Positron annihilation in gaseous hydrogen and hydrogen-neon mixtures. I. Low-energy positrons

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Annihilation lifetime spectra have been measured for positrons in H_2 gas at 293, 250, and 77 K at densities in the range 5.9–429 amagat, and in H_2-Ne gas mixtures at 77 K having H_2 partial densities in the range 1.9–286 amagat and with Ne concentrations in the range 0.02–0.98. The annihilation rate of slow positrons with H_2 has a complex dependence on gas density and temperature. Particularly at low H_2 densities, the presence of various partial densities of Ne can dramatically affect the positron-H_2 annihilation process. The slow-positron annihilation rates are discussed in terms of positron-H_2 collision complexes and the self-trapping of positrons within clusters of H_2 molecules. The annihilation in H_2 of positrons bound in Ps atoms is discussed in paper II of this series.

I. INTRODUCTION

Recent experimental and theoretical studies of the scattering and annihilation of low-energy positrons in noble gases have contributed significantly toward an understanding of positron-atom interactions. Positron annihilation studies with diatomic and simple polyatomic gases, and their mixtures with noble gases, are now beginning to reveal the influence of molecular excitation states and positron-molecule resonance states on the annihilation process. However, many aspects of positron-molecule collision and annihilation interactions remain only qualitatively understood, or not understood at all.

Because H_2 and N_2 can be obtained with a high degree of purity, remain in the gaseous state to very low temperatures, have well-characterized molecular properties and intermolecular interactions, and are sufficiently simple in structure to allow *ab initio* calculations, these diatomic gases are well suited for further investigations of positron-molecule interactions. Moreover, differences in the molecular properties of H_2 and N_2, for example, in their rotational and vibrational excitation threshold energies and in their quadrupole and polarization interactions, might influence the annihilation processes, and thus a comparison of the measured annihilation behavior of positrons in these otherwise similar gases might provide additional insight into positron-molecule interactions.

We report here on the annihilation of low-energy positrons in gaseous H_2 and H_2-Ne mixtures as a function of temperature (293, 250, and 77 K) and H_2 and Ne densities. Similar measurements with gaseous N_2 and N_2-Ne mixtures have been previously reported.[1] Variations in gas temperature and density and in Ne concentration are found to strongly affect one or more of the following positron-hydrogen or positron-nitrogen annihilation parameters: the annihilation rate of positrons which do not form positronium, the annihilation rate of positrons bound in positronium atoms, the fraction of positrons which form positronium, and (in N_2 only) the shoulder width of the lifetime spectrum.

Since in the absence of externally applied electric fields the process by which positrons form positronium or become slow positrons is irreversible, the two groups of positrons can be regarded as distinct species. Following a discussion in Sec. II of the data acquisition and analysis techniques employed, the annihilation rates measured for low-energy positrons in pure H_2 gas at 293 and 250 K and in pure H_2 at 77 K will be reported in Secs. III and IV, respectively. In Sec. V, we report on the measured annihilation rates of slow positrons in mixtures of H_2 and Ne at 77 K. Finally, in Sec. VI, a discussion of the annihilation processes available to low-energy positrons in H_2 is presented. The formation and annihilation of positronium in H_2 and H_2-Ne mixtures is discussed in the following paper.

II. EXPERIMENTAL

Commercially supplied[2] ultrahigh-purity grade H_2 (minimum purity 99.999%; maximum 1-ppm O_2, 1-ppm CO plus CO_2, 0.8-ppm hydrocarbons, 50-ppm He, 5-ppm H_2O) and research-grade Ne (minimum purity 99.995%, maximum 1-ppm O_2, 1-ppm N_2, 5-ppm H_2, 50-ppm He, 1-ppm Ar, 0.5-ppm CO_2, 0.5-ppm hydrocarbons) were used. The usual cleaning procedures[1] were applied to the stainless-steel gas handling system in order to prevent the introduction of impurities into the gas samples, and several times during course of the experiment the gas samples were replaced with fresh ones with no resulting change in the annihila-

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tion spectra being observed.

The positron sources were prepared on single strips of ~0.7 mg/cm^2 Mylar foil by depositing an aqueous solution of high specific activity ^{22}NaCl and then evaporating to dryness. The source activities were about 40 μCi for the 293- and 250-K runs, and about 30 μCi for the 77-K runs. Each source was centrally suspended in a one-piece cylindrical (diameter ~8.9 cm, height ~10.2 cm) stainless-steel experimental chamber. The chambers were immersed either in a temperature controlled oil bath or in a liquid-nitrogen bath. Oil bath temperatures were measured with a commercially calibrated platinum resistance thermometer and were automatically recorded at 10-min intervals. The temperature of the liquid-nitrogen bath was assumed constant at 77.4 K. Gas pressures were measured several times during the course of a run, using high-precision Bourdon gauges with overlapping ranges, and were corrected for barometric fluctuations. Average densities for the different runs were calculated from the measured temperature-pressure data using (i) the second and third virial coefficients for H_2 reported by Sengers *et al.*[3] for H_2 densities less than 155 amagat, (ii) the 17-parameter equation of state for H_2 adapted by Roder and Goodwin[4] from the Benedict, Webb, Rubin equation for H_2 densities above 155 amagat, and (iii) the second and third virial coefficients for Ne reported by Sengers *et al.*[3] The deviation of the densities due to all causes is estimated to be less than 2%. Over the ranges of pressures investigated, the H_2 densities differ from the corresponding ideal-gas densities by less than 9% at 293 and 250 K, and by less than 7% at 77 K.

