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Fusion rates for hydrogen isotopic molecules of relevance for "cold fusion"

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In response to the recent announcements of evidence for room-temperature fusion in the electrolysis of D_2O, we have analyzed how the fusion rate depends on the reduced mass of the fusing nuclei, the effective mass of a "heavy" electron, and the degree of vibrational excitation. Our results have been obtained both by accurately solving the Schrödinger equation for the hydrogen molecule and by using the WKB approximation. We find that in light of the reported d-d fusion rate, the excess heat in the experiment by Fleischmann, Pons, and Hawkins [J. Electroanal Chem. **261**, 301 (1989)] is difficult to explain in terms of conventional nuclear processes.

A recent article by Fleischmann, Pons, and Hawkins[1] of inducing nuclear fusion in metallic palladium electrodes via the electrolysis of D_2O has attracted much attention. They have reported the detection of neutrons and tritium, which presumably were produced in the reactions

$$d+d \rightarrow {}^3\mathrm{He}(0.82\ \mathrm{MeV})+n(2.45\ \mathrm{MeV}), \quad (1)$$

$$d+d \rightarrow t(1.01\ \mathrm{MeV})+p(3.02\ \mathrm{MeV}), \quad (2)$$

consistent with a fusion rate of about 10^{-19} sec^{-1} per d-d pair. They have also described the generation of excess heat by a factor of 10^7 to 10^{10} greater than can be accounted for by the above d-d fusion reactions. Meanwhile, Jones *et al.*[2] have performed a similar experiment involving the electrolysis of D_2O using palladium and titanium electrodes. They have measured a neutron count five standard deviations above background, peaking around 2.5 MeV, consistent with the occurrence of reaction (1) at the rate of about 10^{-23} s^{-1} per d-d pair.

Besides the immediate issue of the unexplained origin of the excess heat in Fleischmann, Pons, and Hawkins' experiment,[1] a number of questions arise: (i) How close must deuterons be brought to account for the d-d fusion rates of 10^{-19} to 10^{-23} s^{-1} per d-d pair? (ii) Under such conditions, at what rates would other fusion reactions, such as

$$p+d \rightarrow {}^3\mathrm{He}(5\ \mathrm{keV})+\gamma(5.4\ \mathrm{MeV}), \quad (3)$$

$$d+d \rightarrow {}^4\mathrm{He}(76\ \mathrm{keV})+\gamma(23.8\ \mathrm{MeV}), \quad (4)$$

$$d+t \rightarrow {}^4\mathrm{He}(3.5\ \mathrm{MeV})+n(14.1\ \mathrm{MeV}), \quad (5)$$

occur? (iii) In light of the experimental evidence[2] that the occurrence of the fusion reactions (1) and (2) is not merely a concentration effect, but depends critically on the achievement of nonequilibrium conditions, how do the fusion rates depend on the degree of vibrational excitation?

In an effort to model the fusion phenomena inside or at the surface of the electrodes, we have performed accurate calculations, within the adiabatic approximation, of the rates of the fusion reactions (1)–(5) for various vibrational states of the D_2, HD, HT, and DT molecules. In a D_2 molecule under ordinary conditions the fusion rate is about 10^{-64} s^{-1} (see below). However, if the electrons are replaced by muons, which are 207 times heavier, the fusion rate increases by 75 orders of magnitude (for a recent review of muon-catalyzed fusion see Ref. 3). Thus the fusion rate displays a strong dependence on the mass of the particle which chemically binds the nuclei together. To assist in the investigation of whether a "heavy" or "sluggish" electron arising from complicated collective solid-state effects could play a role in the enhanced fusion rates seen in the experiments, we study how the Coulomb barrier penetration factor depends on the mass of a hypothetical particle (or quasiparticle) of charge -1 and on the reduced mass of the pair of nuclei. We have also calculated the fusion rates using the WKB approximation as modified by the Langer correction. We discuss various mechanisms which might be thought to explain the excess heat reported by Fleischmann, Pons, and Hawkins.[1]

