Positronic Water, Ps_2O

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(Received 22 May 1998)

We demonstrate the chemical stability of a compound containing two positrons, Ps_2O, which may be considered an extreme isotopic variant of ordinary water. We introduce a dynamical determination of the step length into the diffusion quantum Monte Carlo method, and find that Ps_2O is more stable than its lowest dissociation threshold, PsO + Ps, by 1.27 ± 0.08 eV. We estimate its annihilation rate to be 4.6 ns^{-1}. This paper is the first demonstration of the stability of a two-positron compound since Wheeler's work on diatomic positronium, Ps_2 [Ann. N.Y. Acad. Sci. **48**, 219 (1946)]. [S0031-9007(98)07861-2]

PACS numbers: 36.10.Dr, 02.70.Lq, 03.65.Ge, 31.15.Ar

Chemical compounds comprising both ordinary matter and antimatter, in the form of electrons and positrons, have been of interest for fifty years [1]. Several molecules which contain one positron have been shown recently, by both calculations and experiments, to be stable to dissociation, i.e., to be chemically stable [2–4]. Such compounds undergo electron-positron annihilation, but this process is sufficiently slow to permit their detection and characterization.

Experiments [2] are presently more difficult and less precise than calculations [3,4] for studies of mixed electron-positron systems. In this Letter, we report accurate quantum mechanical calculations on Ps_2O, of which there is no previous mention in the literature known to us. Our calculations indicate that the energy of Ps_2O is 2.11 ± 0.08 eV below that of O + 2Ps. Since the binding energy of Ps_2 is 0.43545 eV [5], it follows that Ps_2O is more stable than O + Ps_2 by 1.67 ± 0.08 eV. The contrast with the ordinary water molecule is stark: The energy of H_2O is below that of H_2 + O by 5.11 eV. The effect of the lighter mass of the positron compared to that of the proton is evident, and may be viewed as an extreme example of a reduced mass effect.

In order to assess the accuracy and reliability of our method of calculation, we perform calculations on the species O and O^-, as well as on PsO and Ps_2O. In this way we calculate the electron affinity of atomic oxygen, which is well known from experiments. Our calculated total energy of atomic oxygen, relative to the complete separation of electrons and the nucleus, is −75.0495 ± 0.0016 a.u. This accounts for 93.1% of the correlation energy, and is comparable to the best previous calculations for this system [6]. It is higher than the best estimate of the exact eigenvalue of the nonrelativistic Schrödinger equation [7] by only 0.48 ± 0.04 eV; in other words, the error in our calculated total energy is only 0.023%. Our calculated electron affinity of atomic oxygen, 1.38 ± 0.05 eV, is comparable to the more precise experimental value from laser photodetachment threshold measurements, 1.46 eV [8]. Evidently, the errors in our energy calculations for O and O^- cancel to within 0.08 ± 0.05 eV. Our calculated positronium affinity of atomic oxygen, or the Ps-O bond energy of the molecule PsO, is 0.84 ± 0.18 eV (slightly larger than that reported by Bressanini *et al.* [4]). Thus the energy of Ps_2O is 1.27 eV below that of PsO + Ps. This is the lowest dissociation threshold of Ps_2O.

Method of calculation.—We use the fixed node diffusion quantum Monte Carlo (DMC) method with importance sampling. This well-tested method has been reviewed recently [9] and is described in a textbook [10]. The Schrödinger equation is transformed into a diffusion equation in imaginary time, solutions of which are simulated by the movements of a large number of "walkers" in $3n$-dimensional space. (n in the present application is the number of light particles, i.e., electrons and positrons.) We improve the efficiency of the approach by dynamically adjusting the time steps of the walkers so that drift distances are approximately uniform in the ensemble. The moves of the walkers are synchronized every few time steps, and all of the walkers move for the same total time.

