Annihilation of Positrons in Nitrogen†

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The positron annihilation lifetime spectra in nitrogen have been measured by a new apparatus consisting of two time-to-amplitude converters. The annihilation of positrons in nitrogen as a function of nitrogen densities from 2 to 45 amagats has been investigated. The free annihilation rate is found to be 5.80 ± 0.07 μsec^{-1} amagat^{-1}, and the o-Ps quenching rate, 0.22 ± 0.06 μsec^{-1} amagat^{-1}. Both rates are found to be linear for densities up to 45 amagats. A distinctive shoulder has been observed in the positron annihilation lifetime spectra for nitrogen with densities less than 10 amagats. The shoulder width is estimated to be 14 ± 3 nsec amagat. The value of Z_{eff} for free-positron annihilation at thermal energy is found to be 30. The value of Z_{eff} for free-positron annihilation at energy about 0.5 eV or higher is estimated to be only about 23.

I. INTRODUCTION

It has been known for many years that when a radioactive element is used as a source of positrons the measured positron annihilation lifetime spectrum in a gaseous medium consists of three components, two of them associated with para- and ortho-positronium and the third with positrons. Several years ago, it was shown by Tao, Bell, and Green,[1] Paul,[2] Falk and Jones,[3] and Osmon,[4] that the latter component, either called the "free"- or the "direct"-positron annihilation component, is nonexponential in the noble gases. It consists of a more or less flat shoulder and an exponential tail. This is attributed to the fact that the positrons emitted by a radioactive element possess energies far greater than thermal energy and they annihilate during the slowing down process. Therefore, if the slowing-down process is slow and the free-positron annihilation rate is energy dependent in the energy region concerned, the resultant annihilation spectrum will be nonexponential. It has been shown that in noble gases during thermalization a positron spends most of its time with an energy of less than a few electron volts.[5] The nonexponential behavior of the free-positron annihilation is a very interesting topic to both experimentalists and theoreticians because it concerns the collision process in the low-energy region. The relationship between the energy-dependent cross sections and the resultant free-positron annihilation lifetime spectrum has been demonstrated lately by Tao and Kelly.[6]

Recently, Paul and Leung[7] investigated the positron slowing-down process both in mixtures of argon and nitrogen and argon and methane. From the decrease of the shoulder width associated with the admission of nitrogen into argon, they concluded indirectly that the thermalization time for positrons in pure nitrogen should be about 16 nsec amagat. We have made a series of direct measurements of the positron annihilation spectra in pure nitrogen of densities from 2 to 45 amagats using a time-to-amplitude converter system of good resolution. The better resolution of the lifetime measuring instrument reveals the fine structure of the lifetime spectrum. The nonexponential behavior of the positron annihilation component also exists in pure nitrogen. This paper will report the results of the work in this field.

II. EXPERIMENTAL

For measuring positron annihilation lifetime spectra in a gaseous medium, a time-to-amplitude converter with a total range of 300 nsec or more is required because of the long mean life of o positronium in most gases. For a total range of 300 nsec, if a multichannel analyzer of 1000-channel capacity is used to store the coincidence information, the minimum channel width will be 0.3 nsec. In order to resolve a fine structure in a spectrum, sometimes a narrower channel width is required. If a longer total range and a narrower channel width are both necessary, a multichannel analyzer with a memory space of 2000 or more words is required to store all the information. This requires a large and expensive multichannel analyzer and a large amount of labor for data reduction.

If only a fraction of the time spectrum requires a high resolution, a different arrangement can be made to save the memory space required as well as the labor. The whole spectrum is recorded in only a few hundred channels with a channel width of about 1 nsec. Only the section of the time spectrum where high resolution is required is recorded with a channel width of about 100 psec. Two time-to-amplitude converters of different ranges are used. The block diagram of such a system is shown in Fig. 1.