Positron lifetime spectra were obtained with a standard, fast-slow timing spectrometer operated on time-to-pulse-height converter time ranges appropriate to the mean lives being measured.[1] The full width at half maximum for ^{60}Co prompt peaks was less than 0.5 nsec on the 400-nsec time range used for most of the measurements, and the spectrometer was calibrated to less than 1% standard error with commercial time calibration electronics.

The computer program POSITRONFIT EXTENDED[5] was used to resolve the measured spectra into three lifetime components. The shortest-lived component results from the annihilation of free positrons in the walls of the experimental chamber and of p-Ps atoms. The longest-lived component, with an annihilation rate $\lambda_{o\text{-Ps}}$, results from the annihilation of positrons bound in o-Ps atoms. The intermediate component, with an annihilation rate λ, is attributed to annihilations in the gas of low-energy positrons which do not form positronium. At 293 and 250 K and at H_2 densities lower than those reported in Fig. 2, the o-Ps lifetime components could not be unambiguously resolved from background, and $\lambda_{o\text{-Ps}}$ was constrained in the spectrum analyses to values determined by linear fits to the data at higher densities. A similar constraint on $\lambda_{o\text{-Ps}}$, described in Sec. V, was imposed on the spectrum analyses for H_2-Ne mixtures at very low H_2 and Ne partial densities. These constraints on $\lambda_{o\text{-Ps}}$ had only minimal effect on the fitted λ values. At low H_2 densities ($D < 38$ amagat) at 77 K, where it was desired to obtain precisely measured $\lambda_{o\text{-Ps}}$ values, backgrounds were determined in a manner previously described[1] and were held fixed in the analyses. These were the only constraints used in any of the analyses. No source corrections were incorporated because the contribution to the lifetime spectra from positrons annihilating in the single thickness of 0.00025-in. Mylar was experimentally determined to have only a small effect on the fitted parameters compared to their statistical standard deviations.

Nonlinear least-squares fits of one or two Gaussian functions to measured ^{60}Co prompt peaks were used to represent the time-resolution function of the spectrometer, and the spectrum analyses included several data channels on the negative time side of the spectrum peak. Test analyses begun several channels beyond the peak on the positive time side, where no contribution remains from the shortest-lived component and the analyses are relatively insensitive to the details of the resolution function and to starting channel, yielded values for $\lambda_{o\text{-Ps}}$, λ, and the ratio $I_{o\text{-Ps}}/I$ of the corresponding relative intensities that were in good agreement with those obtained from analyzing the entire spectrum.

A lifetime spectrum for positrons annihilating in 77-K H_2 at 260 amagat is shown in Fig. 1. The contributions of the o-Ps component and the background are also shown, together with the data remaining after these contributions and the shortest-lived component are subtracted. The slope of the latter data is a measure of the rate at which low-energy positrons annihilate in the gas.

III. H_2 AT 293 AND 250 K

The annihilation rate of low-energy positrons in a gas is usually expressed as

$$\lambda(E) = \pi r_0^2 c n_0 D Z_{\text{eff}}(E) , \tag{1}$$

where E is the energy of the positron, r_0 is the classical radius of the electron, c is the speed of light, n_0 is the standard number density, and D is the density of the gas in amagat. $Z_{\text{eff}}(E)$ is an empirical parameter which for the direct annihilation

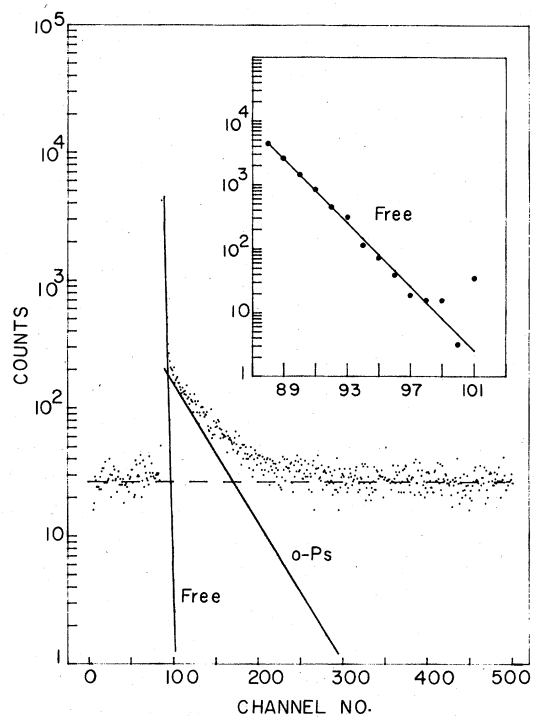

FIG. 1. Lifetime spectrum for positrons annihilating in pure H_2 gas at 77 K and 260 amagat. The time width of each channel is 0.74 nsec. The solid lines represent the free positron and o-Ps annihilation contributions, and the dashed line represents the background contribution. The insert shows part of the data remaining after the background, and the o-Ps and shortest-lived components have been subtracted from the raw data.

of free positrons with electrons is independent of density, and can in that case be interpreted as the effective number of electrons per molecule available for singlet annihilation with positrons. The energy dependence of Z_{eff} arises from an energy-dependent positron wave function Ψ_+^E according to

$$Z_{\text{eff}}(E)=\sum_{i=1}^{z}\int|\Psi_+^E(\vec{r})|^2|\Phi_i(\vec{r})|^2 d\vec{r}\,, \qquad (2)$$

where Φ_i is the wave function of the ith electron of a gas having z electrons per molecule. At low positron energies, $Z_{\text{eff}}(E)$ increases with decreasing E because of the greater molecular polarization produced by the colliding positron.

