lifetime experiments have been performed on CO_2 and SF_6 gases at temperatures in the range 297–400 K and at densities up to 10 amagat. The ensemble-averaged $\langle Z_{\mathrm{eff}}\rangle$ parameter has been extracted at each temperature from the observed density dependence of the annihilation rates. The latter was found to be consistent with annihilation via positron interactions both with single molecules and with pairs. The three-body (positron-plus-two molecules) annihilation coefficient, $\langle b\rangle$, has also been obtained at each temperature. Both $\langle Z_{\mathrm{eff}}\rangle$ and $\langle b\rangle$ are found to be approximately independent of temperature in the range investigated. A simple three-body collision model for $\langle b\rangle$ is developed and discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The interactions of positrons in various media have been of interest for many years, and positron annihilation spectroscopies have found use as probes of, for instance, local electronic or defect densities in condensed matter and materials science (see e.g. [1–3]). However, interest in the fundamental behaviour of positrons in gaseous systems continues to be high, and in particular there is much current activity concerning annihilation in molecular gases. At low gas densities, the mean positron annihilation rate, $\langle\lambda_e\rangle$, is expected to vary with the temperature and density of the gas and is usually written [4] in terms of the (temperature-dependent) parameter, $\langle Z_{\mathrm{eff}}\rangle$, the effective number of electrons available to the positron for annihilation, as

$$\langle\lambda_e\rangle = \pi r_0^2 cn\,\langle Z_{\mathrm{eff}}\rangle. \tag{1}$$

Here r_0 is the classical radius of the electron, c is the speed of light, n is the number density of gas atoms or molecules and $\pi r_0^2 c/v$ is the Dirac free positron–electron annihilation cross section, with v the positron speed. The brackets denote an ensemble average over the positron energy distribution, which here will be characteristic of the temperature of the gas.

It has been known from early studies of positron annihilation in molecular gases (see e.g. [5, 6]) that for some molecular species (e.g. hydrocarbons and some of their derivatives) $\langle Z_{\mathrm{eff}}\rangle$ exceeds the actual number of molecular electrons, Z, by orders of magnitude. More recently, work performed under single-collision conditions using a positron accumulator, and a narrow energy width beam of positrons derived from it, has identified the presence of resonant features in the annihilation cross sections at low energies which are responsible for the high values of $\langle Z_{\mathrm{eff}}\rangle$ [7, 8]. Some of this work has recently been reviewed [9, 10], with [10] including a comprehensive discussion of theoretical models of the annihilation process in high-$\langle Z_{\mathrm{eff}}\rangle$ species [11, 12].

Intriguing features are also to be found in the behaviour of positrons in dense gases, typically at densities of the order of 1 amagat ($= 2.69 \times 10^{25}$ m^{-3}) or greater. In particular, the presence of three-body effects has recently been isolated in positron-molecule annihilation in a selection of species at room temperature [13, 14]. In [14], it was argued that the three-body process may proceed via a reaction of the type

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

where M is a molecule, by analogy with the two-body process

$$e^+ + M \rightarrow e^+M^* \rightarrow 2\gamma + M^+. \tag{3}$$

For these reactions, the intermediate complexes, e^+M^* and e^+MM^*, are thought to form in those cases for which $\langle Z_{\mathrm{eff}}\rangle \gg Z$, which involve temporary binding of the positron to the molecular system. The star in these cases denotes some internal excitation of the complex, since the kinetic energy of the positron must be momentarily distributed therein. Clearly in these instances, annihilation is in competition with break-up of the complex into its original constituents. In $\langle Z_{\mathrm{eff}}\rangle \gg Z$

species, there are two contributions to the annihilation cross section, so-called resonant and direct [11, 12]. The latter will occur for all molecules, irrespective of whether intermediate complexes are formed, but the former, which completely dominates in many cases, must involve temporary resonant attachment.

