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Comments and Addenda

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Quenching of positronium in nitrogen dioxide*

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The quenching mechanism of positronium in NO_2 was investigated by measuring both positron lifetimes and two-photon angular-correlation curves of annihilating positron-electron pairs in NO_2 adsorbed on silica gel. It is found that instead of a conversion reaction by NO_2, chemical quenching is responsible for the quenching of positronium. The quenching cross section for NO_2 is compared with the conversion cross sections of O_2 and NO gases and also with the chemical quenching cross sections of Br_2 and I_2 molecules. The cross sections for chemical quenching are at least two to three orders of magnitude larger than the cross sections for conversion quenching of Ps. The bond strengths of these molecules are found to play an important role in Ps quenching process.

I. INTRODUCTION

Positron lifetimes in nitrogen dioxide and nitric oxide gases were carefully determined previously.[1] The very high positronium quenching rate found in nitrogen dioxide gas was attributed to the conversion of the Ps atoms, i.e., $o\text{-Ps} \rightleftharpoons p\text{-Ps}$ transition, on paramagnetic NO_2 molecules.

Such a conversion reaction can be observed experimentally by measuring the two-photon angular correlation of annihilating positron-electron pairs. The conversion of Ps atoms intensifies the low-momentum component of the angular distribution curve, while chemical quenching of Ps atoms causes an increase of the high-momentum component.[2] However, it is difficult to perform two-photon angular-correlation experiments in either NO_2-gas or NO_2-liquid mixtures.

Recently, porous oxides, such as silica gels and alumina powders, have been used to produce long-life and high-intensity *o*-Ps atoms for investigating physical and chemical properties of positronium and molecule-positronium interactions.[2-6] In this paper, we apply the same technique to investigate NO_2 quenching of positronium in a NO_2-silica-gel system using both the positron-lifetime and the angular-correlation method.

II. EXPERIMENTAL

Davison grade 05 silica gel was used as a substrate in this investigation.[7] Silica gel was first dried in the oven at 250°C for 24 h. A McBain type of adsorption system with a precision cathetometer was used for preparing the NO_2 adsorbed samples. The sample for the lifetime measurements was 2.5 g of dried silica gel and a 5 μCi Na^{22} positron source in a glass bucket. It was suspended on a quartz spiral spring which was hung in a long glass tube. The sample for the angular-correlation experiments was 18 g of dried silica gel in a glass container having a thin Mylar window (1 mg/cm^2). Both samples were connected to a vacuum system. A large glass flask for storing NO_2 gas was also connected onto the same system. The whole system was outgassed at a pressure of about 10^{-4} Torr for 24 h. NO_2 gas (minimum stated purity 99.5%) was transferred and stored in the large flask. Both the positron-lifetime and the angular-correlation measurements were performed on degassed silica gel first. Then a small amount of NO_2 gas was transferred from the flask to both sample containers. A cathetometer was used to determine the concentration of NO_2 adsorbed on silica gel by measuring the extension of the calibrated quartz spring. The positron lifetime and the angular-correlation experiments were measured again. The concentration of NO_2 was determined to be 1 mg of NO_2 per gram of silica gel.

The angular-correlation apparatus used was a standard long-slit type which has been described elsewhere.[2,8] A detailed description of the positron-lifetime apparatus has also been reported previously.[3,9]

III. RESULTS AND DISCUSSION

Three positron lifetimes were observed in degassed silica gel, $\tau_1 = 0.55 \pm 0.5$ nsec, $\tau_2 = 3.0 \pm 0.3$ nsec, and $\tau_3 = 32.0 \pm 0.5$ nsec. The relative intensities of the two long-lifetime components were $I_2 = 4 \pm 1\%$ and $I_3 = 29 \pm 1\%$. The τ_1 component can be understood as being due to the direct annihilation of free positrons and the annihilation of p-Ps. The τ_2-component can be attributed to the annihilation of o-Ps inside silica particles. The τ_3 component has been shown to be due to the annihilation of o-Ps in the pores or voids between silica particles.[3,10] With the presence of NO_2 gas in silica gel (1 mg of NO_2 per gram of gel), the longest lifetime τ_3 was completely quenched. There were only two lifetime components observable, $\tau_1 = 0.52 \pm 0.02$ nsec and $\tau_2 = 2.75 \pm 0.05$ nsec, with $I_2 = 11 \pm 1\%$. From the lifetime measurements, it is clear that all the o-Ps atoms inside the pores of silica gel were quenched by NO_2 molecules adsorbed on the pore surface of silica gel. However, in order to determine whether conversion quenching or chemical quenching is responsible for the quenching of positronium in the presence of NO_2, one must study the angular-correlation curves.

Two-photon angular-correlation curves of annihilating positron-electron pairs in degassed silica gel and NO_2 adsorbed silica gel are shown in Fig. 1. The two angular distribution curves were normalized to the same area. For comparison, we also plot momentum distributions of annihilating positron-electron pairs for both samples in Fig. 2.

