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Optical spectroscopy of molecular positronium

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We report optical spectroscopic measurements of molecular positronium (Ps_2), performed via a previously unobserved $L = 1$ excited state. Ps_2 molecules created in a porous silica film, and also in vacuum from an Al(111) crystal, were resonantly excited and then photoionized by pulsed lasers, providing conclusive evidence for the production of this molecular matter-antimatter system and its excited state. Future experiments making use of the photoionized vacuum $L=1$ Ps_2 could provide a source of Ps^+ ions, as well as other multipositronic systems, such as Ps_2H^+ or Ps_2O .

The realisation that the negative energy electron states of Dirac's relativistic quantum theory [1] actually exist [2] constitutes one of the most remarkable scientific discoveries of the last century. We now know that all particles have a corresponding negative energy state, or antiparticle, and according to the CPT theorem antiparticles and particles have opposite additive quantum numbers (such as electric charge or lepton number) but are otherwise identical.

Combinations of particle-antiparticle pairs may form exotic atomic states, the most well known example being positronium (Ps), the bound state between an electron and a positron [3]. Although Ps will decay via self-annihilation, its lifetime is long enough that it has a well defined atomic structure, and it is even possible for two Ps atoms to form a molecular state known as Ps_2 [4]. This molecule is stable [5] but has a shorter lifetime against annihilation than Ps, so its existence may be inferred from changes in the Ps decay rate that depend on the Ps density. This was done in previous experiments [6,7], but such observations are necessarily indirect since other processes can also affect the Ps decay rate in a similar way.

In this letter we report observations of optically induced changes in the annihilation yield of dense Ps over a narrow range of wavelengths near 251 nm consistent with what would be expected for electric dipole transitions between the ground state of Ps_2 and a predicted but previously unobserved $L = 1$ excited state [8]. These observations provide conclusive evidence for the production of the di-positronium molecule under conditions allowing Ps-Ps interactions and verify the existence of one of its excited states. Using the methods we describe here it should be possible to measure the transition frequency accurately enough to test relativistic energy corrections [9], and photoionizing excited state Ps_2 provides a way to produce Ps^+ ions that could be used in the formation of exotic two-positron systems such as positronic water, Ps_2O [10].

The experiments were performed by implanting intense pulses of 1-4 keV positrons [11] from an accumulator [12] into either a porous silica film [6, 13] or an Al(111) crystal [7], resulting in the creation of ~ 10 million Ps atoms in

around 1 ns. A 2.3 T magnetic field at the target compresses the positron pulse to an areal density of up to 10^{11} cm^{-2} , which produces interacting Ps atoms [14]. We note that at this magnetic field, $m = 0$ triplet Ps atoms have a lifetime < 2 ns, and so in the following when we refer to long-lived triplet states we mean only $|m| = 1$ atoms, whose vacuum lifetime is 142 ns, regardless of the magnetic field [3].

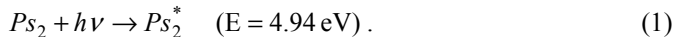
We measure the amount of Ps produced using single shot positron annihilation lifetime spectroscopy [15]. The fraction of our measured lifetime spectra in the interval 50-300 ns after the positron pulse yields the parameter f_d , a measure of the amount of long-lived triplet Ps present [6]. When a high density positron beam is implanted into certain targets, we observe density dependent changes in the Ps decay rate that we ascribe either to spin exchanging scattering events that change triplet Ps atoms into short lived ($m=0$) states [14], or to the formation of Ps_2 (whose lifetime in the ground state is ~ 0.22 ns). Distinguishing between different quenching signals is not possible using only lifetime spectroscopy with our present experimental arrangement.

Fortunately, there is thought to be at least one excited state of the Ps_2 molecule [8], which means that this system may be studied via optical spectroscopy. The $L = 1$ excited molecular state can, in simplistic terms, be thought of as a 2P atom bound to a 1S atom, with the latter acting as though it were a dielectric medium [9], changing the wavelength of the 1S-2P transition from ~ 243 nm for free Ps to ~ 251 nm for Ps_2 . This difference is large enough that there will be no confusion between atomic and molecular Ps excitation, which is important given that any experimental conditions that result in the production of Ps_2 will invariably also produce atomic Ps in much larger quantities.