Each anode output of the photomultipliers is fanned out into two and fed into two time-pulse shapers, one to produce a time pulse of 40 nsec in width and another to produce a time pulse 400 nsec

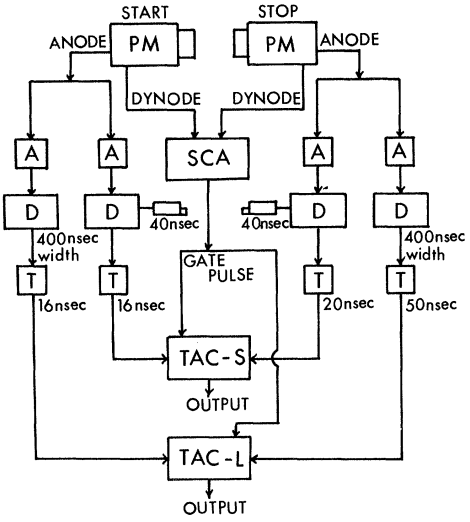

FIG. 1. Block diagram of the time-to-amplitude converter system. (PM, photomultiplier; TAC-S, time-to-amplitude converter, short range; TAC-L time-to-amplitude converter, long range; A, attenuator; D, discriminator; T, time delay.)

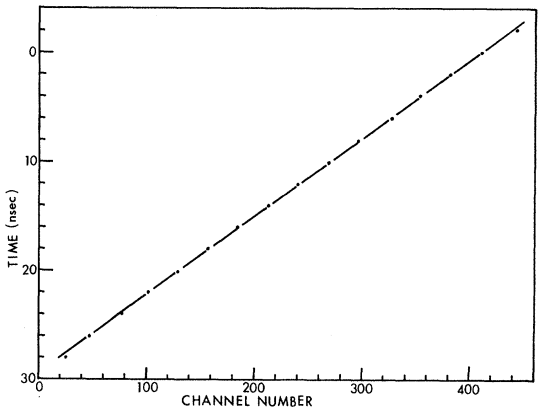

FIG. 2. Linearity of the short-range time-to-amplitude converter (straight line, 68.5 psec/ch).

in width. In order to reduce the attenuation that occurs in a long delay line, the start pulse is not delayed to the full width of the pulse. Thus, a negative time scale is produced. The two time-to-amplitude converters are gated by a single coincidence unit, which is controlled by energy discriminators which act as single-channel analyzers fed by the dynode outputs of the photomultipliers. Since the side-channel elements are also fast, a delay of 10 nsec for the timing pulses is ample for both the time-to-amplitude converters to operate properly. This fast-fast coincidence arrangement reduces the effect of pile-up considerably.

The timing and side-channel circuitry are constructed by Chronetics Nanologic modules. The overlap principle is used for the time-to-amplitude converter. An ND2200 system is used as the multichannel analyzer.

Two analog-to-digital converters are employed to receive the outputs of the two time-to-amplitude converters. One of the outputs is delayed 10 μsec to allow the memory of the ND2200 system to accept both of them in real time. The outputs of the analog-to-digital converters are routed to two separated halves of a selected section of the memory through a Digiplex made by Nuclear Data. After each experiment, the contents of the memory can be read out via various means.

In order to achieve a good resolution, plastic instead of NaI scintillators are used. A resolution of better than 0.6 nsec full width at half-maximum (FWHM) for an Na22 source can be achieved when this system is fed by a pair of 56 AVP photomultipliers coupled with NATON 136 scintillators of $1\frac{1}{2}$ in. diam and 2 in. length. A useful linear region of 32 nsec is obtained for the short-range time-to-amplitude converter and 320 nsec for the long-range one. The linearities of both time-to-amplitude converters are good. A calibration diagram for the short-range time-to-amplitude converter is shown in Fig. 2 as an example. The time interval between two neighboring data points is 2.0 nsec, and the solid line is a straight line. The deviation of the data points from the straight line is negligible, particularly within the range 0–26 nsec. No obvious systematic short-range fluctuations are observed in the linearity of the time-to-amplitude converters.

