Positron annihilation in gaseous nitrogen and nitrogen-neon mixtures at 77 K

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Annihilation lifetime spectra have been measured for positrons in N_2 gas at 77 K at densities in the range 1.9–3.6 amagat, and in N_2-Ne gas mixtures at 77 K having N_2 partial densities in the range 0.5–3.7 amagat and with Ne concentrations in the range 0.34–0.98. The annihilation rate of positrons with N_2 was found to be independent of the Ne concentration in the gas mixtures. $(Z_{eff})_{N_2}$ remains constant at 40.0 ± 0.9 at N_2 densities below about 2.3 amagat, but increases to about 108 at 3.7 amagat. Shoulder regions in the lifetime spectra of positrons in N_2 and in N_2-Ne mixtures have been observed which have a constant width of about 14 nsec amagat at N_2 densities below about 2 amagat, but which increase to about 24 nsec amagat at 3.7 amagat of N_2. For N_2 densities in the range 2–3.7 amagat, the measured shoulder widths correspond to a constant time of about 7 nsec. The slow-positron annihilation rates and the shoulder widths are discussed in terms of the self-trapping of positrons within clusters of N_2 molecules.

I. INTRODUCTION

In recent years, as the scattering and annihilation of low-energy positrons in the rare gases have become better understood, increased experimental and theoretical attention has been devoted to positron interactions in molecular gases and in monatomic-molecular gas mixtures. Several of the most interesting annihilation features reported for the noble gases have also been observed in molecular gases, but they are often modified by the existence of excited molecular states and by positron-molecule resonance processes. Two of the earliest investigations[1,2] demonstrated that positrons in many molecular gases annihilate at rates far in excess of those reasonably expected for direct annihilation during positron-molecule collisions and suggested instead the formation of positron-molecule collision complexes. The ranges of temperatures and densities over which such enhanced annihilation rates occur were subsequently investigated for several diatomic and simple polyatomic gases. However, many aspects of positron collision and annihilation processes in molecular gases are not as yet understood.

The diatomic gases H_2 and N_2 offer attractive properties for further investigations of positron-molecule interactions. These gases can be obtained with a high degree of purity, the intermolecular interactions have been well characterized, they remain in the gaseous state to very low temperatures, and they are sufficiently simple in structure to allow *ab initio* calculations. We report here on the annihilation of low-energy positrons in gaseous N_2 and N_2-Ne mixtures at 77 K as a function of N_2 and Ne densities. This research was undertaken in order to further investigate certain annihilation features observed with H_2 and H_2-Ne mixtures; a detailed comparison of the H_2 with the N_2 results

will be published elsewhere.

In Sec. II of this paper we shall describe the experimental and data-analysis techniques used. In Secs. III and IV we shall report on the annihilation of slow positrons in N_2 and N_2-Ne mixtures, respectively. Finally, in Sec. V, we shall discuss positron thermalization and annihilation processes in N_2.

II. EXPERIMENTAL

Positron lifetime spectra were obtained with a standard, fast-slow timing spectrometer which utilized ~4.5 cm×5 cm plastic scintillators optically coupled to RCA 8575 photomultiplier tubes. Constant-fraction timing discriminators provided a full width at half maximum (FWHM) for ^{60}Co prompt peaks of about 0.45 nsec with 50% wide energy windows. The biased time-to-pulse-height converter, which for most of the measurements was operated on a time range of 400 nsec, was calibrated to less than 1% standard error with commercial time-calibration electronics. The calibration was 0.74 nsec per channel for the 400-nsec time range.

Commercially supplied oxygen-free grade N_2 (minimum purity 99.99%, maximum O_2 0.5 ppm) and research-grade Ne (minimum purity 99.995%; maximum He 50 ppm, O_2 1 ppm, N_2 1 ppm, H_2 5 ppm, Ar 1 ppm, CO_2 0.5 ppm, hydrocarbons 0.5 ppm) were used. The initial cleaning of the stainless-steel gas-handling system was done with extreme care to avoid the introduction of impurities into the gases, and standard baking and flushing techniques were used prior to the introduction of final gas samples. The one-piece cylindrical stainless-steel experimental chamber, which has a diameter of ~8.9 and a height of ~10.2 cm, was suspended in a liquid-nitrogen bath. Gas pres-

sures were measured several times during the course of a run, using high-precision Bourdon gauges, and were corrected for barometric fluctuations. Densities corresponding to the average gas pressures for the different runs were determined using the second virial coefficient for N_2 reported by Gyorog and Obert[3] and the second and third virial coefficients for Ne reported by Sengers, Klein, and Gallagher.[4] The deviation of the densities due to all causes was estimated to be less than 2%. Over the range of pressures investigated, the N_2 densities differed by less than 4% from the corresponding ideal-gas densities.

A positron source of about 35 μCi was prepared by depositing an aqueous solution of high specific activity ^{22}NaCl on 0.7-mg/cm^2 Mylar film and then evaporating to dryness. The source was suspended at the center of the experimental chamber. Contributions to the lifetime spectra from positrons annihilating in the source were experimentally determined to be small compared to statistical deviations, and thus no source corrections to the data were made.