For positrons in thermal equilibrium with the gas molecules, the measured annihilation rate represents an average over the thermal energy distribution and is expressed as

$$\lambda=\pi r_0^2 c n_0 D Z_{\text{eff}}\,. \qquad (3)$$

The temperature dependence of λ, and thus of Z_{eff}, has been observed with Ar (Ref. 6) and with N_2.[1]

The annihilation of nonthermalized positrons in gases is evidenced in the positron lifetime spectra by nonexponential shoulder regions which result from the slowing-down process for positrons in the gas and the variation of the annihilation cross section with positron velocity. The widths of the shoulder regions for the noble gases vary from 200 nsec amagat for Xe to over 2300 nsec amagat for Ne.[7]

Because of more rapid positron thermalization times, the shoulder regions in molecular gases would be considerably smaller. The only molecular gas for which a shoulder region has been directly observed is N_2 (about 14 nsec amagat).[1] Indirect measurements of positron thermalization times in several molecular gases have been made using mixtures of the molecule gases with Ar.[8] In this manner a thermalization time of about 3 nsec amagat has been measured for H_2 gas at 295 K.[9] Thus even at the lowest density of H_2 investigated in this experiment, the entire shoulder region would be contained in the first positive time channel of the lifetime spectrum and would thus be unobservable.

Plotted in Fig. 2 are the annihilation rates of thermalized positrons in H_2 gas at 293.4 ± 0.1 K

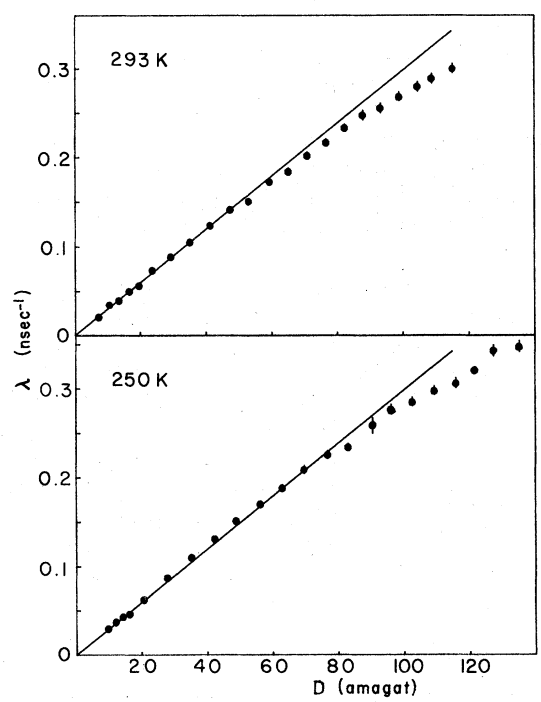

FIG. 2. Annihilation rates of thermalized positrons vs H_2 gas density at 293 and 250 K. The statistical standard deviations in the annihilation rates fall within the data-point symbols unless otherwise shown. The solid line represents a weighted least-squares fit to the combined data for densities less than 47 and 21 amagat at 293 and 250 K, respectively.

and at 249.8 ± 1.3 K versus gas density. At gas densities below temperature-dependent values, the annihilation rates at both temperatures appear to have the same linear dependence on density. A weighted linear least-squares analysis of the 293-K data for densities less than about 47 amagat, and constrained to pass through the origin, yielded a slope corresponding to $Z_{\rm eff} = 14.8 \pm 0.2$. A similar fit to the 250-K data for densities less than about 21 amagat gave $Z_{\rm eff} = 14.7 \pm 0.3$.

A nonconstrained weighted fit to the combined data gave a zero-density intercept of about -1×10^{-4} nsec^{-1}, a $Z_{\rm eff} = 14.8 \pm 0.3$, and a linear correlation coefficient of 0.99, whereas a weighted fit to the combined data, constrained to pass through the origin, yielded

$$Z_{\rm eff} = 14.8 \pm 0.2\,, \tag{4}$$

and is shown as solid lines in Fig. 2. This value of $Z_{\rm eff}$ is considerably larger than the older measurement by Osmon[10] of 11.7 ± 0.08, and is also larger than the value of 13.64 ± 0.09 recently measured with high statistical precision by Coleman *et al.* at 295 K in the density range 12–39 amagat.[11] The origin of the latter discrepancy is not known.

At H_2 densities above 50 amagat at 293 K, the measured λ values fall below those predicted by the linear density dependence observed at lower densities (solid lines). For H_2 at 250 K and densities above 25 amagat, the λ values appear to initially rise above the extrapolated low-density predictions. They then fall off at high densities in the same manner as do the 293-K data. Although the increase above the extrapolated low-density predictions of the 250-K λ data in the 25–60-amagat range is only marginally observable, it is believed to be real since (a) the effect is obvious for H_2 gas at 77 K (see Sec. IV), (b) similar behavior with density has been observed for λ in CH_4 (Ref. 12) and C_2H_6 (Ref. 13) gases, and (c) for these latter gases the deviation of λ from a linear dependence on density occurs at lower densities at lower temperatures. Observation (c) would not hold for H_2 were the 250-K λ data considered to increase linearly with density up to about 75 amagat.

IV. H_2 AT 77 K

The annihilation rates of thermalized positrons in H_2 gas at 77.4 K are plotted as a function of gas density in Fig. 3. Although the variations of λ with density are seen to be considerably larger at 77 K then at the two higher temperatures, the overall density dependence is qualitatively similar.