Another method of detecting the short-range fluctuation in the linearity of the time-to-amplitude converter is to measure the fluctuation of the ran-

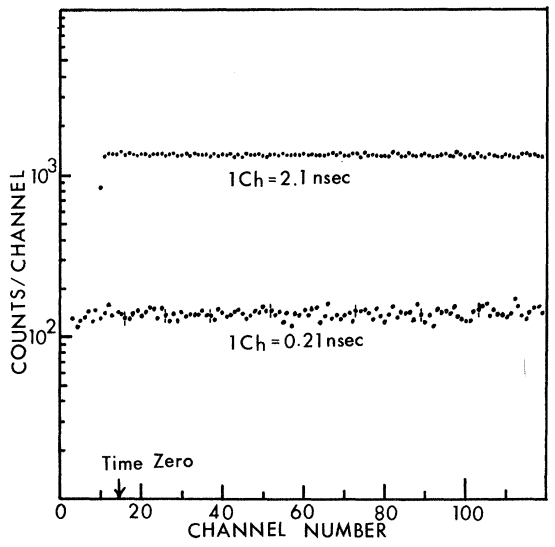

FIG. 3. Background of the short- and long-range time-to-amplitude converters.

dom background of the output of the time-to-amplitude converter. The result is shown in Fig. 3. Two Na^{22} sources serving two separate detectors were arranged for this experiment. No obvious systematic fluctuations other than random ones can be observed.

The random background of the system depends strongly on the source strength, and the signal-to-random ratio has been found to be inversely proportional to the activity of the source.[8] The strength of the Na^{22} source used in this series of experiments gives a total signal-to-random ratio of about 25.

The gas chamber is a spherical vessel of 5 in. diam made from stainless steel with a polished surface. The whole gas system, including the gas inlet and the vacuum side for the evacuation of the system, is made of stainless steel. All joints are either welded or sealed by metal packings. The system is designed to sustain a maximum pressure of 1500 psia. The nitrogen gas used in this experiment is the Prepurified Grade supplied by Matheson. The positron source is 5 μCi Na^{22} deposited on a very thin mica sheet, centered in the gas chamber. The experiments were carried out at room temperature, 24 °C. The pressure was measured by a calibrated pressure gauge with accuracy of 1%. The densities of the nitrogen gas were calculated after correction.[9] The total deviation of the density due to various causes was estimated to be less than 3%.

III. RESULTS

A. Higher Nitrogen Density

No significant shoulder is observed in the positron annihilation spectra in nitrogen of densities greater than 10 amagats. The spectra appear as a curve of three-component exponential decay after the background is subtracted. The directly measured mean life of the shortest-lifetime component which respresents the annihilation of p positronium and positrons trapped inside the wall material of the gas chamber is found to be about 0.4 nsec from the spectra measured by the short-range time-to-amplitude converter. The data on the lifetime spectra obtained from the long-range time-to-amplitude converter (excluding the prompt peak, which consists mainly of the shortest-lifetime component) are fitted with a curve of two-component exponential decay by using a standard procedure.[10] The mean life of the shorter-lifetime component represents the free annihilation of low-energy positrons and the mean life of the longer-lifetime component, the annihilation of o positronium.

After the data reduction, the free-positron and o-positronium annihilation rates are determined and are plotted against nitrogen density in Figs. 4 and 5.

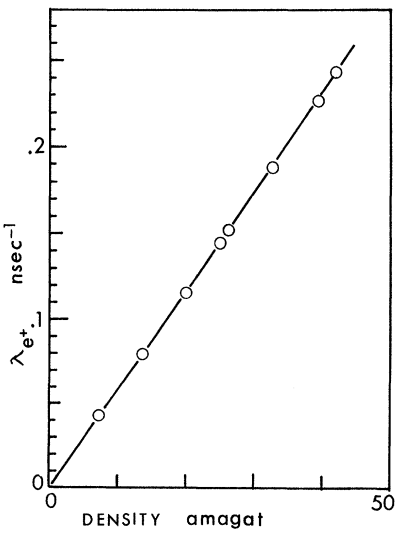

FIG. 4. Dependence of the free annihilation rate of positrons on nitrogen density. The solid line represents the line $\lambda_{e^+} = 5.80D$. The errors are less than the size of the points.