The computer program POSITRONFIT EXTENDED was used to analyze the measured lifetime spectra.[5] The spectrum obtained for 60.7-amagat room-temperature N_2 gas exhibited no detectable shoulder region, and was resolved into three lifetime components. The longest-lived component, with an annihilation rate $\lambda_{o\text{-}Ps}$, results from the annihilation of positrons bound in o-Ps atoms, whereas the shortest-lived component results from the annihilation of p-Ps atoms and of positrons in the walls of the experimental chamber. The intermediate-lifetime component, with an annihilation rate λ, is attributed to annihilations in the gas of positrons which do not form positronium. The lifetime spectra obtained at 77 K were characterized by distinct shoulder regions and were resolved into only two components, $\lambda_{o\text{-}Ps}$ and λ. Details of these analyses are discussed in Sec. III and IV.

III. PURE N_2

A. Results at 293 K

In order to check the performance of the lifetime spectrometer and the accuracy of the data-analysis techniques, lifetime spectra were measured in pure room-temperature N_2 gas at densities of 10.2 and 60.7 amagat. Recent measurements of annihilation rates of positrons in room-temperature N_2 at densities up to 72.5 amagat by Coleman et al.,[6] demonstrated a linear dependence of $\lambda_{o\text{-}Ps}$ on density according to

$$\lambda_{o\text{-}Ps} = (7.24 + 0.804 \, ^1Z_{\text{eff}} D) \, \mu\text{sec}^{-1} \quad (1)$$

with $^1Z_{\text{eff}} = 0.258$. $^1Z_{\text{eff}}$ is the effective number of electrons per molecule that are available for pick-off quenching of o-Ps atoms and D is the gas density in amagats. No errors were quoted for this relation, but its fit to the measured data appears to be excellent and it is in good agreement with previous results obtained at lower densities.[7] Analyses of our data yielded $\lambda_{o\text{-}Ps}$ values of 20 ± 1 μsec^{-1} at 60.7 amagat and 10 ± 2 μsec^{-1} at 10.2 amagat. Although the statistics of our spectra, particularly that at the lower density, were inadequate for very precise determinations of lifetimes, these rates agree within errors with those predicted by Eq. (1), 19.8 and 9.3 μsec^{-1}, respectively.

The annihilation rate of low-energy positrons in a gas is often written

$$\lambda = \pi r_0^2 c n_0 D Z_{\text{eff}} \, , \quad (2)$$

where r_0 is the classical radius of the electron, c is the speed of light, and n_0 is the standard number density. Z_{eff} is an empirical constant which for direct annihilations is independent of gas density, and can in that case be interpreted as the effective number of electrons per molecule available for singlet annihilation with thermalized positrons. For direct annihilations, Z_{eff} is generally observed to be slightly larger than Z, the actual number of electrons per molecule, because of molecular polarization.

For room temperature N_2, Coleman et al.,[6] have measured a Z_{eff} which linearly decreases with gas density according to

$$Z_{\text{eff}} = (30.6 \pm 0.2) - (0.091 \pm 0.002)D \, . \quad (3)$$

The value of about 30 obtained at low gas densities is in reasonable agreement with previous low density measurements.[7,8] A three-component analysis of our data at 60.7 amagat yielded a $Z_{\text{eff}} = 26 \pm 1$, which is in agreement with the value of 25.1 ± 0.2 predicted by Eq. (3). A similar fit to the data at 10.2 amagat resulted in a Z_{eff} considerably less than the 29.7 ± 0.2 from Eq. (3). The lower value resulted in part from the inclusion in the analysis of the shoulder region of the lifetime spectrum. This region, which has a width of about 14 nsec amagat as reported by others,[6-9] is not apparent in our 293-K data because of inadequate statistics obtained on an inappropriate time range. Beginning a two-component analysis of the 10.2 amagat spectrum at a channel corresponding to a delay of 26 nsec amagat (chosen larger than 14 nsec amagat to avoid contributions from the short lifetime component as well as the shoulder region) gave a $Z_{\text{eff}} = 28 \pm 2$, in better agreement with Eq. (3).

B. Results at 77 K

A lifetime spectrum for positrons annihilating in 77 K N_2 at 750 torr (3.65 amagat) is shown in Fig. 1. This spectrum shows a distinct nonexponential shoulder region corresponding to the slowing-down process for positrons in the gas and the variation of the annihilation cross section with positron velocity. The contributions of the o-Ps component and the background are also shown in Fig. 1, together with the data remaining after these contributions are subtracted. The slope of the exponential portion of the latter data corresponds to the average annihilation rate of positrons in thermal equilibrium with the gas molecules, as described by Eq. (2). For nonthermalized positrons, Eq. (2) must be generalized to

$$\lambda(E) = \pi r_0^2 c n_0 D Z_{\text{eff}}(E) , \tag{4}$$

where E is the positron energy.