As can be seen from the insert plot in Fig. 3,

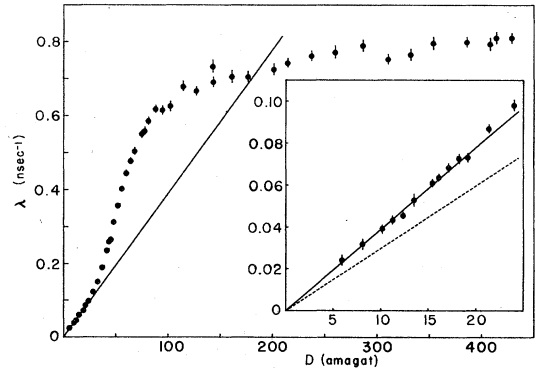

FIG. 3. Annihilation rates of thermalized positrons vs H_2 gas density at 77 K. The statistical standard deviations fall within the data-point symbols unless otherwise shown. The solid line represents a weighted least-squares fit to data for densities less than 19 amagat. The insert shows the low-density data. For comparison, the weighted least-squares fit to the combined data at 293 and 250 K of Fig. 2 is shown by the dashed line.

which shows the low-density λ data, λ initially increases linearly with density. A weighted linear least-squares fit to the λ versus density data for densities less than about 19 amagat and constrained to pass through the origin is shown as solid lines in Fig. 3. The slope of these lines corresponds to

$$Z_{\rm eff} = 19.3 \pm 0.4\,. \tag{5}$$

For comparison, the line corresponding to the $Z_{\rm eff}$ of 14.8, measured for low densities at 293 and 250 K, is shown dashed in the insert plot in Fig. 3.

The values of $Z_{\rm eff}$ calculated from Eq. (3) for each of the measured annihilation rates, are plotted as a function of density in Fig. 4. $Z_{\rm eff}$ is

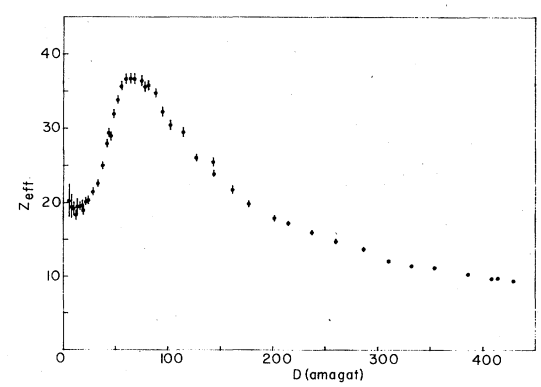

FIG. 4. $Z_{\rm eff}$ for thermalized positrons vs H_2 gas density at 77 K. Unless otherwise shown, the statistical standard deviations fall within the data symbols. For reasons of clarity, not all the data have been shown at the lower densities where $Z_{\rm eff}$ is constant.

seen to increase from its density independent value of 19.3 at low densities to a maximum of about 37 near 65 amagat, and then to decrease to about 9.5 at 429 amagat, the highest density reached in the experiment.

V. H_2-Ne MIXTURES AT 77 K

Positron lifetime spectra have been measured as a function of H_2 partial density at 77.4 K in H_2-Ne mixtures containing constant Ne partial densities of 6.8, 32.8, 52.4, and 101.1 amagat. As has been discussed elsewhere,[1] the annihilation rate of low-energy positrons in Ne is nearly independent of positron energy and can be described to nearly liquid Ne densities at 77 K by Eq. (3) with $Z_{\rm eff} = 5.97 \pm 0.15$.[14] Assuming that the low-energy positron annihilation rate with Ne is unaffected by the presence of H_2 (see Sec. VI), $(Z_{\rm eff})_{H_2}$ values for positrons annihilating with the H_2 component of the mixture were calculated from

$$\lambda^{\rm mix} = \pi r_0^2 c n_0 [(Z_{\rm eff})_{H_2} D_{H_2} + (Z_{\rm eff})_{\rm Ne} D_{\rm Ne}], \qquad (6)$$

where $\lambda^{\rm mix}$ is the measured annihilation rate of low-energy positrons in the mixture, and $(Z_{\rm eff})_{\rm Ne}$ is taken as 5.97 ± 0.15.

The results obtained for $(Z_{\rm eff})_{H_2}$ in H_2-Ne mixtures are plotted as functions of H_2 partial density in Fig. 5. The solid curves in Fig. 5 are smoothed fits to the $Z_{\rm eff}$ values measured in pure H_2 at 77 K and shown in Fig. 4. It is seen, particularly at low H_2 densities, that the presence of various partial densities of Ne can dramatically affect the positron-hydrogen annihilation mechanism. This was not found to be the case when Ne was added to N_2 at 77 K.[1]

In order to further investigate this effect, positron lifetime measurements were made as a function of Ne partial density in H_2-Ne mixtures containing a constant H_2 partial density of 12.86 amagat. The results for $\lambda^{\rm mix}$ are plotted versus Ne partial density in Fig. 6. The data taken at Ne densities greater than 25 amagat in Fig. 6, as well as all the data shown in Fig. 5, were obtained from spectra analyzed into three lifetime components with no constraints. However, at Ne densities less than 25 amagat, the data in Fig. 6 were ob-