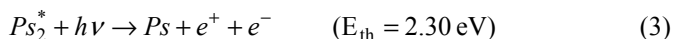
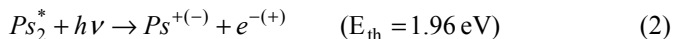
Spectroscopy of Ps_2 molecules was performed with essentially the same methods as our experiments with Ps, as described elsewhere [13]; we use a Nd-YAG-pumped dye laser to generate tunable ultra-violet (uv) light pulses around 251 nm, with a bandwidth of ~ 100 GHz. Residual green light from the pump laser is used to ionize the excited state molecules, with pulse energies of ~ 1 mJ and 30mJ for the uv and green lasers respectively. The ~ 2 mm FWHM uv laser

beam and the ~ 0.15 mm FWHM positron beams were aligned using a phosphor screen and CCD camera, and the 6 mm FWHM green laser was adjusted to overlap the uv light.

We excite Ps_2 molecules to the first excited state [8] using ~ 251 nm light:



Excited state molecules created by the uv light were subsequently ionized with green light (532 nm; 2.33 eV) obtained from the (doubled) output of the pump laser via the following mechanisms:



We note that these processes have different energy thresholds, E_{th} , so that in principle one could select process 2 or 2 & 3 using a tunable ionization laser. Process 3 may be thought of as the photoionization of a 2P Ps atom in the presence of (i.e. weakly bound to) a spectator ground state Ps atom. A third possibility, photodissociation into two Ps atoms: $\text{Ps}_2^* + h\nu \rightarrow \text{Ps} + \text{Ps}^*$, will likely have a small probability for occurring but could include a rich series of resonances [16] corresponding to Rydberg Ps states that would be interesting to examine experimentally.

The Ps_2 detection mechanism relies on observing changes in the Ps decay rate that are correlated with the laser wavelength. That is, when long-lived atoms combine at high density to form Ps_2 the decay rate increases, and f_d will decrease. If these molecules are resonantly excited and photoionized, as in eq (3), this effect will be counteracted due to the production of some long lived triplet Ps, but there will be no observable effect if Ps ions [17] are produced as shown in eq (2) as these will also annihilate rapidly [18]. However, a green light pulse sufficient to ionize Ps_2^* will also ionize Ps^\pm ions, so regardless of whether process (2) or (3) occurs, we shall end up with a free positron and electron and a Ps atom, the last being in a long-lived ($|m|=1$) triplet state 50% of the time [19]. Thus, of all the positronium molecules that are excited to the $L = 1$ state, we should expect to observe an increase in f_d due to, at most, half of them (assuming the liberated positrons annihilate quickly with bound electrons in the target, which is likely since they will not have sufficient energy to make further Ps atoms).

Ps_2 molecules produced inside an open porous silica matrix will not, for the most part, be able to escape into vacuum owing to their short lifetime. Thus, laser spectroscopy of such molecules has to occur inside the pores. Experiments with confined Ps atoms [20] have demonstrated that it is feasible to make such measurements. Figure 1a shows the laser induced change in f_d as a function of the wavelength, measured with

the high density positron beam implanted into a porous silica target. The measured signal is $\Delta f_d = f_d(\text{on}) - f_d(\text{off})$ (on and off refer to the lasers) for four runs, each made up of 52 pairs of single shot measurements of f_d with laser-on and laser-off at various wavelengths. For each run the subtraction of the laser off measurements was done using a straight line fit to the laser off measurements versus measurement number. The errors were assigned so as to make the straight line fits have unity reduced chi square. Figure 1b shows the same data as 1a, ordered by uv wavelength and averaged over independent sets of 8 neighboring measurements with the wavelength and signal both weighted by the inverse square of the individual errors. The square point in Fig. 1b is from a separate run made up of 36 pairs of measurements of $\Delta f_d = f_d(\text{on}) - f_d(\text{off})$, where on and off refer to uv light on and off resonance, at 251.0 nm and 250.55 nm. The Δf_d value for this run, $\Delta f_d = (0.18 \pm 0.02)\%$, was shifted to include the $-(0.10 \pm 0.02)\%$ laser-off background and its error determined from the Gaussian fit to the measurements in Fig 1a. A peak is observed at a wavelength close to the calculated value [8,9] of $\lambda_0 = (250.9179 \pm 0.0011)$ nm. The data of Fig 1 were obtained using an arrangement in which the wavelength was automatically tuned, and was measured using a wavemeter, giving an accuracy of ± 0.005 nm.