The details of the shoulder region can be better

FIG. 2. Instantaneous $[Z_{\text{eff}}]_{N_2}$ vs tD for several densities of N_2 gas at 77 K. The horizontal lines represent $[Z_{\text{eff}}]_{N_2}$ values corresponding to the annihilation rate of thermalized free positrons with N_2 gas. The data at densities of 3.7 and 3.0 amagat were taken with pure-N_2 gas, whereas the lower three sets of data were taken with N_2-Ne mixtures having partial N_2 densities of 2.6, 2.0, and 1.8 amagat.
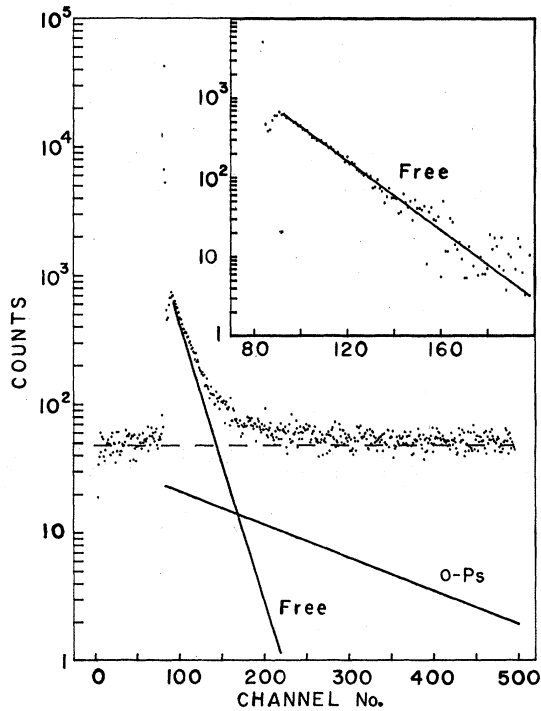

FIG. 1. Lifetime spectrum for positrons annihilating in pure-N_2 gas at 77 K and 3.65 amagat. The solid lines represent the free positron annihilation and o-Ps annihilation contributions obtained from the computer analysis of the data. The dashed line represents the background contribution to the spectrum. The insert shows part of the data remaining after the background and properly normalized o-Ps component have been subtracted from the raw data. A distinct, nonexponential shoulder region is obvious in the insert.
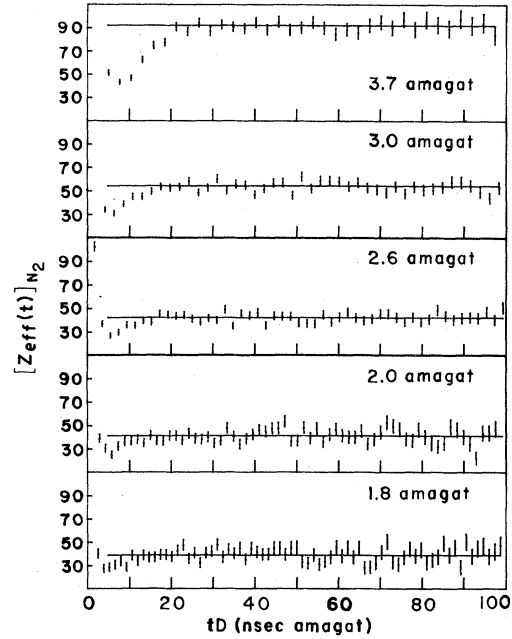
observed by investigating the instantaneous annihilation rate $\lambda(t)$, or equivalently the instantaneous $Z_{\text{eff}}(t)$, defined by

$$\lambda(t) = \pi r_0^2 c n_0 D Z_{\text{eff}}(t)$$

$$= \frac{-dN(t)/dt}{\int_t^\infty [-dN(t')/dt']dt'} . \tag{5}$$

$[-dN(t)/dt]dt$ is the probability of annihilation of positrons between times t and $t+dt$, and is obtained by subtracting the o-Ps component (of appropriately normalized intensity) and the background from the measured lifetime spectrum. The results so obtained for $Z_{\text{eff}}(t)$ are plotted against tD in Fig. 2 for several densities of N_2 gas. The horizontal lines represent the average Z_{eff} values given by Eq. (2) for the annihilation of thermalized positrons. Shoulder widths were estimated from a hand-smoothed fit to the $Z_{\text{eff}}(t)$ data at each density as the time required for the $Z_{\text{eff}}(t)$ to reach $0.9(Z_{\text{eff}})_{\text{equilibrium}} + 0.1(Z_{\text{eff}})_{\text{minimum}}$, which is the criterion of Paul and Leung.[9,10] For N_2 pressures less than 400 torr (1.9 amagat), the shoulder region is not clearly visible in the instantaneous Z_{eff} plots; it is the higher values of the equilibrium
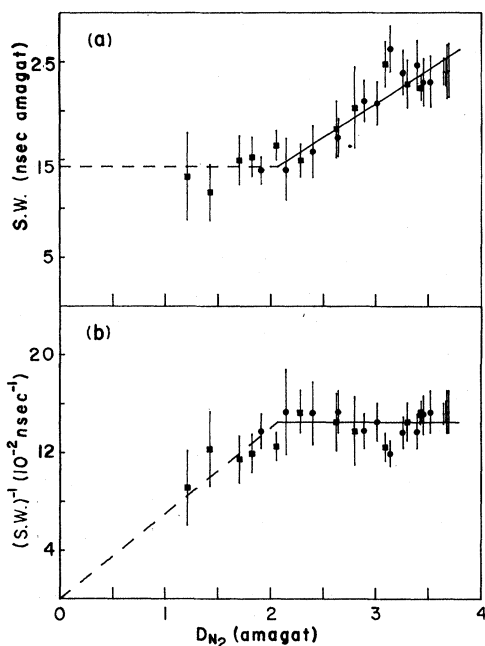
FIG. 3. (a) Shoulder width vs (partial) density of N_2 gas in pure N_2 (circles) and in N_2-Ne mixtures (squares) at 77 K. The bars indicate estimated errors. For reasons of clarity, symbols have not been used for the four highest density points; the three highest of these are derived from N_2-Ne mixtures. The dashed line is obtained from a weighted least-squares fit to the reciprocal shoulder-width data of Fig. 3(b) for N_2 densities up to 2 amagat and constrained to pass through the origin. The solid line represents a weighted average of the reciprocal shoulder-width data of Fig. 3(b) for N_2 densities above 2 amagat. (b) Reciprocal shoulder width vs (partial) density of N_2 in pure N_2 and in N_2-Ne mixtures at 77 K. The symbols and the lines are as described in Fig. 3(a).