All our calculations have been performed within the adiabatic approximation. In this approximation the nuclei move in a potential consisting of the Born-Oppenheimer (clamped nuclei) potential plus the adiabatic correction term. (We have also included the electron relativistic corrections in the potential which, however, have a negligibly small effect on the quantities discussed in this paper.) The potential was taken from Ref. 4, which contains the most accurate values available for the hydrogen molecule. The details of the method are described in Ref. 4. This approach neglects the nonadiabatic effects which are extremely small for electronic molecules (these effects, however, do play a significant role in muonic molecules[5]). The vibrational equation was solved numerically using an integration step of 0.00002 bohr. At this distance even for the electronic case the vibrational wave function is within a few percent of its value at $r=0$. To obtain the value of the wave function at zero we have extrapolated using ten equally spaced points between 0.00006 and 0.00024 bohr. We used the following masses of the particles: $m_\mu=206.7683$,[6] $M_p=1836.1527$,[6] M_d

$=3670.4806$,[7] and $M_t=5496.918$.[7]

The fusion rate is given by[8]

$$\lambda_f = A_0 \frac{m^3}{4\pi a_0^3} |\chi(0)|^2 \tag{6}$$

where $\chi(r)$ is the radial part of the vibrational wave function and A_0 is the nuclear reaction constant equal to 5.2×10^{-22}, 1.48×10^{-16}, 4.76×10^{-21}, and 1.2×10^{-14} cm^3s^{-1} for the p-d, d-d, p-t, and d-t reactions, respectively.[9] For the d-d case A_0 is the sum of the constants for channels (1) and (2). The distance a_0 is the Bohr radius ($0.529\,177\times10^{-8}$ cm) and m is the mass of the negatively charged particle expressed in electron masses. The factor $1/4\pi$ results from the angular part of the wave function describing the relative motion of the two nuclei.

A simpler estimate of the fusion rate can be obtained by using the WKB approximation, as modified by the Langer correction.[10] We follow here the approach used by Jackson in his fundamental paper on muon-catalyzed fusion.[8] To compute the fusion rate we approximate $|\chi(0)|^2$ by the square of the WKB wave function at $r=0$

$$[\chi_{WKB}(0)]^2 = N^2 \exp[-\lambda(0)], \tag{7}$$

where

$$\lambda(0) = \int_0^{r_i} \left[2\left[2M[V(r)-E] + \frac{1}{4r^2} \right]^{1/2} - \frac{1}{r} \right] dr + \ln(r_i/2), \tag{8}$$

is the barrier penetration integral and

$$N^2 = \left[2\int_{r_i}^{r_o} \{2M[E-V(r)]\}^{-1/2} dr \right]^{-1}, \tag{9}$$

is the normalization constant. In the above equations M denotes the reduced mass of the two nuclei, $V(r)$ is the internuclear potential, E is the energy level, and r_i and r_o are, respectively, the inner and outer classical turning points. We use units such that $\hbar=e=m=1$, unless otherwise stated.

Equations (6)–(9) reveal that the overall fusion rate is the product of the intrinsic nuclear reaction factor and a molecular factor arising from tunneling through the Coulomb barrier. The general trend for reactions involving hydrogen isotopes is that the intrinsic nuclear reaction factor increases with the number of neutrons in the nuclei and hence with their mass. However, the tunneling through the Coulomb barrier decreases with the reduced mass of the pair of nuclei since $\lambda(0)\sim(M/m)^{1/2}$. Thus the overall fusion rate reflects a competition between these effects, and relative fusion rates for different pairs of hydrogen isotopes can change dramatically with the mass m of the negatively charged particle.

Table I shows our results on the fusion rates for the relevant isotopes of H_2 for various masses of the negatively charged particles. For $m=1$ our result for the p-d fusion rate agrees to within 2 orders of magnitude with the estimate of Zel'dovich and Gershtein,[11] but our result for the d-d fusion rate is 7 to 16 orders of magnitude larger than the range of estimates of Van Siclen and Jones.[12]

We have also investigated the relations of the fusion rates between molecular ions (containing only one heavy fermion) and the respective molecules (containing two heavy fermions). We have performed a calculation using the potential-energy curve for the H_2^+ ion from Ref. 13. Our rate for D_2^+ equal to 0.45×10^{-76} agrees reasonably well with the value 0.83×10^{-76} computed by Rafelski *et al.*[14] For the muonic ion $td\mu$ we obtained a fusion rate of 0.66×10^{12}, which agrees very well with the accurate fully nonadiabatic result 0.63×10^{12} of Ref. 15. Thus even for muonic molecules the nonadiabatic effects play a minor role for the ground state. Comparison with Table I shows that the presence of the second muon increases the fusion rate by a factor of 14. For $m=1$ the effect is much larger, e.g., for D_2 the second electron increases the fusion rate by 13 orders of magnitude. This conclusion disagrees with a conclusion reached in Ref. 14.