The intensity of the low-momentum component I_N for degassed silica gel was determined from Fig. 2 to be $16 \pm 1\%$. This component is attributed to the annihilation of p-Ps.[11] For the NO_2 adsorbed samples, I_N reduces to $3 \pm 1\%$, and the most probable momentum of the high-momentum component increases substantially, as shown in Fig. 2. Since the conversion of o-Ps to p-Ps will enhance the value of I_N, as it was seen in oxygen adsorbed silica gel in which I_N increased to 28%,[2] it is clear that the NO_2 quenching of positronium is not due to the conversion process. The enhancement of the high-momentum component by the presence of a small amount of NO_2 in silica gel suggests that the reactions

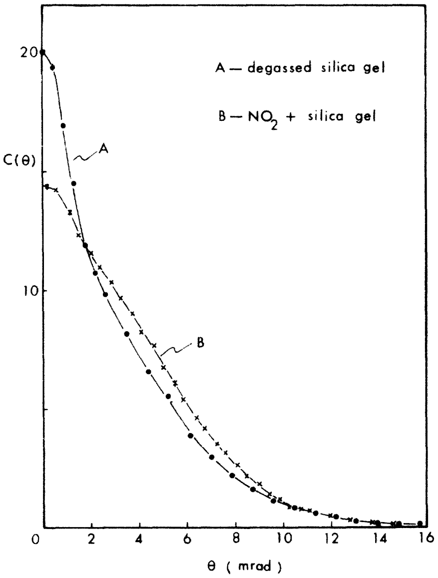

FIG. 1. Angular distributions of annihilating positron-electron pairs in (a) degassed silica gel and (b) NO_2 + silica gel; the concentration of NO_2 was 1 mg per gram of gel. Both curves are normalized to the same area.

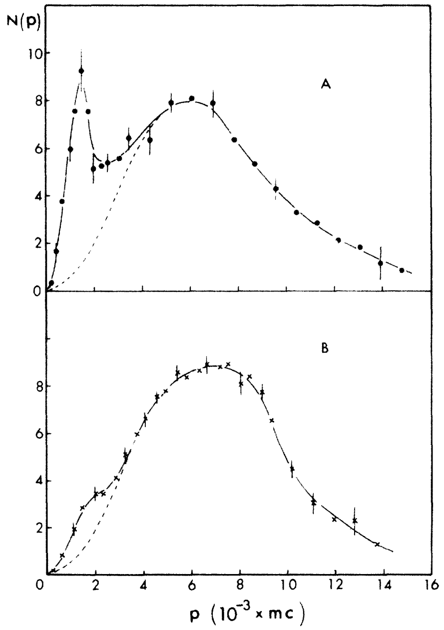

FIG. 2. Momentum distributions of annihilating positron-electron pairs. (a) Degassed silica gel; (b) NO_2 + silica gel.

TABLE I. Quenching cross sections and bond strengths of various quenching molecules in the gaseous state.

Quenching molecule	$\sigma_q v$ (cm^3 sec^{-1})	σ_q (cm^2)	Bond strengths [a] (eV)	Quenching process
NO_2	171×10^{-10}	26×10^{-16}	3.17 (O-NO) 0.56 (O_2N-NO_2)	chemical
I_2	3.78×10^{-10}	0.57×10^{-16}	1.56 (I-I)	chemical
Br_2	3.43×10^{-10}	0.52×10^{-16}	1.74 (Br-Br)	chemical
O_2	1.75×10^{-12}	2.65×10^{-19}	5.16 (O-O)	conversion
NO	5.58×10^{-12}	8.45×10^{-19}	6.49 (N-O)	conversion

[a] Reference 12.

$$e^+ + NO_2 \rightarrow e^+NO_2\,, \qquad (1)$$

$$Ps + NO_2 \rightarrow PsNO_2\,, \qquad (2)$$

have very high reaction rates. In other words, the probability for positrons, either free or bound in positronium, to annihilate with orbital electrons of NO_2 molecules is very high.

From the above results, we can conclude that NO_2 quenching of positronium is due to chemical quenching, as shown in reaction (2), and is not due to conversion quenching, as was generally believed previously.

The quenching cross section σ_q for NO_2 was determined to be 26×10^{-16} cm^2 from the lifetime measurements by taking 6.6×10^6 cm sec^{-1} as the mean thermal velocity (v) of the Ps atoms.[1] This cross section is comparable with the physical cross section of the NO_2 molecule.

It is interesting to compare the quenching cross section for the NO_2 molecule with the cross sections for other quenching molecules studied previously, such as iodine,[3] bromine,[2] oxygen,[2] and nitric oxide.[1] In Table I we list the values of the volume quenching probabilities ($\sigma_q v$) and also the quenching cross sections (σ_q) for the above mentioned molecules. For comparison, we also list the bond strengths (or dissociation energies) of these molecules.

Two significant correlations can be found in Table I. First, the cross sections for chemical quenching molecules are at least two to three orders of magnitude larger than those for conversion quenching molecules. Second, all chemical quenching molecules have much smaller bond strengths than those of conversion quenching molecules. This clearly indicates that bond strengths of these molecules play an important role in the quenching of the Ps atoms. Hence, the different Ps quenching phenomena observed in O_2, NO, and NO_2 gases can be understood. Because of the small bond strengths in nitrogen dioxide gas (either NO_2 or N_2O_4), the Ps compound formation is possible and is in fact dominant in the whole quenching process. Conversely, owing to the large bond strengths in NO and O_2 gases, the Ps compound formation is less likely and the paramagnetic conversion quenching of the Ps atoms is dominant.

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