Z_{eff} that produce the better-defined shoulder regions at the higher N_2 densities. The measured shoulder widths and their reciprocals are plotted (points) as a function of N_2 density in Fig. 3. These results will be discussed in Secs. IV and V together with results from the N_2-Ne mixture data.

The lifetime spectra at 77 K were analyzed according to the following procedure:

(i) Two-component analyses were begun in channels chosen sufficiently beyond the time-zero channel to ensure that the nonexponential shoulder regions were excluded from the fits.

(ii) The locations of zero time in the lifetime spectra were constrained to experimentally measured positions. The analyses proved to be almost completely insensitive to small variations in the time-zero positions; however, accurate determinations of the time-zero positions are required for computing thermalization times.

(iii) The o-Ps annihilation rates were constrained according to Eq. (1). This assumes that the pick-off annihilation rate [density-dependent term in Eq. (1)] in 77 K N_2 gas is unchanged from that observed at room temperature. However, at our densities, this rate constitutes less than 10% of the total o-Ps annihilation rate of Eq. (1), the predominant contribution being the o-Ps vacuum annihilation rate (7.24 μsec^{-1}). Thus, even if significant differences in the pick-off annihilation rates at the two temperatures were to exist, they would have little effect on the values of $\lambda_{o\text{-Ps}}$ and, as experimentally verified, almost negligible effect on the determination of λ.

(iv) The ratios of the measured background rate to the total counting rate were monitored. For the higher-density runs, none of these ratios deviated from their mean by more than 4%; this mean ratio was used to constrain the background in the analyses of the spectra obtained at lower densities. The background counting rates were always in agreement with those measured on the negative-time portions of the spectra. Because the o-Ps component was so long lived, the background was observed to be strongly correlated with the o-Ps relative intensity, but to have little influence on the much-shorter-lived (by factors of 2 to 8 at our densities) low-energy positron component.

The Z_{eff} and λ values measured for thermalized positrons are plotted (points) in Figs. 4 and 5, re-
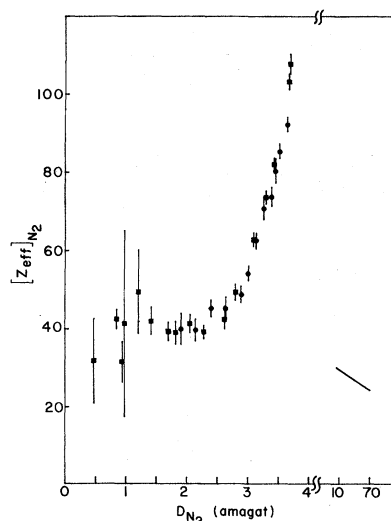

FIG. 4. Z_{eff} values for thermalized positrons annihilating with N_2 molecules in pure N_2 (circles), and in N_2-Ne mixtures (squares) vs (partial) N_2 density at 77 K. The bars indicate statistical standard deviations and the line represents the results of Coleman *et al.* (Ref. 6) for pure-N_2 gas at room temperature.
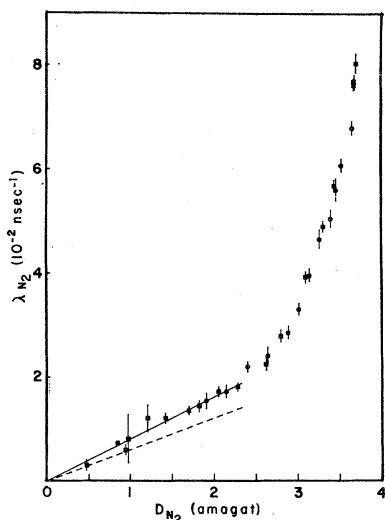
FIG. 5. Annihilation rates for thermalized positrons
with N_2 vs (partial) N_2 density in pure N_2 (circles)
and N_2-Ne mixtures (squares) at 77 K. The bars indi-
cate statistical standard deviations. The solid line
represents a weighted least-squares fit to the data at
densities less than 2.3 amagat and is constrained to
pass through the origin. This line corresponds to a
$(Z_{eff})_{N_2} = 40$. The dashed line corresponds to a $(Z_{eff})_{N_2}$
$= 30$.

spectively, as functions of N_2 density. They will
be discussed more fully in Secs. IV and V.