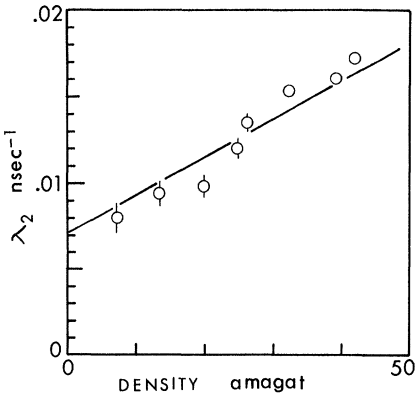

FIG. 5. Dependence of the o-positronium quenching rate on nitrogen density. The solid line represents the line $\lambda_q = 0.22D$.

B. Lower Nitrogen Density

For positron annihilation in nitrogen with a density less than 10 amagats, a distinctive shoulder appears, particularly in the lifetime spectra measured by the short-range time-to-amplitude converter. The appearance of the shoulder becomes more significant as the density of nitrogen becomes lower. This can be traced in the positron annhilation lifetime spectra in nitrogen with densities of 7.3, 4.1, 2.8, and 2.2 amagats measured by both the long- and short-range time-to-amplitude converters. These are reproduced in Figs. 6–9. The background has been subtracted from these spectra. Straight lines are drawn in Figs. 7 and 9 to show the deviation from the straight line. The effect of

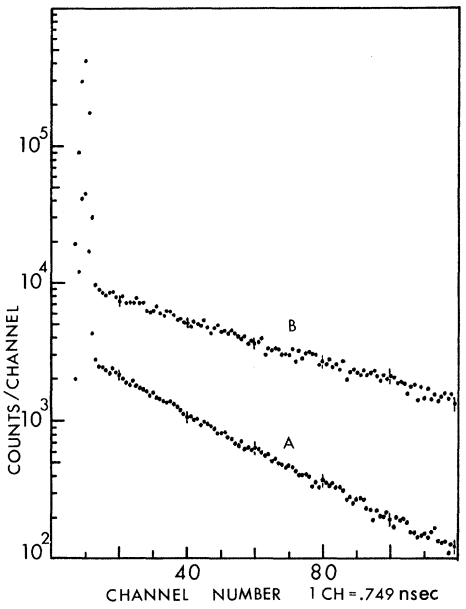

FIG. 6. Positron annihilation lifetime spectra in nitrogen. (From the long-range time-to-amplitude converter, nitrogen density A, 7.3 amagats; B, 4.1 amagats.)

any background fluctuation on these spectra is quite negligible, since at the shoulder region the background is less than $\frac{1}{10}$ of the signal value at a nitrogen density of 2.2 amagats, and less than $\frac{1}{70}$ at 7.3 amagats.

The shoulders are particularly significant in the spectra shown in Figs. 8 and 9. They cannot be attributed to chance fluctuation due to the random nature of the coincidence events. A simple statistical evaluation using the χ^2 test can prove the chance is less than 0.001. The shoulders cannot be attributed to systematic errors either. If they are due to the nonlinearity of the time-to-amplitude converter, such a small shoulder should exist at the same location for all spectra including the annihilation lifetime spectra in gases other than nitrogen, such as argon at low density. This has been found to be not the case. The random background shown in Fig. 3 also does not support the existence of such a shoulder. Furthermore, the effect of pile-up, if it exists, tends to remove the shoulder instead of enhancing it. Therefore, this shoulder, although small, should be real.

However, it is very difficult to determine the shoulder width accurately from Figs. 6–9. The shoulder width can be more clearly defined by the time-dependent free-positron annihilation rate $\lambda(t)$. The values of $\lambda(t)$ are plotted against time in Figs. 10 and 11. Certainly no shoulders can be traced in $\lambda(t)$ plots measured by the long-range