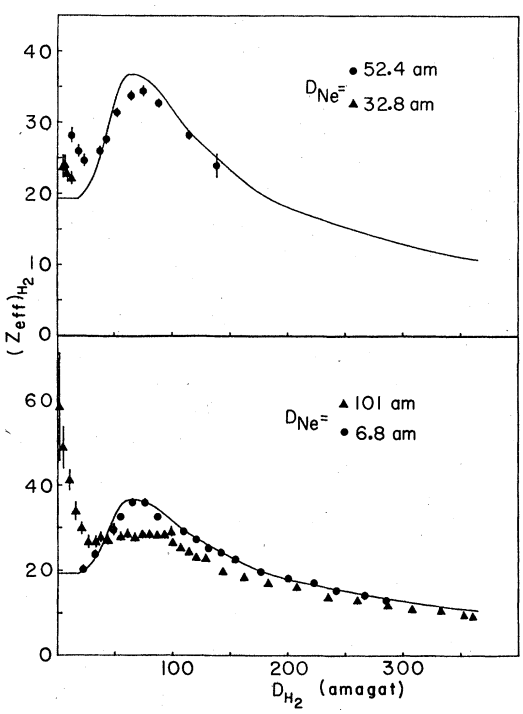

FIG. 5. $(Z_{\rm eff})_{H_2}$ for thermalized positrons annihilating with H_2 molecules in H_2-Ne mixtures at 77 K containing constant partial densities of Ne. The statistical standard deviations are within the point symbols unless otherwise shown. The solid curves represent a smoothed fit to the $Z_{\rm eff}$ vs H_2 density data measured in pure H_2 at 77 K and shown in Fig. 4.

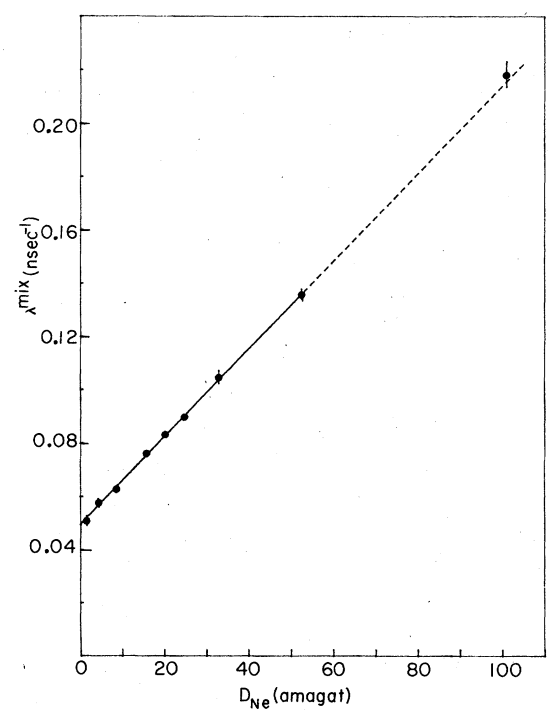

FIG. 6. Annihilation rates of thermalized positrons in H_2-Ne mixtures containing a constant H_2 partial density of 12.86 amagat vs Ne partial density at 77 K. The statistical standard deviations fall within the size of the data symbols unless otherwise shown. The solid line represents a weighted least-squares fit to data up to Ne partial densities of 52.4 amagat, and the extrapolation to higher Ne partial densities is shown by the dashed line. The data point at Ne partial density of 101 amagat represents an average of $\lambda^{\rm mix}$ for H_2 partial densities of 16.2 and 10.8 amagat.

tained by constraining the annihilation rate $\lambda_{o\text{-Ps}}^{\text{mix}}$ of o-Ps in the mixture according to

$$\lambda_{o\text{-Ps}}^{\text{mix}} = \{7.24 + 0.804[({}^1Z_{\text{eff}})_{\text{H}_2} D_{\text{H}_2} + ({}^1Z_{\text{eff}})_{\text{Ne}} D_{\text{Ne}}]\}\ \mu\text{sec}^{-1}, \qquad (7)$$

where D_{H_2} and D_{Ne} are the partial densities of H_2 and Ne, respectively. $({}^1Z_{\text{eff}})_{\text{Ne}}$ and $({}^1Z_{\text{eff}})_{\text{H}_2}$, which are measures of the pickoff annihilation of o-Ps atoms with Ne and H_2, are taken as 0.235 ± 0.008 and 0.194 ± 0.004, respectively. These are the temperature-independent values measured for pure Ne[7] and H_2 (Ref. 15) gases. Equation (7) is shown in the following paper to be correct for H_2 partial densities less than about 40 amagat at 77 K, indicating that at these densities the o-Ps annihilation process with either H_2 or Ne is unaffected by the presence of the other gas.

At least at the single 77-K H_2 density investigated, which falls in the linear λ vs D region in pure H_2, the λ^{mix} values of Fig. 6 increase linearly with Ne partial density. A least-squares fit to these data, shown in Fig. 6 as a solid line, gave a $D_{\text{Ne}} = 0$ intercept corresponding to $(Z_{\text{eff}})_{\text{H}_2} = 19.1 \pm 0.4$, in good agreement with Eq. (5) for pure H_2 at 77 K. $\lambda_{\text{H}_2}^{\text{mix}}$, the rate calculated from Eq. (6) for annihilations with the H_2 component of the mixture, increases with added Ne by the amount $(1.64 \pm 0.04) \times 10^{-3}$ (nsec amagat Ne)$^{-1}$ (see Sec. VI). The $D_{\text{Ne}} = 101$-amagat point in Fig. 6 actually represents an average λ^{mix} for measurements taken at 16.2 and 10.8 amagat of H_2, and was not included in the analytical fit.