IV. N_2-Ne MIXTURES

Canter and Roellig[11] have shown that the annihi-
lation rate of positrons in Ne gas at 77 K increases
linearly with density to nearly liquid Ne densities
with a $Z_{eff} = 5.97 \pm 0.15$. This result is in excellent
agreement with the Z_{eff} values determined by other
investigators for Ne at room temperature: Cole-
man et al.,[12] 5.99 ± 0.08; Mao and Paul,[13] 6.02
± 0.16; and Goldanskii,[14] 5.47 ± 0.50. A shoulder
width of 2300 ± 200 nsec amagat for positrons in
room-temperature Ne was determined by Coleman
et al.,[12] whereas a minimum thermalization time
of 2700 nsec amagat was measured by Mao and
Paul.[13] Canter and Roellig,[11] however, were unable
to resolve a nonexponential region in their lifetime
spectra, and yet obtained a Z_{eff} in agreement with
the results of others who analyzed only the data for
thermalized positrons. Thus the annihilation rate
of low-energy positrons in Ne is nearly indepen-
dent of positron energy, and can be described by
$Z_{eff} = 5.97 \pm 0.15$. Additionally, $^1Z_{eff}$ for o-Ps in Ne
has been measured by Coleman et al.,[12] to be 0.235
± 0.008 at room temperature, and by Canter and
Roellig[11] to be unchanged at 77 K up to about 180
amagat.

The analyses of the lifetime spectra for posi-
trons in N_2-Ne mixtures were performed following
a procedure similar to that used for pure N_2. As-
suming that the o-Ps annihilation process with ei-
ther N_2 or Ne is unaffected by the presence of the
other gas, the annihilation rates corresponding to
the o-Ps component of the spectra were con-
strained according to

$$\lambda^{mix}_{o\text{-}Ps} = \{7.24 + 0.804[(^1Z_{eff})_{N_2} D_{N_2} + (^1Z_{eff})_{Ne} D_{Ne}]\} \ \mu sec^{-1} , \quad (6)$$

where $(^1Z_{eff})_{N_2} = 0.258$, $(^1Z_{eff})_{Ne} = 0.235$, and D_{N_2} and
D_{Ne} are the partial densities of N_2 and Ne, respec-
tively, in amagat. The $(Z_{eff})_{N_2}$ for positrons an-
nihilating with the N_2 component of the mixtures
were calculated from

$$\lambda^{mix} = \pi r_0^2 c n_0 [(Z_{eff})_{N_2} D_{N_2} + (Z_{eff})_{Ne} D_{Ne}] , \quad (7)$$

where $(Z_{eff})_{Ne} = 5.97 \pm 0.15$. This again assumes in-
dependent annihilation processes with N_2 and Ne
in the mixture.

Total annihilation rates were measured for N_2-
Ne mixtures containing a constant Ne partial den-
sity of 1.84 amagat and six N_2 partial densities
between 0.97 and 2.28 amagat. A weighted least-
squares fit to the λ^{mix} vs D_{N_2} data, which had large
statistical errors at the smaller D_{N_2}, gave a D_{N_2}
$= 0$ intercept of 3.4 ± 3.1 μsec^{-1}. Using Eq. (7),
this rate corresponds to a $(Z_{eff})_{Ne}$ of 9 ± 8, in at
least rough agreement with the value of 5.97 dis-
cussed above.

Following Eqs. (5) and (7), the instantaneous an-
nihilation rate $\lambda^{mix}(t)$ for positrons in the mixture
is related to $[Z_{eff}(t)]_{N_2}$ according to

$$\lambda^{mix}(t) = \pi r_0^2 c n_0 \{[Z_{eff}(t)]_{N_2} D_{N_2} + (Z_{eff})_{Ne} D_{Ne}\} , \quad (8)$$

where

$$\lambda^{mix}(t) = \frac{-dN(t)/dt}{\int_t^\infty [-dN(t')/dt'] \, dt'} . \quad (9)$$

The $[Z_{eff}(t)]_{N_2}$ calculated from Eqs. (8) and (9) were
used to determine shoulder widths for positrons in
the mixture.