In accordance with the proportionality of λ to $(M/m)^{1/2}$, the barrier penetration probability is largest for the p-p system (for $m=1$ the molecular factor for p-p fusion is larger by 22 orders of magnitude than for d-d fusion). However, since the nuclear reaction constant A_0 for p-p fusion is smaller by 23 orders of magnitude[9] than for d-d fusion (because $p+p\rightarrow d+e^++\nu$ can proceed only via the weak interaction), this process is not relevant to explaining the electrolytic fusion experiments and will not be further discussed here. For $m=1$ the molecular contribution to the p-d fusion rate is 14 orders of magnitude larger than for d-d fusion, while A_0 is 6 orders of magnitude smaller, so the p-d fusion rate is 8 orders of magnitude larger than the d-d fusion rate. However, the ratio of molecular contributions decreases rapidly with m, so that for $m\approx5$, required to reach the d-d fusion rate reported by Fleischmann, Pons, and Hawkins,[1] the molec-

TABLE I. Dependence of the fusion rate on the mass of the negatively charged particle for the HD, D_2, HT, and DT molecules in the $v=0$ vibrational state. Numbers in brackets denote power of ten.

	HD		D_2		HT		DT	
m	$\chi(0)$	λ_f	$\chi(0)$	λ_f	$\chi(0)$	λ_f	$\chi(0)$	λ_f
1	0.153 [−28]	0.654 [−55]	0.157 [−35]	0.197 [−63]	0.202 [−30]	0.105 [−57]	0.365 [−39]	0.863 [−69]
2	0.173 [−19]	0.665 [−36]	0.219 [−24]	0.306 [−40]	0.835 [−21]	0.143 [−37]	0.618 [−27]	0.197 [−43]
3	0.162 [−15]	0.197 [−27]	0.174 [−19]	0.649 [−30]	0.139 [−16]	0.134 [−28]	0.148 [−21]	0.383 [−32]
4	0.362 [−13]	0.234 [−22]	0.139 [−16]	0.984 [−24]	0.439 [−14]	0.315 [−23]	0.229 [−18]	0.217 [−25]
5	0.142 [−11]	0.702 [−19]	0.130 [−14]	0.168 [−19]	0.217 [−12]	0.151 [−19]	0.336 [−16]	0.912 [−21]
6	0.209 [−10]	0.264 [−16]	0.364 [−13]	0.228 [−16]	0.381 [−11]	0.801 [−17]	0.132 [−14]	0.241 [−17]
m_μ	0.441 [−01]	0.480 [07]	0.212 [−01]	0.316 [12]	0.366 [−01]	0.302 [08]	0.140 [−01]	0.112 [14]

ular contribution to the p-d fusion rate is only 6 orders of magnitude larger than for d-d fusion, so that the overall p-d and d-d fusion rates (per nucleon pair) should be the same within an order of magnitude.

In Table II we show results of our calculations for D_2 using the WKB approximation, employing the same potential as for the solution of the Schrödinger equation. Comparison with the results of Table I shows that the WKB approximation gives a very accurate description of the barrier penetration yielding a result only slightly different from the nearly exact quantum value. The results of Table II show that the fusion rates grow dramatically with the vibrational excitation level. For high vibrational levels of ordinary D_2 the rate is 8 orders of magnitude larger than for the ground state. These results can be qualitatively understood in terms of the decrease of the classical inner turning point r_i with v. For high vibrational states just below the dissociation threshold the fusion rate slightly *decreases* with E since the anharmonic widening of the potential well causes the normalization factor N^2 to decrease.