The simulated diffusion is guided by a trial wave function Ψ_T which is not provided by the DMC method. The conventional choice for Ψ_T for a purely electronic system is a product of Slater determinants of electronic orbitals and Jastrow factors for electron pairs. We use a straightforward extension of this scheme for the electronic part of our Ψ_T: For the electronic orbitals, we use those of O^- as given by Clementi and Roetti [11]. We use a Jastrow factor for each pair of light particles of the form $\exp[ar/(1 + br)]$, where r is the radial distance between the particles of the pair, the parameter a is the proper cusp value for that pair, and b is chosen by variational QMC calculations. We multiply this by two functions, one for each positron, of the form $(c + r)\exp(-dr)$, where r is a positron-nucleus distance. The parameters c and d are chosen to satisfy the positron-nuclear cusp condition, leaving one remaining parameter which is determined by variational QMC calculations.

We use about 800 walkers, each taking $\sim 10^4$ to 10^5 average time steps from about 0.0006 to 0.0025 a.u. [12]. Four independent runs are made for each system at each

TABLE I. Energies calculated for each system as a function of the average time step (see text). Energies in the last row are extrapolated. Uncertainties in the last decimal figure are shown in parentheses.

δt_{ave} (a.u.)	O	O$^-$	PsO	Ps$_2$O
0.0025	−75.0548(10)	−75.1116(8)	−75.3447(17)	−75.6540(33)
0.001875	−75.0548(14)	−75.1060(8)	−75.3452(20)	−75.6455(50)
0.00125	−75.0527(7)	−75.1053(12)	−75.3394(72)	−75.6356(45)
0.000625	−75.0502(17)	−75.1034(8)	−75.3289(57)	−75.6343(13)
0.0	−75.0495(16)	−75.1001(11)	−75.3284(62)	−75.6270(22)

of four values of the time step, implying that more than 10^8 configurations in $3n$-dimensional space are sampled for each system. Extrapolations to zero time step are made for each system, and the differences in total energies so calculated yield the binding energies of interest. The calculated energy values for each time step are given in Table I. Expectation values of powers of interparticle coordinates for Ps$_2$O are given in Table II.

Annihilation rates of Ps$_2$O *and* PsO.—If the wave function Ψ for a mixed positron-electron system is known, and if the electrons and positrons are in closed shells, the annihilation rate λ takes a particularly simple form [13]. In atomic units,

$$\lambda \approx \pi \alpha^3 \left\langle \Psi \,\middle|\, \sum_{e,p} \delta^3(\mathbf{r}_{ep}) \,\middle|\, \Psi \right\rangle, \tag{1}$$

where $r_{ep} = |\mathbf{r}_e - \mathbf{r}_p|$. This can be written as [14]

$$\lambda \approx 50.5 n_{ep} \langle \Psi | \delta^3(\mathbf{r}_{ep}) | \Psi \rangle \ \mathrm{ns}^{-1}, \tag{2}$$

where n_{ep} is the number of electron-positron pairs in the system, and where the subscripts e and p denote any particular electron and positron in the argument of Ψ. The DMC method does not provide a wave function in a convenient form, but easily yields expectation values for operators which only multiply (such as those given in Table II) by simple sampling techniques. However, delta functions present difficulties for DMC [15]; there has been no report to our knowledge of a calculated annihilation rate within the DMC method for any electron-positron system with more than four light particles. We therefore resort to an expediency which allows us to approximate the annihilation rate. We define a distribution function ρ for the electron-positron radial distance r_{ep}:

$$\rho(r_{ep}) = \int |\Psi|^2 \frac{dV}{4\pi r_{ep}^2 dr_{ep}} . \tag{3}$$

The integration is over the spatial and spin coordinates of the light particles, except r_{ep}. The values given in the fourth row of Table II are evidently equivalent to $\langle r_{ep}^n \rangle$ and can be expressed as

$$\langle r_{ep}^n \rangle = \int r_{ep}^n |\Psi|^2 dV = 4\pi \int_0^\infty r^n \rho(r) r^2 dr . \tag{4}$$