There are many molecular systems, however, in which $\langle Z_{\rm eff}\rangle \approx Z$ [4, 6, 15], but which still display a wealth of density and temperature-dependent features in their positron annihilation rates (see e.g. [15, 16]). In particular, at temperatures below about twice the critical temperature of the gas, positrons can undergo annihilation in clusters of gas atoms or molecules. The clusters may pre-exist in the gas, or perhaps nucleate around the positron. In any case, annihilation rates are enhanced and at very high densities tend to saturate. At high temperatures, it has been found that the annihilation rates for several gases fell gradually below the linear rise predicted by equation (1). A binary collision model was developed to explain this behaviour [17], as will be discussed in section 3.

The main motivation for the work presented here was to extend the earlier study of Charlton and co-workers [14] to the species CO_2 and SF_6, but at several temperatures in the range 297–400 K. Our density range was restricted to be below $\rho = 10$ amagat. One aim was to benchmark the behaviour of the three-body annihilation reaction in gases without the added complication of resonant behaviour in the process; i.e. to study species for which $\langle Z_{\rm eff}\rangle \approx Z$.

We note, following [14], that assuming both reactions (2) and (3) can occur (with or without the intermediate complex) then the positron annihilation rate must be re-written as

$$\langle \lambda_e\rangle = \langle a\rangle\,\rho + \langle b\rangle\,\rho^2 = \omega\,\langle Z_{\rm eff}\rangle\,\rho + \langle b\rangle\,\rho^2. \qquad (4)$$

Here $\langle \lambda_e\rangle$ is in units of μs^{-1}, with ρ the gas density in units of amagat, and the pre-factor $\omega = 0.201\ \mu s^{-1}$ amagat^{-1} is the density-normalized Dirac rate for a free electron gas. Fitting $\langle \lambda_e\rangle$ yields the parameter $\langle Z_{\rm eff}\rangle$, characteristic of the two-body e^+–M interaction, and the three-body coefficient, $\langle b\rangle$.

In this study, we report the first systematic investigation of the temperature dependence of positron annihilation in molecular gases within the context of the three-body model. The remainder of this paper is organized as follows. Experimental details are presented in section 2, with results, discussion and comparisons to previous work given in section 3. Section 4 contains pertinent conclusions.

2. Experimental details

The positron lifetime spectrometer used was a conventional time-to-amplitude-converter/multi-channel analyser-based system (see e.g. [4]). The positrons were derived from a 150 kBq ^{22}Na source sandwiched between two kapton foils of 10 μm thickness and mounted in a purpose-built holder in the centre of a gas chamber. The delayed coincidence between the nuclear gamma quantum, with an energy of 1.274 MeV (start signal), and one of the 0.511 MeV photons emitted in the annihilation of the positron (stop signal) was measured. The gamma rays were registered by two plastic scintillator–photomultiplier tube arrangements located on either side of the chamber.

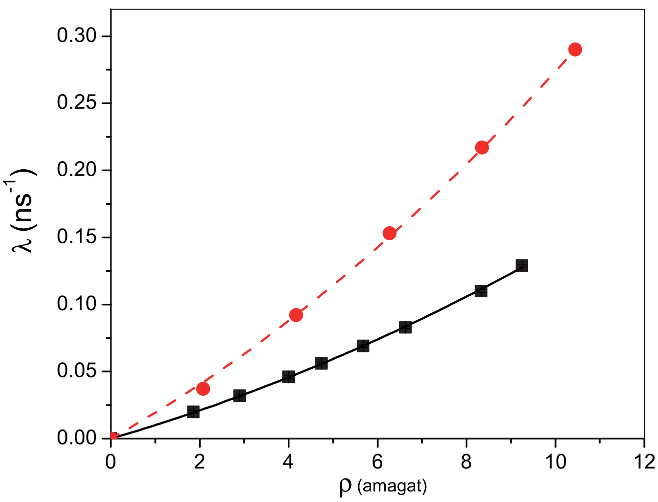

Figure 1. The behaviour of the free positron annihilation rate versus gas density for SF_6 (●) and CO_2 (■) at $T = 297$ K. The lines are the fits according to equation (4).