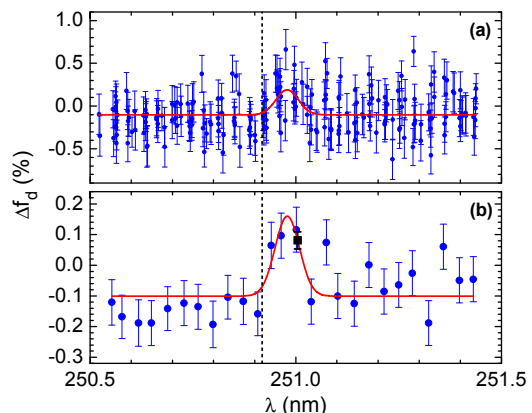


FIG. 1. (color online) Ps_2 resonance measured inside a porous silica film. All data recorded in four separate runs as a function of the laser (vacuum) wavelength (a) and rebinned data (b). The vertical scale is the change in the delayed fraction in percent. The measurement for the single square point in (b) was obtained as described in the text. The solid lines are simple Gaussian fits to the data from which we determine a line center of $\lambda_0 = (250.979 \pm 0.006)$ nm, amplitude $(0.027 \pm 0.008)\%$, and a full width at half maximum (FWHM) of (0.069 ± 0.026) nm. The dashed vertical line indicates the theoretical resonant wavelength for the Ps_2 excitation in vacuum.

The observed line center is (250.979 ± 0.006) nm, which is (0.061 ± 0.006) nm longer than expected for Ps_2 in vacuum. In fact, because the Ps_2 was observed inside a confining pore we had thought that the resonance frequency might be shifted from the vacuum level, but to a *shorter* wavelength, as was observed for atomic Ps in a similar target material, where a shift of -0.05 nm was measured [20]. This was attributed to

the effect of the cavity on the larger 2P state of the atom; the opposite effect observed for Ps_2 is not presently understood theoretically. It can, however, be explained qualitatively if the Ps and Ps_2 internal energies are reduced by similar amounts due to Van der Waals interactions with the cavity walls, whereas, due to its higher mass, the positive confinement energy shift for Ps_2 is only half that of Ps.

The measured linewidth is (0.069 ± 0.026) nm; that this is the same as the 0.070 nm Doppler width expected for free Ps_2 at a temperature of 300 K is undoubtedly fortuitous since the thermalization time for Ps in porous silica is of the order of 10 ns, far longer than the 0.22 ns Ps_2 lifetime. Thus, after the Ps_2 is formed, with release of its ~ 0.4 eV binding energy [8] to its center of mass, it will not have time to fully thermalize. However, we expect that Ps_2 optical transitions in the porous material will be line narrowed [21], and that the observed linewidth actually has nothing to do with the usual Doppler effect, and is more likely to be related to some property of the sample, such as the distribution of cavity sizes [20].

Although porous silica films are very useful for confining Ps atoms, and thus also for observing Ps-Ps interactions [14], for spectroscopic investigations it is preferable to produce Ps_2 in vacuum. Moreover, using silica films has the disadvantage that intense laser light can cause significant and permanent damage to the target material, reducing the amount of Ps (and Ps_2) formation. The accumulation of laser damage means that one cannot collect data indefinitely, limiting the available statistics. In addition to this, temporary damage sites produced during the laser pulse [20] further reduce the amount of Ps formation, which is why the off resonance background of Fig 1b is negative.