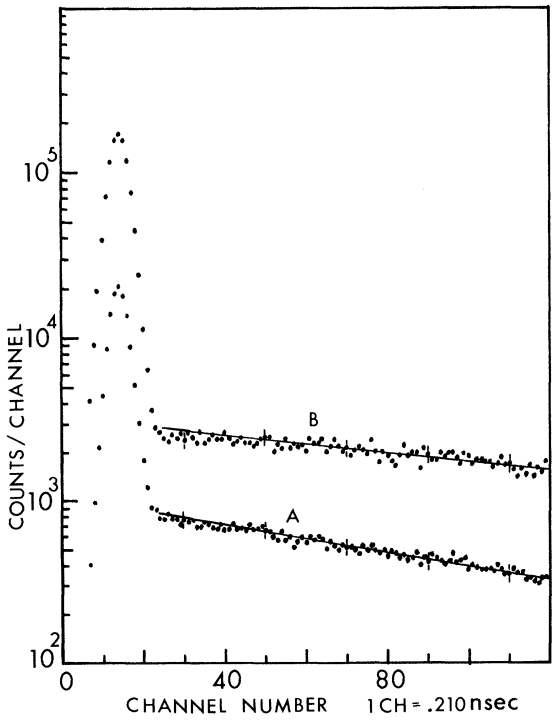

FIG. 7. Positron annihilation lifetime spectra in nitrogen. (From the short-range time-to-amplitude converter; nitrogen density A, 7.3 amagats; B, 4.1 amagats.)

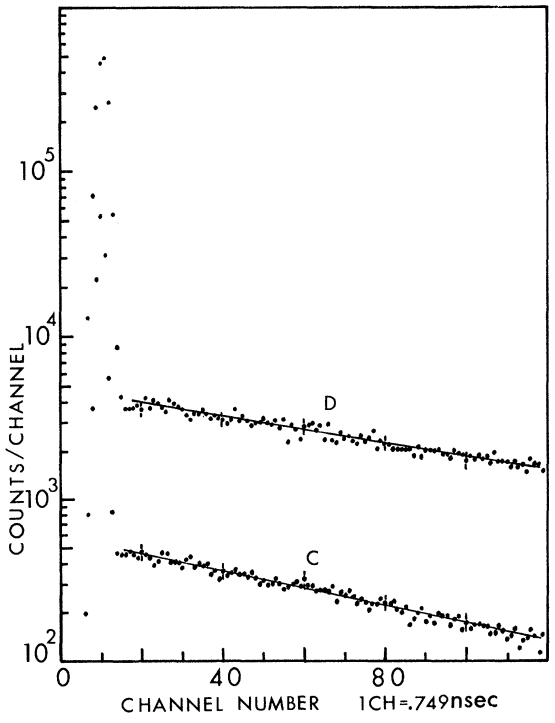

FIG. 8. Positron annihilation lifetime spectra in nitrogen. (From the long-range time-to-amplitude converter, nitrogen density C, 2.8 amagats; D, 2.2 amagats.)

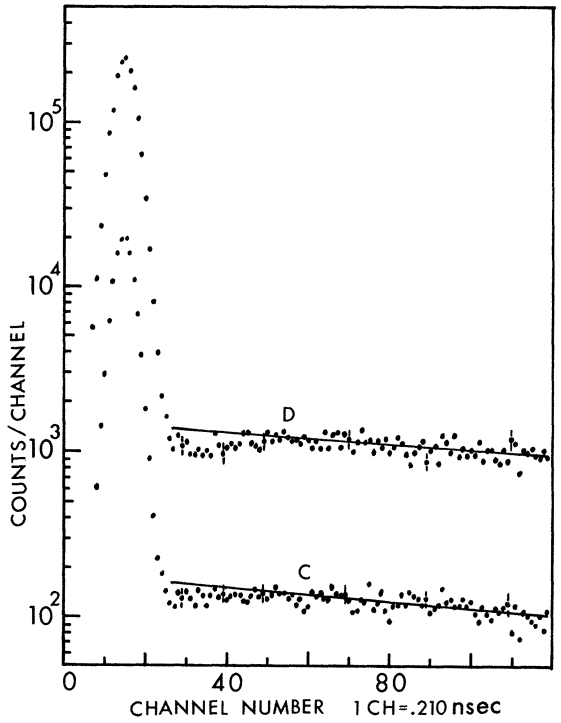

FIG. 9. Positron annihilation lifetime spectra in nitrogen. (From short-range time-to-amplitude converter, nitrogen density C, 2.8 amagats; D, 2.2 amagats.)