The gas chamber consisted of a stainless steel cylinder, of inner diameter 35 mm and length 210 mm, into which the sample gases could be admitted at pressures up to 10 atmospheres. For the measurements taken above room temperature, the chamber was heated using an insulated resistance heater wire wrapped directly around the chamber. The temperature of the outer chamber wall was measured using a thermocouple, and the chamber was allowed to stabilize for several hours following a change of temperature before a new run was started. It was found that the temperature was uniform to within ±5 °C across the cell. The gas pressure was recorded using a Druck PDCR 4010 pressure transducer. Gas densities were computed from the temperatures and pressures using accepted first-order virial coefficient corrections [18].

In all cases, the lifetime spectra contained a large prompt peak due to positron annihilations in the source holder and at the chamber wall. After this peak, the events due to the positrons stopped in the gas could be fitted by two overlapping exponentials with a constant background. For the gases studied here, the faster of these two components was that due to the free positrons (the other was due to the annihilation of ortho-positronium atoms created during slowing down of the positrons in the gas), such that $\langle \lambda_e\rangle$ could be extracted at each density/temperature.

3. Results and discussion

Examples of the results for the positron annihilation rates in CO_2 and SF_6 at a temperature of 297 K are presented in figure 1. The fitted lines are those corresponding to equation (4) which allowed values for $\langle Z_{\rm eff}\rangle$ and $\langle b\rangle$ to be obtained, as summarized in table 1 for the two gases at each temperature.

The values for $\langle Z_{\rm eff}\rangle$ at 297 K are noticeably lower than the textbook values of 53 (CO_2) and 97 (SF_6) [4, 15]. The older results were given without uncertainties, based upon previous work [19, 20], and we note that the data from those experiments

Table 1. Values of $\langle Z_{\text{eff}}\rangle$ and the three-body parameter for four different temperatures for CO_2 and SF_6. (Here the three-body coefficient is given as $\langle b\rangle/\omega$, where ω is defined in the text.)

	$\langle Z_{\text{eff}}\rangle$		$\langle b\rangle/\omega$ (amagat^{-1})	
T(K)	CO_2	SF_6	CO_2	SF_6
297	47.8 ± 1.0	82.6 ± 6.5	2.2 ± 0.2	4.8 ± 0.4
320	46.5 ± 0.8	75.1 ± 5.0	2.1 ± 0.1	4.0 ± 0.8
350	48.1 ± 3.6	76.1 ± 6.5	1.9 ± 0.4	2.9 ± 0.8
400	46.0 ± 1.6	74.8 ± 2.7	2.1 ± 0.2	3.4 ± 0.6

were not analysed taking into account the possibility of three-body effects, which may have led to an overestimate of $\langle Z_{\text{eff}}\rangle$.

The values of $\langle Z_{\text{eff}}\rangle$ and $\langle b\rangle/\omega$ at the various gas temperatures show that there is no statistically significant variation in either parameter between 297 and 400 K. The present data exhibit similar phenomena to those of Heyland and co-workers [19], though the latter are only given in graphical form, and the region below 10 amagat was not studied in detail. The increase in $\langle Z_{\text{eff}}\rangle$ apparent in the 350 K SF_6 data of [19] with respect to their data at lower temperatures is, however, not reproduced here. To the best of our knowledge, the only theoretical work for comparison is that of Gianturco and Mukherjee [21] for the case of CO_2. These authors used their energy-dependent values for Z_{eff} to compute $\langle Z_{\text{eff}}\rangle$ for assumed thermal distributions at temperatures of relevance for this experiment. They found $\langle Z_{\text{eff}}\rangle$ to vary little with temperature and to be ~ 51, in reasonable accord with experiment.