We also conducted experiments using an Al(111) target, from which it is possible to produce molecular positronium in vacuum [7]. The Al(111) surface was prepared by Ar^+ ion bombardment for 1 hr at 549 °C, but we found that even after cleaning these surfaces were rather unstable, possibly due in part to light induced chemical effects when there is some small amount of oxide present on the surface [22]. The sample instability is evident in the data of Fig. 2a which shows the time sequence of f_d measurements with and without the uv laser. The effect of the increasing amount of Ps formation with subsequent pairs of shots is removed from the data by subtracting the laser off data, represented by its best fitting quadratic curve, from the uv-laser on data. The errors are taken to be those that give unity reduced chi square for the quadratic fit to the laser off data. The Ps_2 resonance is clearly observed in Fig 2b, which shows the measurements with the 532 nm (green) Ps_2^* photo-ionizing laser on. The measurements with the green laser off in Fig. 2c are consistent with no effect, as expected, since the un-ionized Ps_2^* molecules quickly annihilate in ~ 0.44 ns or decay back to the ground state [8] (with a 19% branching ratio [9]), resulting in no signal. These data were taken using our initial laser setup that required hand tuning of the wavelength, which was measured to an accuracy of ± 0.01 nm using a grating spectrometer and a helium $3^1\text{P}-2^1\text{S}$ reference line.

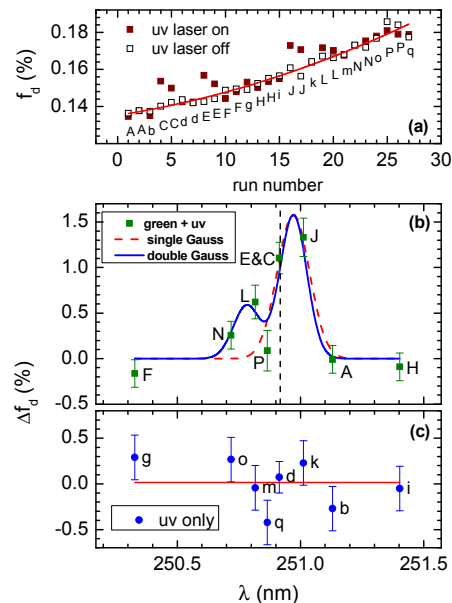


FIG. 2. (color online) Ps_2 resonance measured in vacuum with an Al(111) crystal at room temperature: (a) data with uv laser on and off showing variations in f_d during the measurement and the quadratic fit to the laser off data. Measurements are labelled sequentially using upper (lower) case letters for green photoionizing laser on (off). (b) lineshape measured with the uv and green lasers on. The dashed line in (b) is a single Gaussian fit to the data and the solid line is a Double Gaussian fit (with a single width), as explained in the text. The dashed vertical line indicates the theoretical resonant wavelength for the Ps_2 excitation in vacuum. (c) Measurement with uv laser on and green laser off, showing the best fitting horizontal line, $\Delta f_d = (0.016 \pm 0.087)\%$, consistent with no effect.

A single Gaussian fit to the data of Fig. 2b (dashed (red) line) gives a line center $\lambda_0 = (250.97 \pm 0.02)$ nm, significantly longer than the calculated vacuum wavelength. However, Ps_2 molecules produced at the Al(111) surface will only travel ~ 0.1 mm before annihilation. To obtain maximal overlap with the Ps_2 cloud in vacuum the uv laser was directed into the target at an angle of $\sim 25^\circ$. As a result there will be a Doppler shift of the transition to a longer wavelength for incident light, and to a shorter wavelength for reflected light, as has been observed using Ps formed on Si surfaces [23]. As we expect there to be equal and opposite Doppler shifts associated with the incident and reflected light, we fitted a single-width double Gaussian function to the data in Fig. 2b (solid (blue) line). To obtain convergence, we constrained the amplitude of the main peak to be the same as that of the single Gaussian fit. The amplitude of the peak corresponding to the reflected light depends on the reflection coefficient, which is unknown, but will be < 1 . The center of the two peak positions is (250.88 ± 0.02) nm, which is $\sim 2\sigma$ shorter than the calculated vacuum wavelength. However, even though the improved reduced chi square with respect to the single Gaussian fit ($\chi^2/\nu = 5.46/4$ instead of 15.10/5), supports the conclusion that light reflection should be taken into account, the shape of the assumed double Gaussian lineshape cannot be correct; the

exact value of the transition wavelength for these data is therefore not known as accurately as the double Gaussian fit suggests, and the measurement is broadly consistent with the theoretical value.