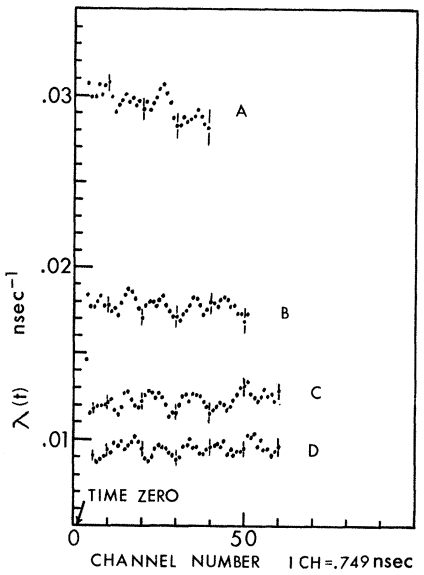

FIG. 10. Time-dependent positron annihilation rate in nitrogen. (From the long-range time-to-amplitude converter, nitrogen density A, 7.3 amagats; B, 4.1 amagats; C, 2.8 amagats; D, 2.1 amagats.)

time-to-amplitude converter for higher nitrogen densities, i.e., curves A and B in Fig. 10. However, the shoulder width can be barely noticed in $\lambda(t)$ plots measured by the short-range time-to-amplitude converter for nitrogen density of 7.3 amagats, i.e., curve A in Fig. 11, and can be measured with better accuracy from other $\lambda(t)$ plots.

The definition of shoulder width here is similar to the one used by Paul.[2,7] The reciprocal of the shoulder width evaluated from Figs. 10 and 11 is plotted against the nitrogen density in Fig. 12.

IV. DISCUSSION

A. Free Annihilation Rate

The dependence of the free annihilation rate on nitrogen density for nearly thermalized positrons, or for positrons represented by the exponential tail, is found to fit a linear function of

$$\lambda_{e^+} = (5.80 \pm 0.07) D \,, \qquad (1)$$

where the units of λ_{e^+} are μsec^{-1} and of D, amagats. Equation (1) is represented by a solid line in Fig. 4. The value 5.80 $\mu\text{sec}^{-1}\text{amagat}^{-1}$ is considerably higher than the value 3.95 $\mu\text{sec}^{-1}\text{amagat}^{-1}$ with density up to 35 atm reported by Osmon.[11] It is slightly higher than the unpublished value of 5.3 $\mu\text{sec}^{-1}\text{amagat}^{-1}$ for nitrogen density < 20 amagats determined by us previously. The value of Z_{eff} calculated from 5.80 $\mu\text{sec}^{-1}\text{amagat}^{-1}$ is 30, which agrees well with the value $Z_{\text{eff}} = 32$ reported by Paul

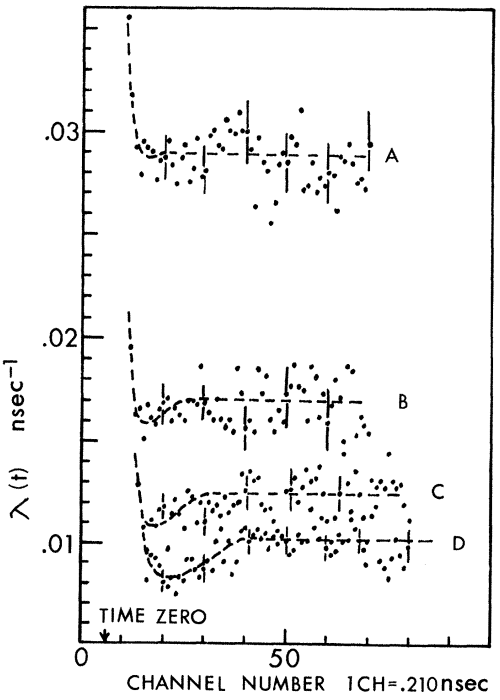

FIG. 11. Time-dependent positron annihilation rate in nitrogen. (From the long-range time-to-amplitude converter, nitrogen density A, 7.3 amagats; B, 4.1 amagats; C, 2.8 amagats; D, 2.1 amagats.)