As briefly mentioned in section 1, Heyland and co-workers [6, 17] have provided an empirical model of the behaviour of a density-dependent $\langle Z_{\text{eff}}\rangle$, denoted as $\langle Z_{\text{eff}}(\rho)\rangle$ to incorporate the density-dependent behaviour, in gases at high temperatures, typically more than twice the relevant critical temperature. They noted that data for several gases were of the form $\langle Z_{\text{eff}}(\rho)\rangle = \langle Z_{\text{eff}}\rangle/(1+\beta\rho)$, with β a positive constant. Re-arranging by writing $\langle \lambda_e\rangle = \omega\rho\,\langle Z_{\text{eff}}(\rho)\rangle$, it can be seen that $1/\langle\lambda_e\rangle = (1/\omega\rho\,\langle Z_{\text{eff}}\rangle + 1/\lambda_l)$, where $\lambda_l = \omega\,\langle Z_{\text{eff}}\rangle/\beta$. The latter was interpreted as a limiting annihilation rate in the gas as ρ tended to infinity. This was further described using a binary model in which the probability of annihilation on collision was $\lambda_l\,\langle\delta t\rangle$, where $\langle\delta t\rangle$ is a mean duration of the collision. By defining the time between collisions as $\langle\tau\rangle$, the annihilation rate can be written as $\langle\lambda_e\rangle = \lambda_l\,\langle\delta t\rangle/(\langle\tau\rangle + \langle\delta t\rangle)$, such that $1/\langle\lambda_e\rangle = \langle\tau\rangle/(\lambda_l\,\langle\delta t\rangle + 1/\lambda_l)$, which is the same form as that empirically derived, as discussed above. Thus, the high-temperature annihilation rate features can be adequately described in a binary-collision model, such that their physical origin is distinct from the many-body effects observed at lower temperatures. This includes the three-body phenomena which are of special concern here.

The positron annihilation rate may be affected by the presence of pre-existing weakly bound pairs of molecules, as mentioned earlier. Certainly at higher densities and lower temperatures, positron annihilation in clusters is an established phenomenon [4, 16, 19, 22, 23] for a variety of atomic and molecular species. Annihilation on pre-existing clusters would be governed by the attractive van der Waals potential, which is related to the leading-order virial coefficient correction for each gas. We have attempted to compare the size of the virial coefficient correction with the three-body annihilation rate, which is effectively a measure of the departure from the classic two-body annihilation relationship. In order to do this, we have constructed the ratios $(\rho - \rho_{\text{id}})/\rho$ and $\langle b\rangle\,\rho^2/\langle\lambda_e\rangle$, where $\rho_{\text{id}} = 273.15P/T$ is the ideal gas density, with ρ_{id} in amagats and P in atmospheres, at a temperature, T. Given the first-order virial coefficient, B, and with $\rho = \rho_{\text{id}}/(1 + BP)$, it is clear that

$$\frac{(\rho - \rho_{\text{id}})}{\rho} = -BP \tag{5}$$

and

$$\frac{\langle b\rangle\,\rho^2}{\langle\lambda_e\rangle} = \left(1 + \frac{\omega\,\langle Z_{\text{eff}}\rangle}{\langle b\rangle\,\rho}\right)^{-1} = \left(1 + \frac{\omega\,\langle Z_{\text{eff}}\rangle\,T(1+BP)}{273.15P\,\langle b\rangle}\right)^{-1}. \tag{6}$$

Using the derived values of $\langle b\rangle$ and $\langle Z_{\text{eff}}\rangle$ from this study (table 1) and tabulated values of B [18], it can be seen, even in our most extreme case (SF_6 at $T = 297$ K at a pressure of 10 atmospheres), that $\langle b\rangle\,\rho^2/\langle\lambda_e\rangle$ is around five times greater than $(\rho - \rho_{\text{id}})/\rho$: in most cases the former exceeds the latter by about a factor of 10. Thus, we conclude that the three-body effects we observe are predominantly a feature of the positron–gas interaction, and not a result of positron interactions with pre-existing molecular dimers.