The shoulder widths, which are the times re-
quired for positrons to slow to near-thermal ener-
gies, in N_2 and in N_2-Ne mixtures are plotted in
nsec amagat of N_2 units as a function of N_2 (partial)
density in Fig. 3(a). The reciprocal shoulder
widths are plotted in $nsec^{-1}$ units vs N_2 (partial)
density in Fig. 3(b). The error bars indicate the
estimated errors in determining the shoulder
widths from the instantaneous Z_{eff} plots. The lines
represent weighted fits to the data; they are dis-
cussed in Sec. V. Within errors, the shoulder
widths measured for pure N_2 agree with those
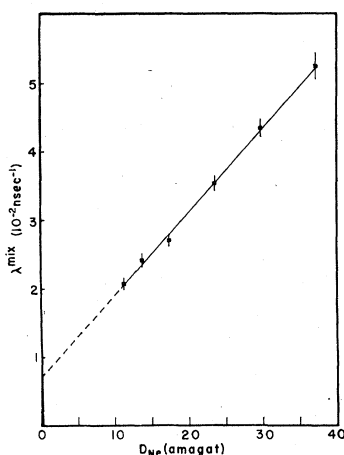measured for N_2-Ne mixtures containing the same

FIG. 6. Total annihilation rates of thermalized positrons in N_2-Ne mixtures vs partial Ne density at 77 K. The mixtures have constant partial density of $N_2 = 0.85$ amagat. The bars indicate statistical standard deviations. The solid line represents a weighted least-squares fit to the data. The dashed line is an extrapolation of this fit.

partial densities of N_2 and having Ne concentrations in the range 0.34–0.61. As can be seen from Fig. 3(a), the shoulder widths are in the 11–15 nsec amagat range near 1.5 amagat, and increase to the 20–25 nsec amagat range near 3.5 amagat.

The values of Z_{eff} measured for thermalized positrons annihilating with N_2 molecules in pure N_2 and N_2-Ne mixtures at 77 K are plotted in Fig. 4 as a function of N_2 (partial) density. The room temperature-results of Coleman et al.,[6] are shown for comparison. The error bars in Fig. 4 represent the statistical standard deviations. No significant differences are observed between the values measured in pure N_2 and those measured in the N_2-Ne mixtures, thus justifying our assumption of independent positron and o-Ps annihilation processes with the N_2 and Ne components of the mixtures.

At densities above about 2.3 amagat, Z_{eff} is seen to increase dramatically with N_2 density, reaching a value of 108 at 3.7 amagat. At the lowest densities investigated, Z_{eff} appears to be approaching a value closer to 40 than to the value of 30 observed by others[6,7,15] at room temperature. This feature is seen more clearly in Fig. 5, where the annihilation rates for thermalized positrons with N_2 are plotted versus N_2 (partial) density. The dashed line corresponds to a Z_{eff} of 30. The solid line is obtained from a weighted least-squares fit to the data at densities less than 2.3 amagat which is forced to pass through the origin. This fit yields

$$\lambda = (8.0 \pm 0.2) \times 10^{-3} D_{N_2} \,, \tag{10}$$

where λ is in $nsec^{-1}$ and D_{N_2} is in amagat. The

Z_{eff} is calculated to be 40.0 ± 0.9.

The equilibrium Z_{eff} for N_2 can also be obtained from an analysis of λ^{mix}-vs-D_{Ne} data measured with N_2-Ne mixtures containing a constant partial density of N_2. Such data are shown in Fig. 6 for $D_{N_2} = 0.85$ amagat. A weighted least-squares fit to the data, shown as a solid line in Fig. 6, gives an intercept of 7.0 ± 1.1 μsec^{-1} at zero Ne density. This rate corresponds to $(Z_{eff})_{N_2} = 41 \pm 7$, in agreement with the more precise result quoted above.

V. DISCUSSION

A. Positron annihilation rates

Although measurements were possible only over a small range of N_2 densities at 77 K, the behavior of Z_{eff} for N_2 as a function of D_{N_2} (Fig. 4) for thermalized positrons annihilating in pure N_2 gas at 77 and 293 K and in gaseous N_2-Ne mixtures at 77 K appears qualitatively similar to that reported for CH_4 (Ref. 16) and H_2.[17] At low densities of these gases, and at sufficiently high temperatures, λ is found to be linearly dependent on density and to be represented, therefore, by constant values of Z_{eff}. The low-density Z_{eff} values of CH_4 and H_2, being about 15 and 8 times the actual number of electrons per molecule, respectively, are larger than those expected for direct annihilations during positron-molecule collisions. For example, a recent theoretical study of the interaction of low-energy positrons with H_2 molecules, which incorporates a sufficiently strong empirical polarization potential to give total elastic cross sections in reasonable agreement with experiment, predicts a Z_{eff} at thermal energies that is an order of magnitude less than the measured values.[18] As previously mentioned, such high values of Z_{eff} might result from the formation of positron-molecule collision complexes.

The values of Z_{eff} measured for thermalized positrons in low-density N_2 exceed the actual number of molecular electrons by factors of only about 2 at room temperature and about 3 at 77 K. Considering that the spherical and anisotropic polarizabilities and the quadrupole moment of N_2 are over twice as large as the corresponding values for H_2, and that the effects of the quadrupole and polarization interactions reinforce each other in N_2 whereas they cancel for H_2,[19] it might be expected that the observed annihilation rates could result entirely from direct annihilations on polarized N_2 molecules. Some support for this picture is obtained from the calculations of Darewych and Baille.[20] These authors investigated the interaction of low-energy positrons with molecular nitrogen in the adiabatic (fixed-nuclei) approximation, using a one center formalism that is in all respects similar to

that used for the positron-H_2 calculations dis-
cussed above. With the effect of the distortion of
the electronic cloud by the incoming positrons in-
cluded through the use of empirical velocity-inde-
pendent polarization potentials that had proven
successful for calculations of electron-N_2 scatter-
ing, they calculate a Z_{eff} which rapidly decreases
from 30 near zero energy to 7 at and above 2 eV.
At thermal energies at 77 and 300 K, the predicted
Z_{eff} values are about 29 and 23, respectively.
These values are less than the measured values of
40 and 30, respectively, by only about 25%, and
the calculated dependence of Z_{eff} on positron ener-
gy is seen to be in good qualitative agreement with
experiment.