In Table III we present fusion rates for ground and high vibrationally excited states as a function of m. Although the vibrational enhancement of fusion rates decreases with m, even for $m=5$ fusion from high vibrational states is 3 orders of magnitude faster than from the ground state. In view of the remark by Jones *et al.*[2] that nonequilibrium conditions, which imply a higher population of the excited states than Boltzmann statistics predicts, are crucial in achieving electrolytic fusion, the observation of enhanced fusion rates out of vibrationally excited states may be of a special significance.

Our analysis has been carried out for the ground electronic state of H_2. However, the principal trends of our results are much more generally applicable since the barrier penetration probability is most strongly influenced by the short-range behavior of the internuclear potential, i.e., where the Coulomb potential $1/r$ is sharply rising. This feature is always present regardless of the environment in which the hydrogens are found. In particular, the isotopic effects should be of a generic nature unless the effective potentials are of very unusual shapes. Elsewhere[16] we will present a simple model of the short-range repulsive potential which allows quite accurate estimation of barrier penetration probabilities.

TABLE II. Dependence of the fusion rate on the excitation level calculated for D_2 using the WKB approximation.

v	Binding energy	$\chi_{WKB}(0)$	λ_f
0	0.1674	0.162 [−35]	0.209 [−63]
2	0.1407	0.232 [−34]	0.427 [−61]
4	0.1161	0.145 [−33]	0.166 [−59]
6	0.0936	0.579 [−33]	0.267 [−58]
8	0.0731	0.175 [−32]	0.244 [−57]
10	0.0548	0.430 [−32]	0.147 [−56]
12	0.0386	0.877 [−32]	0.612 [−56]
16	0.0135	0.220 [−31]	0.384 [−55]
20	0.0006	0.189 [−31]	0.284 [−55]

TABLE III. Dependence of the fusion rate on the excitation level and the heavy fermion mass calculated for D_2 using the WKB approximation.

m	v	Binding energy	$\chi_{WKB}(0)$	λ_f
1.0	0	0.1674	0.162 [−35]	0.209 [−63]
	20	0.0006	0.189 [−31]	0.284 [−55]
2.0	0	0.1646	0.228 [−24]	0.329 [−40]
	12	0.0082	0.132 [−21]	0.111 [−34]
3.0	0	0.1624	0.181 [−19]	0.700 [−30]
	10	0.0063	0.252 [−17]	0.137 [−25]
4.0	0	0.1605	0.145 [−16]	0.106 [−23]
	8	0.0112	0.876 [−15]	0.390 [−20]
5.0	0	0.1589	0.135 [−14]	0.181 [−19]
	8	0.0037	0.422 [−13]	0.177 [−16]

As mentioned above, Fleischmann, Pons, and Hawkins[1] have reported an excess amount of heat (by a factor of 10^7 to 10^{10}) compared to the amount of neutrons and tritium from the d-d reactions (1) and (2). Let us examine whether the p-d reaction could explain this observation. We have found (see Table I) that under the conditions of the experiments, the p-d fusion rate (per p-d pair) is comparable to the d-d fusion rate (per d-d pair). The relative rate of the two reactions depends on the relative concentration of p and d in the electrode. In the experiment[1] the concentration of p in the solution was 200 times smaller than the concentration of d. It cannot, however, be excluded that the ratio of concentrations in the electrodes is different. Nevertheless, even assuming that all the γ-ray energy is converted into heat, one still is at least a factor 10^6 short of accounting for the excess heat. Thus, barring some unexpected enhancement of p-d fusion we see no way to explain the heat by this reaction. A similar analysis applies to the d-d fusion reaction (4), for which $A_0=3.1\times10^{-25}$ cm^{3}s^{-1},[8] more than 8 orders of magnitude slower than the d-d fusion reactions (1) and (2). However, our results suggest an experiment with equal amounts of H_2O and D_2O, and looking for 5.4-MeV γ rays from the p-d fusion reaction (3).