We proceed by constructing a hypothetical three-body annihilation rate, $\lambda_{3\text{b}}$, from a two-body scattering rate, $n\sigma_t v$ (where σ_t is a total scattering cross section), multiplied by the probability at a given density of having a further molecule within a volume $r_{3\text{b}}^3$ of the positron–molecule system. The origin of the distance $r_{3\text{b}}$, which parameterizes the strength of the interaction of the complex, is unknown at present, so that it is added empirically. Given that the fraction of collisions that result in annihilation can be written in terms of an annihilation cross section, σ_a, as σ_a/σ_t, $\lambda_{3\text{b}}$ can be found as

$$\lambda_{3\text{b}} = (n\sigma_t v)\left(nr_{3\text{b}}^3\right)(\sigma_a/\sigma_t) = n^2\sigma_a v r_{3\text{b}}^3. \tag{7}$$

By assuming that σ_a is given by the Dirac cross section (see section 1) multiplied by $\langle Z_{\text{eff}}\rangle$ (i.e. $\sigma_a = \pi r_0^2 c\,\langle Z_{\text{eff}}\rangle/v$), equation (7) becomes

$$\lambda_{3\text{b}} = n^2\pi r_0^2 c\,\langle Z_{\text{eff}}\rangle\,r_{3\text{b}}^3. \tag{8}$$

Thus, the three-body coefficient can be identified as $\langle b\rangle = \pi r_0^2 c\,\langle Z_{\text{eff}}\rangle\,r_{3\text{b}}^3$. As such, the temperature dependence of $\langle b\rangle$ (and $\langle b\rangle/\omega$) should be that of $\langle Z_{\text{eff}}\rangle\,r_{3\text{b}}^3$. Since both $\langle Z_{\text{eff}}\rangle$ and $\langle b\rangle$ have been found to be independent of temperature in the range we have explored, the implication is that $r_{3\text{b}}$ must have a weak, if any, temperature dependence. The observations seem to preclude identifying $r_{3\text{b}}$ as the positron de Broglie wavelength, which would introduce an extra $T^{-1.5}$ effect. Using the experimental results for $\langle b\rangle$, a value of $r_{3\text{b}} \sim 13$ Å can be derived for both CO_2 and SF_6. This can be compared to the mean, ideal gas, inter-molecule spacing of $21/\rho^{1/3}$ Å. Thus, the three-body model is expected to break down close to the maximum density we have investigated (around 10 amagat), and the effects of this have been observed previously

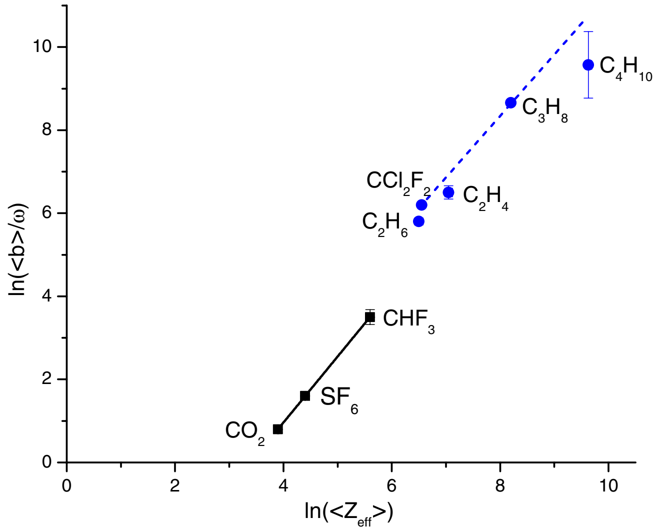

Figure 2. Logarithmic plot of $\langle b\rangle/\omega$ versus $\langle Z_{\mathrm{eff}}\rangle$ for a number of room temperature gases, as labelled. The fits to the two groups of molecules are explained in the text.