It is also evident that the probability of coalescence of the electron-positron pair is

$$\langle \Psi | \delta^3(\mathbf{r}_{ep}) | \Psi \rangle = \rho(0) . \tag{5}$$

We determine the approximate value of $\rho(0)$ by expanding $\rho(r_{ep})$ in a basis,

$$\rho(r_{ep}) = \sum_{i=1}^{N} a_i r_{ep}^{n_i} \exp(-b_i r_{ep}) , \tag{6}$$

and fitting this function to the calculated average powers of the coordinate r_{ep} in Table II and to the known cusp value. By fixing the powers n_i we have left $2N$ variables and six values to fit, so we take $N = 3$. The fitted parameters are given in Table III, from which we find that $\rho(0) \approx 4.54 \times 10^{-3}$. Since there are twenty electron-positron pairs in Ps$_2$O, we arrive at an approximate annihilation rate of

$$\lambda \approx 4.6 \ \mathrm{ns}^{-1}, \tag{7}$$

or a natural lifetime of 220 ps. This is not a quantitative result but rather an extrapolation of sorts, about which little is known. It is a reasonable value, however, as can be seen by the following argument.

Each positron is in a 10-electron environment in which the electron spin seen by a positron in any contact leading to annihilation is equally likely to be parallel as antiparallel to its own. Thus the spin-averaged annihilation rate of positronium, ~2 ns^{-1}, is a reasonable guess for the annihilation rate for one of the positrons,

TABLE II. Averages of powers of interparticle coordinates, in atomic units, for Ps$_2$O. Uncertainties in the last decimal are in parentheses.

	$\langle r^n \rangle$				
Pair	$n = -2$	$n = -1$	$n = 0$	$n = 1$	$n = 2$
e^--nucleus	25.44(5)	2.308(1)	1	1.281(4)	2.77(3)
e^+-nucleus	0.105(2)	0.286(3)	1	4.30(5)	27.05(46)
e^--e^-	1.645(9)	0.789(1)	1	2.036(7)	5.71(6)
e^--e^+	0.122(2)	0.284(3)	1	4.50(4)	24.3(5)
e^+-e^+	0.053(2)	0.193(3)	1	6.38(7)	47.5(9)

TABLE III. Parameters in Eq. (7).

i	n_i	a_i	b_i
1	0	4.54×10^{-3}	1.0
2	2	2.90×10^{-3}	1.0
3	4	-1.3×10^{-8}	0.5

twice that for both. The many-electron environment increases this value, but probably not by very much because of the limiting effects of exclusion and repulsion. The saturation value has been estimated [16] to be ~20% larger than in isolated positronium, which would give an annihilation rate of 2.4 ns^{-1}. An annihilation rate very much like this is found in virtually every molecular material, and is attributed to the annihilation of a single positron surrounded by a large number of electrons with random spins. Twice this is 4.8 ns^{-1}. The good agreement between this result and that given in Eq. (7) is probably fortuitous, because other sets of parameters different from those given in Table III also fit the average powers of r_{ep} and the cusp value but give different values of $\rho(0)$. The fitting exercise merely demonstrates that a fit exists which gives a value of $\rho(0)$ that is consistent with the qualitative notions discussed earlier in this paragraph.

We may regard the total light particle spin S, its z component M_S, the total spin for the electrons S_e, and that for the positrons S_p as "good" spin quantum numbers [17]. For Ps_2O, all of these quantum numbers are zero. When Ps_2O annihilates, PsO is left. The ground state [18] of this species has $S_e = S_p = \frac{1}{2}$, so $S = 0, 1$. We denote the $S = 0$ state as para-PsO, and the $S = 1$ state as ortho-PsO. These two states are, like ortho-positronium and para-positronium, separated by tiny hyperfine and continuum coupling interactions, and have virtually identical wave functions except for the spins of the positron-unpaired electron pair. Para-PsO will annihilate more rapidly, presumably with the spin-averaged saturated rate for one positron, which we approximate as $\frac{1}{2}\lambda$. The positron in ortho-PsO sees only three valence electrons with spin opposite their own (a condition for annihilation producing two gammas) compared to four for para-PsO, and recent observations of the Doppler broadening of annihilation radiation in atoms [19] indicate that the valence electrons in an atom contribute approximately equally to the annihilation rate of a nearby positron, and much more than do core electrons. It follows that the annihilation rate of ortho-PsO is $\sim\frac{3}{8}\lambda$.