As we have seen, the p-d and d-d fusion reactions (3) and (4) involving the production of a γ ray cannot account for the excess heat seen in the experiment of Fleischmann, Pons, and Hawkins.[1]. One might ask whether the crystal environment could open the channels for the radiationless reactions $p+d\rightarrow{}^3$He(5.4 MeV) and $d+d\rightarrow{}^4$He(23.8 MeV) since the crystal could assist in the energy-momentum balancing, in analogy with the Mössbauer effect. To provide some guidance, we refer to the muon-catalyzed radiationless fusion reaction $pd\mu\rightarrow{}^3$He(196 keV)$+\mu$(5.2 MeV). The branching ratio between this channel and ordinary muon-catalyzed p-d fusion, $pd\mu\rightarrow{}^3$Heμ(5 keV)$+\gamma$(5.4 MeV), is 1:7.[17] Thus the presence of a third body, the muon, does open the radiationless channel but the probability of reaction through this channel is still relatively low. The analogous radiationless reaction $dd\mu\rightarrow{}^4$He(725 keV)$+\mu$(23.1 MeV)

has not, to our knowledge, been observed (cf. Ref. 8, p. 332), which suggests that the channels (1) and (2) strongly dominate. In order to explain the excess heat in the experiment of Fleischmann, Pons, and Hawkins in terms of crystal assisted radiationless p-d and/or d-d fusion, one would have to find some way of coupling the nuclei to the lattice even more strongly than they are coupled to the muon in muon-catalyzed fusion. Since the Bohr radius of the muon moving about the fusing hydrogen nuclei is $\frac{1}{400}$ (ordinary) a.u. ≈ 130 fm, this coupling is very strong in the muonic case, and it is difficult for us to conceive of any effect in a crystal which would be even stronger by many orders of magnitude. This is especially so in light of the fact that the deuterons in palladium are highly mobile, and so presumably are not strongly coupled to nearby palladium atoms.

One can also envision a cascade of $d + {}^3\mathrm{He} \rightarrow p + {}^4\mathrm{He}$ reactions, as well as reactions (3) and (5) triggered by the recoiling ^{3}He, t, and p followed by reactions (1) and (2). However, the densities of d, the fusion cross sections, and the stopping ranges are such that these secondary reactions should occur with very low relative probability. Also, in view of the dramatic decrease of the barrier penetration probability with nuclear charge and nuclear mass, it seems highly improbable that nuclei with $Z \geq 2$, or multiple collisions of deuterons, could be involved in production of the excess heat.

In summary, we have obtained accurate solutions to the Schrödinger equation for the motion of nuclei in various isotopes of H_2 for a range of electron masses, and from them calculated how the fusion rates depend on various factors. We have shown that the fusion rates for hydrogen isotopic molecules with $m = 1$ are up to 14 orders of magnitude larger than had previously been estimated,[12] although this is of little practical importance since the fusion rates are so low for $m = 1$. We have found that a "heavy" electron of mass $4 < m < 5$ would be needed to produce the d-d fusion rates reported by Jones *et al.*[2] and by Fleischmann, Pons, and Hawkins[1] on the basis of the neutron measurement. Although effective electron masses in this range occur in the theory of the electronic structure of metals, they arise from long-range correlations, and a plausible mechanism has not yet been suggested to justify using them in the Schrödinger equation to study a short-distance property such as the fusion rate. In fact, our finding that $4 < m < 5$ is required for such rates argues strongly against this to occur at all. The molecular contribution to the fusion rate depends very strongly on the isotopic species of the hydrogen molecule; however, for m between 4 and 5 the p-d and the d-d fusion rates are roughly comparable. We have shown that the WKB-Langer approximation, if applied with an accurate internuclear potential, gives fusion rates in excellent agreement with our accurate solutions of the Schrödinger equation. We have found that fusion out of vibrationally excited states is enhanced by several orders of magnitude, which may be of particular significance in light of the experimental evidence[1] for the importance of nonequilibrium conditions. On the basis of our analysis we have concluded that the excess heat reported by Fleischmann, Pons, and Hawkins cannot be explained in terms of conventional nuclear processes.

After our calculations had been completed we received copies of similar papers by Koonin and Nauenberg[18] and by Shimamura.[19] These authors come to similar conclusions about the fusion rates for various hydrogen isotopes. In 1980, an article was published by Picker,[20] which reported similar p-d and d-d fusion rates for $m = 1$.

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