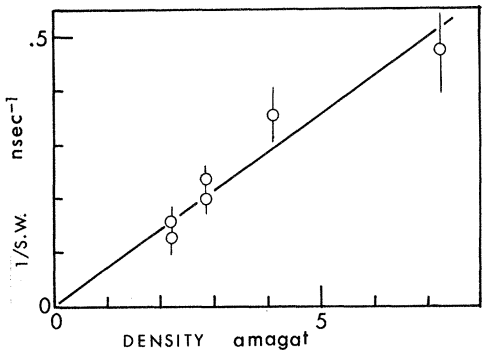

FIG. 12. Dependence of the shoulder width for positron annihilation on nitrogen density.

and Leung[7] for lower nitrogen densities.

The linear relationship of (1) holds very well for densities up to 45 amagats. This implies that at a nitrogen density of 40 amagats, the effect of multicollision is still not significant. This finding is consistent with the result obtained in high-density argon.[12]

B. *o*-Positronium Quenching Rate

The dependence of the *o*-positronium rate on nitrogen density is found to fit a linear function

$$\lambda_q = (0.22 \pm 0.06) D \ , \qquad (2)$$

where

$$\lambda_0 = 0.72 + \lambda_q \ ,$$

where λ_q is in μsec^{-1} and D is in amagats, provided the *o*-positronium annihilation rate in free space is assumed to be the theoretical value 0.72 μsec^{-1}.[13] Equation (2) is represented by the solid line in Fig. 5. The value 0.22 $\mu\text{sec}^{-1}\text{amagat}^{-1}$ agrees very well with the value 0.21 $\mu\text{sec}^{-1}\text{atm}^{-1}$ reported by Celitans, Tao and Green,[14] and Osmon.[11] This implies that the effect of multicollision in nitrogen on *o*-positronium quenching is also not significant up to a density of 40 amagats.

C. Shoulder Width

The dependence of the reciprocal of the shoulder width on nitrogen density is found to fit a linear function of

$$1/(\text{shoulder width}) = (0.071 \pm 0.015) D \ , \qquad (3)$$

where the width is in nsec and D is in amagats. The shoulder width is calculated to be 14 ± 3 nsec amagat. This value supports the "thermalization time" of 16 nsec amagat calculated by Paul and Leung[7] from their indirect method, in which the "thermalization time" is determined from the change of shoulder width in mixtures of argon and nitrogen with various partial pressures of nitrogen. Since full thermalization may not be attained when the end of the shoulder or the start of the exponential tail is reached,[6,7] the actual thermalization time certainly should be greater than 14 nsec amagat.

The discovery of a distinctive shoulder indicates that the free-positron annihilation rate of Z_{eff} in nitrogen is also energy dependent, just like the free-positron annihilation rate in noble gases.

The slowing-down process for positrons in nitrogen was discussed by Paul and Leung[7] in detail. The lowest energy for any form of electronic excitation is 5.1 eV. Apart from energy losses in elastic collisions, positrons below this level will be slowed by vibrational and rotational transitions, and below 0.29 eV, which is the lowest vibrationally excited state, by rotational collisions only. For positrons of 0.29 eV slowing down to 0.025 eV, the time was estimated by Paul and Leung[7] from the equation given by Gerjuoy and Stein[15] to be about 12 nsec at a nitrogen density of 1 amagat.