This set of intrinsic annihilation rates, λ for Ps_2O, $\frac{1}{2}\lambda$ for para-PsO, and $\frac{3}{8}\lambda$ for ortho-PsO, gives rise to a laboratory count of annihilation gammas which might be used as a signature of Ps_2O. It is not difficult to calculate the resulting lifetime spectrum. We find that it has components (lifetime in ps, intensity in %) = (220, 15), (440, 25), and (580, 60).

Structure of Ps_2O.—Positrons are so much lighter than protons that arguments of structure and properties which spring from the protonic analog are not necessarily instructive. For example, the rotational and vibrational degrees of freedom of H_2O are subsumed in Ps_2O into positronic motions more like those of the electrons. The positrons are as mobile and delocalized as the electrons, far more so than are the protons in H_2O. The two positrons can be considered to be in their lowest s-type atomic orbital, which is unlike any electronic s orbital owing to the reversal of Coulomb forces and the high degree of correlation with the electrons. A bound excited triplet P state involving one positron in a p-type orbital is not inconceivable. Annihilation will take place directly from such a state because it is dipole forbidden to deexcite to the ground state. Since the exchange interaction between the positrons is expected to be small, a positronic singlet P state will have a slightly higher energy and might still be bound compared to $Ps_2 + O$. Such a state will optically deexcite to the ground state before it annihilates.

Calculations on these and other excited states are under way. If it develops that no excited state of Ps_2O exists, then the detection of this compound is somewhat simplified.

Possible preparation and detection of Ps_2O.—An experimental program is now under way at Oak Ridge National Laboratory (ORNL) to measure the binding energies of one-positron compounds, such as PsO [20]. In order to prepare the molecule Ps_2O in the laboratory, we must create a higher concentration of positrons than is now possible at ORNL or any other laboratory. If the source of positrons is to be nuclear decay, then the positrons will be spin polarized, and mostly positron-triplet Ps_2O will result, if it exists. On the other hand, if the positrons are unpolarized, and if bound positron-triplet Ps_2O exists, the singlet and triplet will be formed in the ratio 1:3, approximately.

The techniques of time bunching [21] and brightness enhancement [22] of positron beams should be capable of delivering 10^6 slow positrons in nanosecond bursts to a spot size on the order of a micron [23,24]. Ps_2O might be formed on a metal surface with adsorbed oxygen at attainable positron surface concentrations by a process similar to that suggested for the formation of Ps_2 [24].

Alternatively, a BaO target might yield Ps_2O by a modification of the Knotek-Feibelman mechanism [25]. The charge state of oxygen in the BaO lattice is nominally -2, and if it is electrically neutralized by the addition of two positrons the Madellung forces which hold the anion in the lattice are canceled, and the neutral Ps_2O species would be expelled with a kinetic energy of a few eV.

In any case, there seem to be definite possibilities for forming Ps_2O, although details of the chemical and surface dynamics involved are not yet worked out. The detection and characterization of the resulting Ps_2O present more formidable challenges. Perhaps the optical signals discussed in the previous section will provide the necessary signal. It might also be possible to exploit the differences in the production of Ps_2O for polarized and unpolarized positron sources. In this regard, the question of the existence of a bound positron-triplet state of Ps_2O is especially significant.

We acknowledge illuminating discussions with D. E. Ramaker and A. P. Mills, Jr., and a helpful comment from D. T. Haworth. This work is supported in part by the National Science Foundation under Grant No. PHY-9600416.

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