It is apparent from Fig. 5 that the dependence of $(Z_{\text{eff}})_{\text{H}_2}$ on D_{Ne} will be different at different constant D_{H_2}. However, it is observed that for $D_{\text{H}_2} \lesssim 19.1$ amagat, the upper limit of the linear λ vs D region for pure H_2 at 77 K, the increase of $(Z_{\text{eff}})_{\text{H}_2}$ with added Ne depends only on the Ne fraction, $f_{\text{Ne}} = D_{\text{Ne}}/(D_{\text{Ne}} + D_{\text{H}_2})$, of the mixture. This is seen in Fig. 7, where the data includes H_2 partial densities in the range 1.9–19.1 amagat and Ne partial densities in the range 1.4–101 amagat. Note, in particular, the near overlap of the two data points near $f_{\text{Ne}} = 0.72$ which result from mixtures containing D_{H_2} of 12.8 and 19.1 amagat and D_{Ne} of 32.9 and 52.4 amagat, respectively.

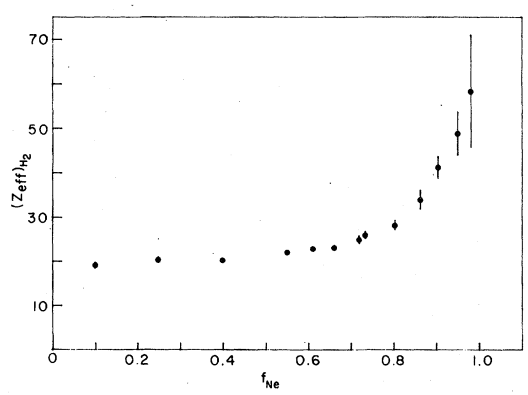

FIG. 7. $(Z_{\text{eff}})_{\text{H}_2}$ for thermalized positions annihilating with H_2 molecules in H_2-Ne mixtures at 77 K vs Ne concentration. H_2 partial densities are in the range 1.9–19.1 amagat and Ne partial densities are in the range 1.4–101 amagat. Unless otherwise shown, statistical deviations fall within the data symbols.

VI. DISCUSSION

A. Positrons in H_2 and H_2-Ne mixtures at low H_2 densitites

The annihilation rate of slow positrons in low densities of N_2 (Ref. 1) and H_2 gases, at sufficiently high temperatures, has been found to vary linearly with gas density, thus corresponding to density-independent values of Z_{eff} and indicating the interaction of positrons with single gas molecules. Similar annihilation behavior has been observed for several other molecular gases.[12,13] The temperature-dependent density ranges over which such behavior is observed will henceforth be referred to as "low-density" regions. The values of Z_{eff} measured for thermalized positrons in low-density N_2 gas exceed the actual number of molecular electrons by factors of about 2 at room temperature[1,16] and about 3 at 77 K.[1] As has been discussed elsewhere,[1] these thermal energy values of Z_{eff} can be predominately, if not totally, attributed to the direct annihilation of positrons on polarized N_2 molecules, the higher Z_{eff} at 77 K resulting from the greater polarization distortion of the molecular electron cloud at the lower thermal energies.

The values of Z_{eff} measured at low densities of H_2 gas exceed the number of electrons per molecule by factors of about 7.5 and 9.5 at room temperature and 77 K, respectively. Considering that the spherical and anisotropic polarizabilities and the quadrupole moment of H_2 are less than one half as large as the corresponding values for N_2, and that the effects of the polarization and quadrupole positron-molecule interactions cancel for H_2 whereas they reinforce each other in N_2,[17] these Z_{eff} values appear much too large to result from direct annihilations on polarized H_2 molecules. This conclusion is corroborated by the recent theoretical study by Baille *et al.*[18] of the interaction of low-energy positrons with H_2 molecules. Their calculations, which used the adiabatic nuclei approximation and which incorporated a sufficiently strong empirical polarization potential to produce total elastic cross sections in reasonable agreement with experiment, predict a Z_{eff} at

room-temperature thermal energies that is an order of magnitude less than the measured value. Similar calculations for positron-N_2 interactions[19] yield Z_{eff} values in reasonable agreement with the measured values, and a calculated dependence of Z_{eff} on positron energy that is in good qualitative agreement with experiment. Hara[20] investigated positron-H_2 interactions using the two-center formalism, and also calculated Z_{eff} values that are nearly an order of magnitude less than observation. However, the latter calculation neglected the effect of distortion of the molecular electron cloud.

The high values of Z_{eff} measured in low-density H_2 gas might result from the formation of compound states in which a positron is trapped in the neighborhood of a H_2 molecule. It is well known that the formation of resonance states is pervasive in low-energy electron scattering from atoms and molecules, and often dominates electron collision processes (vibrational and rotational excitation, electronic excitation, elastic scattering, dissociative attachment, three-body attachment, ionization, and others).[21] The resonance formation of a vibrationally excited positron-CH_4 compound was initially postulated to explain high positron annihilation rates in the low-density regions of room-temperature CH_4 gas,[22] but later measurements have shown that a single-level Breit-Wigner resonance near the vibrational excitation threshold cannot in this case be the correct explanation.[12,23]

Electron scattering experiments with H_2 have demonstrated the existence of a single-particle shape resonance at about 2.3 eV and of both core-excited Feshbach and shape resonances at higher energies.[21] The formation and subsequent decay of the electron-H_2 compound states were found to strongly influence inelastic electron-H_2 scattering near these energies. Electron swarm experiments have provided additional knowledge of electron-H_2 interactions at very low electron energies. The results of swarm experiments in low-density H_2 gas at 77 K, and the pressure dependence of the electron drift velocity in several gases, have been explained by the presence of resonance scattering associated with the temporary formation of rotationally excited electron-molecule states.[24,25] Additionally, low-energy electron-H_2 scattering measurements have shown resonancelike structure in the transmitted electron current approximately at the threshold energies for the $J=0\rightarrow 2$ and $J=1\rightarrow 3$ rotational excitations of H_2.[26] Recently, Matsuzawa[27] has briefly reviewed the question of electron-molecule rotational resonances, with particular application to ultralow-energy electron-H_2 scattering.