However, it must be noted that the calculations
of Darewych and Baille yield total scattering cross
sections that appear to have the wrong shape in the
energy range 3–10 eV. Gillespie and Thompson[21]
have further investigated the positron-N_2 scatter-
ing problem and conclude that a velocity-indepen-
dent potential which reproduces the thermal-energy
experimental Z_{eff} will not give a good scattering
cross section in the higher-energy range ($\gtrsim 1$ eV)
where measurements can currently be made. They
attribute the failure of Darewych and Baille to pre-
dict the correct dependence of the cross section on
positron energy to the use of a very strong attrac-
tive potential. Using a weaker velocity-indepen-
dent potential, which is the direct molecular
counterpart of that used for positron-atom scatter-
ing, Gillespie and Thompson calculate positron-N_2
cross sections which are in fair agreement with
experiment. Although they report no Z_{eff} values,
comparison with positron-atom scattering calcula-
tions leads them to suppose that their potential will
be too weak to yield the large thermal-energy val-
ues of Z_{eff}.

It is thus not possible at this stage in the devel-
opment of positron-molecule scattering theory to
decide whether the large thermal energy values of
Z_{eff}, measured at those N_2 densities where λ is
directly proportional to D_{N_2}, can be totally at-
tributed to the polarization distortion of the molec-
ular electrons. The above discussion indicates,
however, that should positron-N_2 scattering in-
volve the formation of collision complexes, then
either the formation process cannot be highly
probable or the resulting states must be short
lived relative to the lifetime of the bound positron.

At gas densities above specific temperature-de-
pendent values, the annihilation rates of thermal-
ized positrons in CH_4,[16] H_2,[17] and N_2 deviate from
the linear dependence on density observed at lower
densities. For 77 K N_2 at densities greater than
about 2.3 amagat, Z_{eff} is seen (Fig. 4) to increase
rapidly with density, indicating the interaction of

positrons with two or more N_2 molecules.

A possible explanation for a nonlinear depen-
dence of λ on D_{N_2} would be the formation of nitro-
gen dimers. The probability of dimer formation
would increase with gas density, and since the
binding energy of such dimers is very small, the
equilibrium dimer concentration would be enhanced
by low gas temperatures. Following Stogryn and
Hirschfelder[22] and Frommhold[23] we write for the
dimer density N_d

$$N_d = X_2 N , \tag{11}$$

where N is the neutral density and X_2 is the mole
fraction of dimers. X_2 is a function of temperature
and is proportional to N; thus, N_d is proportional
to N^2. Assuming a Lennard-Jones 6-12 potential,
with constants given by Hirschfelder et al.,[24]
Frommhold calculates

$$X_2/p = 43 \times 10^{-6} \text{ torr}^{-1} \tag{12}$$

for N_2 at 77 K and pressure p. At our maximum
pressure of 750 torr, this treatment predicts an
equilibrium mole fraction of about 0.03. Further,
measured dimer concentrations for many molec-
ular gases are much lower than those theoretically
predicted in this manner.[25] In particular, for 750
torr of N_2 at 300 K the experimentally determined
dimer concentration is found to be smaller than
that predicted by more than two orders of magni-
tude.[25] We conclude that, at the pressures and
temperatures used in our measurements, dimer
formation contributes negligibly to the annihilation
rates.

It has been experimentally[26] and theoretically[27]
demonstrated that, in He gas near the gas-liquid
critical point, attractive electrostatic forces cause
the clustering of He atoms about low-energy posi-
trons leading to a gas-liquid-like phase transition
at temperatures both below and above the critical
temperature of ordinary He liquid. The minimum
gas densities at which this self-trapping of posi-
trons in high-density clusters begins is observed
to increase with temperature. The onset of clus-
tering is seen as an increase in λ from the linear
density dependence observed at constant tempera-
ture at lower densities to values corresponding to
liquid He densities.[26,28] These transitions in λ
have a finite density width which is likely due to
the finite number of atoms in the droplet. The
positron localized within the droplet samples an
effective density which is obtained by weighting the
density profile of the droplet with the square of the
positron wave function. Fluctuations in the droplet
size, which increase considerably near the critical
point of the droplet phase, thus appear as a
smearing of the transitions.

Such a breaking down of the linear density depen-

dence of the annihilation rate is also evident in Fig. 5 for positrons in N_2 gas at 77 K, indicating the possible beginning of N_2 molecule clustering about positrons. Assuming a Z_{eff} as low as 13.8, the value reported for liquid N_2,[29] the annihilation rate for 3.6 amagat N_2 corresponds to an effective density of only 24 amagat. The density of liquid N_2 is about 650 amagat. It appears, therefore, that at the highest gas densities available at 77 K, the clustering process in N_2 is still embryonic. Positron lifetime measurements at temperatures closer to, and above, the critical temperature will be important to the further investigation of positron-induced clustering in N_2.