(see, e.g., [19]). The reason that, in our analysis, r_{3b} is the same for both gases is likely to be fortuitous and is due to the assumption that $\langle Z_{\mathrm{eff}}\rangle$ can be used to construct λ_{3b}.

Gribakin [24] has also recently described three-body effects in gases with $\langle Z_{\mathrm{eff}}\rangle \gg Z$. His model assumes that the additional contribution to the annihilation in the positron–molecule complex (see equations (1) and (2)) arises due to collisional stabilization of the complex by a second molecule. An assumption is that $\langle b\rangle$ is approximately proportional to $\langle Z_{\mathrm{eff}}\rangle$, such that the three-body effect acts upon the complex and is not an extra pathway to annihilation. This is in accord with the simple model given above.

In order to explore further the scaling behaviour of the three-body coefficient and $\langle Z_{\mathrm{eff}}\rangle$, we have combined the room temperature data for CO_2 and SF_6 from this study with the room temperature values for a selection of $\langle Z_{\mathrm{eff}}\rangle \gg Z$ gases from earlier work [13, 14]. A log–log plot of $\langle b\rangle/\omega$ versus $\langle Z_{\mathrm{eff}}\rangle$ is shown in figure 2, where the gases have been grouped into two sets, namely those with $\langle Z_{\mathrm{eff}}\rangle \approx Z$ and those where $\langle Z_{\mathrm{eff}}\rangle \gg Z$. The motivation for this is that the two-body annihilation mechanisms are quite different for the two classes and involve temporary binding of the positron to the molecule for those with $\langle Z_{\mathrm{eff}}\rangle \gg Z$ (see equation (3)). The lines fitted to the data have similar slopes, having an approximate behaviour as $\langle b\rangle/\omega \propto \langle Z_{\mathrm{eff}}\rangle^{(1.5\pm0.1)}$, though there seems to be an offset, or jump, in $\langle b\rangle/\omega$ between the two groups. The slope suggests a stronger dependence on $\langle Z_{\mathrm{eff}}\rangle$ than predicted from the two models described above.

4. Conclusions

We have presented measurements for the gases CO_2 and SF_6 at temperatures between 297 and 400 K of the parameters $\langle Z_{\mathrm{eff}}\rangle$ and $\langle b\rangle/\omega$ which, respectively, characterize positron annihilation by two- and three-body mechanisms. Both parameters have been found to have no significant variation with temperature in the current range. A simple, empirical, three-body scattering model has been developed to yield an expression for $\langle b\rangle$, though given present uncertainties in the data, no firm conclusions can be drawn as to its validity. A comparison of all available data for $\langle b\rangle/\omega$ at room temperature has revealed that this parameter scales roughly as $\langle Z_{\mathrm{eff}}\rangle^{1.5}$, over a range of $\langle Z_{\mathrm{eff}}\rangle$ values from around 50 to 15000. The physical basis of this scaling is not understood and is contrary to the simple model developed herein. In addition, there is evidence of an offset in $\langle b\rangle/\omega$ between those gases in which temporary binding of the positron to the molecule can occur and the others. Both of these phenomena are worthy of further study, and data for more molecular species may be helpful.

It would also be interesting to measure absolute values for the temperature dependences of $\langle Z_{\mathrm{eff}}\rangle$ and the three-body coefficient for a range of gases with $\langle Z_{\mathrm{eff}}\rangle \gg Z$. In these cases, annihilation via the intermediate state in equations (2) and (3), in which strong energy-dependent features are known to play a role [7–12], would be present. Such a study will be undertaken in our laboratory in the near future.

Acknowledgments

The authors are grateful to the technical staff in the Department of Physics at Swansea for their help with the construction of the apparatus. MGC is grateful to the EPSRC for the provision of a postgraduate studentship. We thank Dr Gleb Gribakin for useful discussions and communications.

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