The slowing-down time from higher energies to 5.1 eV and from 5.1 eV to the lowest vibrational resonance should be very fast. The order of magnitude of the slowing-down time can be roughly estimated by the following method. If the slowing down of positrons in nitrogen is due to elastic collisions only, and the elastic scattering cross section σ_s is nearly a constant, we have the slowing-down time[5]

$$t = (2m)^{1/2}(E_1^{-1/2} - E_0^{-1/2})/\xi N\sigma_s \ ,$$

provided the thermal effect is neglected. The ratio of the slowing-down time from higher energies to 0.29 eV and the slowing-down time from 0.29 to 0.025 eV is

$$1/0.29^{1/2}(0.025^{-1/2} - 0.29^{-1/2}) = 1/2.4 \ .$$

Since, below 0.29 eV, positrons are slowed down by rotational transitions and elastic collisions and above this energy level the slowing down is assisted with additional contributions from vibrational transitions, this ratio 1/2.4 should be a reasonable upper limit. Therefore, the slowing-down time from higher energies to 0.29 eV in nitrogen should be less than 1/2.4 of 12 nsec, i.e., 5 nsec amagat. Similarly, the slowing-down time from higher energies to about 1 eV should be less than 3 nsec amagat.

The above results point out that (i) for positrons of several electron volts, slowing down to the lowest vibrational resonance, say 1 eV, the time is very short, less than 3 nsec amagat; and (ii) for positrons of 0.29 eV, slowing down to thermal energy the time required is roughly about 12 nsec amagat. In a light noble gas such as helium, the slowing-down time for positrons of 18–5 eV is quite short and the shoulder of the free-positron annihilation component is found to be due to a minimum in the free-positron annihilation rate at about 3 eV.[6]

Here we may infer that it is possible that such a minimum in the free-positron annihilation rate also exists in nitrogen. If such a minimum does exist, it is reasonable to assume that it exists even at low positron energy corresponding to the minimum in the $\lambda(t)$ plot (Figs. 10 and 11). Since the minimum in the $\lambda(t)$ plot occurs within 2 nsec amagat (?) of $t = 0$, that is, the probable time for slowing down to 0.29 eV the minimum in the free-positron annihilation rate should exist at an energy about or higher than 0.29 eV. A reasonable guess would be about 0.5 eV. The free annihilation rate at the minimum is estimated from the $\lambda(t)$ values shown in Figs. 10 and 11 to be about 4.5 $\text{nsec}^{-1}\text{amagat}^{-1}$, which is equivalent to $Z_{\text{eff}} = 23$.

ACKNOWLEDGMENTS

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Stark and Zeeman Effects on the Protonic Structure of Molecules*

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The effect of a homogeneous electric field on the protonic coordinates of neutral hydrides is shown to be identical to the effect on the electronic coordinates. For ionized hydrides, the effects on the protonic coordinates are shown to be proportional to $(1 - Nm_p/M)$ where m_p and M are the protonic and total mass, respectively, and N is the degree of ionization. A homogeneous magnetic field affects the protonic coordinates through terms proportional to $\mathcal{H}^2 m_p/M$ and $N_e \mathcal{H}^2 m_p^2/M^2$, where $\mathcal{H}$ is the strength of the field and N_e is the number of electrons in the molecule. The terms of first order in $\mathcal{H}$ are found to be negligible for the protonic coordinates. The effects of both the electric and magnetic fields on the motion of the center of mass are also given. We show that in the presence of a homogeneous magnetic field in the z direction, the center of mass of neutral atoms or molecules will vibrate in the xy plane with a frequency of $\omega = (N_e q_e^2 \mathcal{H}^2/4Mm_e c^2)^{1/2}$, where c is the velocity of light.

In several papers we have established theoretically the existence of a protonic structure in molecules completely analogous to the electronic structure.[1] The field free Hamiltonian which we used was, in hartrees,

$$H = \sum_i \left(\frac{-1}{2m_i} \nabla_i + \sum_{j>i} \frac{q_i q_j}{r_{ij}} \right),$$

where the sums over i and j run over all the nuclei and electrons of the molecule, m_i and q_i are the mass and charge of the ith particle, and r_{ij} is the distance between particles i and j.

In this paper, we will add to the field free Hamiltonian external homogeneous electric and magnetic fields.

Our wave functions are in center-of-mass coordinates; therefore, we must transform the operator

$$H' = -F(q_a z_a + \textstyle\sum_i q_i z_i) \qquad (1)$$

to those coordinates defined by