Although the mean lifetime for autoionization of such low-energy compound states would be short compared with the mean free time between collisions, it would be long compared with the interaction time in normal collisions. In fact, an upper limit of 4×10^{-9} sec has been estimated from the results of electron drift measurements for the lifetime of the lowest-energy electron-H_2 resonance state.[28] Thus if it were the case that thermal positrons also form temporary compounds with H_2 molecules by means of Feshbach-type resonances associated with rotational excitation of the molecules, then the positron annihilation rates would be substantially larger than those expected for normal collisions.

The lowest excitation threshold for H_2, which is that for molecular rotational $J=0\rightarrow 2$ at 44 meV, is not far above the thermal energy distribution at 300 K, but is more than six times higher than the most probable positron energy at 77 K. Thus relatively few positrons in thermal equilibrium with the gas at 77 K have energies approaching the threshold of the lowest excitation of H_2. A similar condition exists for the $J=1\rightarrow 3$ threshold at 73 meV. However, the Z_{eff} measured for H_2 at 77 K is about 30% greater than that measured at both 250 and 293 K. It appears very unlikely that the energy dependence of Z_{eff} for free positrons in H_2 (Ref. 18) could be sufficiently strong so as to produce the observed net increase in Z_{eff} at 77 K if there were a large accompanying reduction in the contribution to Z_{eff} from rotational resonances. We conclude that if the resonance formation of positron-H_2 compounds are responsible for the high Z_{eff} measured in low-density H_2, then the positrons must enter into these compounds during the thermalization process. Furthermore, at 77 K only the $J=0$ and $J=1$ rotational states of normal H_2 are populated: 24.8% and 75.0%, respectively. Since the probabilities for transitions with $\Delta J=\pm4$ or greater are much smaller than those with $\Delta J=\pm2$, the above results demonstrate that the mechanism for compound formation during positron thermalization cannot be one associated with pure rotational excitations. Assuming that the high Z_{eff} values measured in low-density H_2 gas do primarily result from the formation of positron-H_2 compound states during positron thermalization, then the further enhancement in Z_{eff} at 77 K over the value at room temperature can be qualitatively attributed to the combined effects, at the lower thermal energies, of larger compound state formation cross sections and higher Z_{eff}'s being experienced by those positrons which have remained free.

Further support for this picture is provided by the H_2-Ne mixture results. As was discussed in Sec. V, the addition of various partial densities of Ne to low densities of H_2 can greatly increase

the positron-H_2 annihilation rates. A positron undergoing an elastic collision with a Ne atom suffers a fractional energy loss which is small compared with those suffered during rotational or vibrational excitation of H_2 molecules. It is reasonable, therefore, to hypothesize that Ne is primarily effective in moderating more positrons during thermalization into the resonance energy region(s) associated with the formation of positron-H_2 compound states, thereby enhancing $\lambda_{H_2}^{mix}$ and $(Z_{eff})_{H_2}$. According to this interpretation, an appreciable number of positrons in pure H_2 must avoid compound state formation to annihilate from the free state, and the resonance energy region(s) for compound state formation must be predominately located below the electronic excitation threshold of Ne at 16.6 eV. The admixture of H_2 to Ne would produce a more rapid thermalization of positrons than in pure Ne, but, as was assumed in Eq. (6), would not detectably alter the annihilation rate of positrons with the Ne component of the mixture (see Sec. V). For H_2 concentrations sufficiently high that positron-H_2 collisions are still likely to occur in the resonance energy region(s), $(Z_{eff})_{H_2}$ would be expected to increase with Ne partial density and with Ne concentration as in Figs. 6 and 7, respectively. It is shown in Sec. VIB that the net reduction in $(Z_{eff})_{H_2}$ that results when Ne is added to 77-K H_2 at densities above the low-density region is also consistent with this picture.

B. Positrons in H_2 and H_2-Ne mixtures at high H_2 densities

The temperature-dependent regions of H_2 density in which λ deviates from a linear density dependence, indicating the interaction of positrons with two or more H_2 molecules, will here be referred to as "high-density" regions. At the 293-, 250-, and 77-K temperatures of H_2 gas investigated, the high-density regions begin at about 53, 28, and 21 amagat, respectively. Considering first the measurements in 77-K H_2 gas (Fig. 3) in the high-density region, λ initially increases more rapidly with density than in the low-density region, indicating the onset of a new multimolecule annihilation process characterized by an annihilation rate higher than those for the single-molecule processes that are dominant at lower H_2 densities. As the H_2 density is further increased, the λ versus density data pass through an inflection point, corresponding to a maximum in Z_{eff} (Fig. 4), and then become nearly independent of density at the highest densities investigated.