B. Shoulder widths

Shoulder widths have now been accurately measured for positrons in all of the rare gases through xenon.[30] When expressed in time-density dimensions, they are found to be independent of the gas density,[31] with values ranging from 200 nsec amagat for xenon to over 2300 nsec amagat for neon. For N_2 gas at 77 K, the shoulder widths in nsec amagat units [Fig. 3(a)] are also observed to be independent of density for N_2 densities less than about 2 amagat. It is also for these densities that a linear dependence of the equilibrium rate on N_2 density is found. The dashed line in Fig. 3(b) represents a weighted least-squares fit to the reciprocal shoulder-width data at densities up to 2 amagat, which is constrained to pass through the origin. The fit yields a shoulder width of 14 nsec amagat with an estimated error of 2 nsec amagat. This is to be compared with the density independent values of 14 ± 3 and 14 ± 2 nsec amagat measured by Tao[15] and by Coleman et al.,[6,32] respectively, for low-density N_2 at room temperature.

At N_2 densities greater than about 2 amagat, the measured shoulder widths in nsec amagat units are no longer constant, but now increase in an approximately linear manner with N_2 density.[33] The solid line in Fig. 3(b) represents a weighted average of the reciprocal shoulder-width data for N_2 densities above 2 amagat. This average and its estimated error correspond to a density-independent shoulder width of 7.0 ± 0.5 nsec.

As discussed by Paul and Leung[9] and by Tao,[15] the time required for positrons in N_2 gas to be moderated from 5.1 eV, the lowest energy for any form of electronic excitation, to the vibrational-excitation threshold at 0.29 eV is only about 1 nsec amagat. The slowing-down time from higher energies to 5.1 eV is also known to be very fast.[15] Thus during thermalization in low-density N_2, a positron spends most of its time at energies where rotational excitation of N_2 molecules and elastic

scattering are the only available modes of energy loss. So long as this remains the case, the shoulder width should remain constant in nsec amagat units as the N_2 density increases. This thermalization picture is consistent with the observations[6,8,9,32] and calculations[6,9] of shoulder widths for room temperature N_2 and with our measurements at 77 K below 2 amagat; the preliminary results of Coleman et al.,[6] indicate that the thermalization time calculated using current values for the rotational- and momentum-transfer cross sections[19,20] is consistent with the measured room-temperature shoulder width.

In order for the shoulder width at densities above 2 amagat to become approximately constant in nsec at a value greater than those expected at these densities, a new slower energy-loss mechanism which is nearly independent of density must now favorably compete with the faster density-dependent energy-loss processes. A positron-N_2 interaction which trapped positrons having energies significantly above thermal, for example a vibrationally excited positron-N_2 complex, would also contribute to $Z_{eff}(t)$ at times much less than those at which $Z_{eff}(t)$ reaches its equilibrium values at densities just under 2 amagat. This is not observed. Furthermore, those positrons which escape from (or avoid) such "high-energy" trapping, albeit with reduced energy, must still undergo at least some energy loss below 0.29 eV, which would again result in a density-dependent slowing-down time. We are, therefore, seeking a density independent energy-loss mechanism that is available to positrons having near-thermal energies.

Assuming that the occurrence of changes in the density behavior of both the annihilation rate and the shoulder width at about 2 amagat of N_2 is more than coincidental, we consider the possibility that the onset of self-trapping of low-energy positrons within clusters is responsible for both effects. The existence of a stable cluster requires the positron thermal energy to be much less than its binding energy to the cluster. When clusters first form about suprathermal positrons, this cannot be the case. Until the excess positron energy, including that released by the binding, can be dissipated, the cluster will be unstable towards dissociation. Provided that the dissociation lifetime of clusters formed about suprathermal positrons is sufficiently short, a positron might become trapped several times prior to annihilation. The positron would be emitted with reduced energy from a dissociating cluster since part of its initial excess energy would have been redistributed among the internal degrees of freedom of the cluster. The temporary self-trapping of low-energy positrons within clusters would thus constitute an additional slowing-

down mechanism in competition with rotational excitation and elastic scattering. Further, it would be reasonably expected that the fractional energy loss per cluster dissociation would be significantly larger than that experienced by positrons of similar energy during a few non-cluster-forming positron-N_2 collisions. If the probability per collision for cluster formation is large, then the temporary trapping mechanism would dominate the slowing-down process, and the shoulder width would be primarily determined by the time spent in trapped states. Additionally, in agreement with observation, the shoulder width in nsec would now be (nearly) independent of gas density.

As positron energies approach thermal values, cluster-dissociation lifetimes and the fractional

energy losses suffered by positrons emitted from clusters would become more sensitive to the temperature of the gas. It appears that higher temperatures result in larger, but still density independent, shoulder widths.[33] Additional more precise measurements are needed to accurately determine the temperature and density dependencies of the positron slowing-down time in N_2.

ACKNOWLEDGMENTS

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