The full width at half maximum (FWHM) of the double and single Gauss fits is ~ 0.15 nm, indicating Ps_2 emission energies of ~ 0.2 eV, consistent with the 0.435 eV binding energy and the energetics of Ps_2 formation at an Al(111) surface [24]. The $(1.5 \pm 0.5)\%$ amplitude implies that more than 5% of the $\sim 2 \times 10^7$ slow positrons implanted into the Al target end up forming at least half a million Ps_2 molecules (where we assume that the ~ 100 GHz bandwidth of the laser is power broadened so as to cover $\sim 30\%$ of the $\text{Ps}_2 \rightarrow \text{Ps}_2^*$ Doppler-broadened linewidth, as has been observed in experiments with Ps [25]).

The statistical significance of the 251 nm resonances in Figs. 1 and 2 can be judged from P , the probability that a random sample of data from a population representing the null hypothesis gives a worse fit to a wavelength independent constant than the actual measured data. For Fig 1b, $P = 3 \times 10^{-5}$ or 6×10^{-8} for null hypotheses of an unconstrained constant background or a fixed background, respectively (the latter determined by the Gaussian fit). For the data of Fig 2b, $P = 2 \times 10^{-5}$ or 6×10^{-14} for the null hypothesis of zero background (as determined from the data of Fig. 2c), taking into account the chi square per degree of freedom of the Gaussian or double Gaussian fits respectively. Thus, the spectroscopic data presented in figures 1 and 2 demonstrate the existence of the $L = 1$ excited state predicted by Varga *et al.* [8], confirm our earlier experiment [6] and set the stage for future work in which more detailed measurements will be made.

Ps_2 formed in vacuum by two Ps atoms interacting on a surface will initially carry away some fraction of its binding energy, and so the Doppler width of the excitation line is relatively broad, since the Ps_2 mass is so low. This limits the accuracy with which measurements of the ($L = 1$) line center can be made to ~ 100 ppm. A measurement to ~ 10 ppm would be necessary to test calculations of relativistic contributions to both the ground and excited state Ps_2 energies [9]. Improvements to the experimental method, such as using a different or modified formation target to obtain colder Ps_2 or employing spectral hole burning techniques [26], might make it possible to reach the 10 ppm level.

An excited state with $L = 0$ and even C parity has been predicted [27] that suggests the possibility of a Doppler-free two photon excitation that could provide a ~ 1 ppm measurement (determined by the lifetimes of the ground and excited Ps_2 states). We note, however, that the properties of this state are in question because the group representation [28] used in the calculation may not properly take into account the symmetry of the Ps_2 system [29].

As indicated in Eq (2), ionization of the excited state Ps_2 molecule can result in the production of either positive or negative Ps ions. Although Ps^- ions have been observed before [17,18] and can now be produced quite efficiently [19], Ps^+ ions have not yet been observed experimentally. However, it is

likely that some fraction of the signal in the present work is due to Ps^+ production.

In order to optimize and identify the formation of Ps ions via excited molecular states, one would use a laser just sufficient to ionize Ps_2^* (1.96 eV, 633 nm), and electric fields to control the resulting ions [17]. However, 633 nm light will photoionize Ps^+ ions, with a cross section similar to that of Ps_2^* molecules [19], so the total Ps ion yield would then be approximately half of the Ps_2^* yield. Thus, it should be possible to form a Ps^+ ion beam with $\sim 1\%$ efficiency. An interesting prospect is that collisions using slow Ps^+ ions could provide a means of transferring more than one antiparticle to ordinary matter atoms or molecules. This might be a way to produce and study new exotic multi-positronic systems [30] such as dipositronium hydride, Ps_2H^- [31], or positronic water, Ps_2O [10].

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