Calculations for H_2, similar to those discussed elsewhere for N_2,[1] show that at the pressures and temperatures involved, H_2 dimer formation would contribute negligibly to the annihilation rates. In fact, the dissociation energy of the H_2–H_2 bond is so weak (~0.4 meV) that even at 20 K only about 0.1% of the H_2molecules are in bound $(H_2)_2$ states.[29]

Cova and Zappa[30] have developed a method for predicting Z_{eff} for liquids. They assume that each atom in a molecule contributes to the annihilation of positrons an amount that is typical of that type of atom and is independent of the structural properties of the molecule. Applied to H_2, their empirical method predicts a Z_{eff} of about 4.7. Using this value in Eq. (1), the annihilation rates measured at the highest ambient densities of 77-K H_2 correspond to nearly liquid densities in the immediate vicinity of the positron. This observation suggests that the positron is annihilating with an electron of the H_2 molecules clustered at high densities about it.

It has been recently demonstrated, both experimentally[31] and theoretically,[32-35] that in He gas near the gas-liquid critical point, attractive electrostatic forces cause the clustering of He atoms about low-energy positrons, 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 positrons in high-density clusters begins are observed to increase with temperature. The onset of clustering is seen as an increase in λ from the linear density dependence observed at constant temperature at lower densities to values corresponding to liquid-He densities.[31,36] The positron localized within the cluster samples an effective density which is obtained by weighting the density profile of the cluster with the square of the positron wave function.

The concept of molecular clustering about positrons was first semiquantitatively tested for CH_4 molecules[12] using the Atkins[37] snowball model for the somewhat analogous clustering of molecules about heavy fixed ions in liquid He, although it was known that this macroscopic model fails to produce a self-trapped state for positrons in He.[36] If the gas is treated as a continuum which is electro-restricted about a positron, then the number density $n(r)$ at distance r from the cluster center can be approximately calculated as

$$n(r) = N_0/V', \tag{8}$$

where

$$\int_p^{p'} V'\,dp = \tfrac{1}{2} N_0 \alpha e^2 \epsilon(r)\,. \tag{9}$$

Here N_0 is Avogadro's number, V' is the molar volume at distance r with ambient gas pressure p, $\epsilon(r)$ is the positron's electric field, and α is the molecular polarizability of the gas. From the viewpoint of cluster states, changes in λ should

now be interpreted as due to changes in cluster density, whereas Z_{eff} is taken to be a constant at a given temperature:

$$\lambda(r) = \pi r_0^2 c n(r) Z_{eff} . \quad (10)$$

Using a nonlinear least-squares method and including only the spherical induced polarizability of H_2, this simplistic cluster model was fit to the λ versus density data for 77-K H_2 at densities above 214 amagat, where clustering might be expected to dominate the annihilation process. The best fit, which is shown as a solid line in Fig. 8, was obtained for an "average" $r = 3.6 \pm 0.2$ Å and $Z_{eff} = 4.3 \pm 0.3$. These values are in reasonable agreement with the Cova and Zappa Z_{eff} (4.7) and with the intermolecular separation (4.2–4.6 Å) of H_2 dimers at 30 K.[29] The extrapolation of this cluster calculation to 250 and 293 K is shown in the inset of Fig. 8. Although the temperature dependence of the simple cluster model is somewhat too large at the higher H_2 densities where clustering would predominate, it appears qualitatively correct.[38] It is concluded, therefore, that the nonlinear density dependence of λ in the high-density regions of H_2 results from the self-trapping of positrons in clusters of H_2 molecules.

As has been argued for the case of N_2 gas,[1] the formation of positron cluster states is likely to be a reversible process, particularly near the threshold densities. Annihilation of positrons self-trapped in clusters might then be competitive with the positron single H_2 molecule annihilation processes that dominate the low-density regions. It was suggested in Sec. VIA that the addition of Ne to H_2 increases the probability of positron-H_2 compound state formation. If so, this would allow the lower annihilation rate process of compound state formation to compete more favorably with annihilation from clusters, thereby producing a net reduction in the total annihilation rate in the high-density regions in agreement with Fig. 5.

Several more realistic theoretical approaches to positron-induced cluster formation have been applied to the positron-He system.[32-35] In view of the thus far only semiquantitative success of these studies, we will not attempt a detailed treatment of cluster formation in the more complex positron-H_2 system.

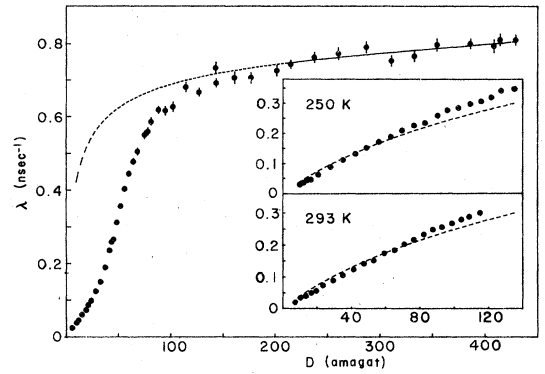

FIG. 8. Annihilation rates of thermalized positrons in H_2 vs H_2 gas density at 77 K. The statistical standard deviations fall within the size of the data symbols unless otherewise shown. The solid curve represents a weighted least-squares fit of a simplistic cluster model to data at densities above 214 amagat, and the extrapolation to lower densities is represented by the dashed curve. The inserts show λ vs H_2 gas density data at 250 and 293 K, where the dashed curves represent an extrapolation of the cluster model calculation to these temperatures.

In summary, we have shown that the annihilation rate of low-energy positrons in H_2 gas is a complex function of both density and temperature, and that the addition of Ne to the H_2 significantly alters the positron-H_2 annihilation process. Although consistent with the measurements, the processes proposed to account for this annihilation behavior have here been treated only in an empirical manner. It is our hope that these preliminary analyses may prove useful in more rigorous and complete theoretical treatments.

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