CHEMICAL CORRECTIONS TO THE MEASURED MUON MAGNETIC MOMENT*

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(Received 10 June 1966)

A plausible description of the behavior of a μ^+ meson in aqueous solutions is given which suggests a reduction of almost 20 parts per million in the measured μ^+ magnetic moment. When combined with muonium hyperfine measurements it supports a value of the fine structure constant which almost halves the disagreement between theory and experiment for the hyperfine structure in hydrogen.

Accurate measurements of the precession frequency of μ^+ mesons in a magnetic field have been performed for mesons stopped in water and aqueous HCl.[1] From the ratio of μ^+ and proton precession frequencies, the ratio of magnetic moments has been inferred to be

$$\mu_\mu/\mu_p = 3.183\,38 \pm 0.000\,04. \qquad (1)$$

When combined with the measured hyperfine splitting in muonium by the Hughes group,[2] it yields an inverse fine-structure constant

$$\alpha^{-1}(\mathrm{H}) = 137.0388 \pm 0.0013, \qquad (2)$$

in much better agreement with the value of Lamb, Triebwasser, and Dayhoff,[3]

$$\alpha^{-1}(\mathrm{L}) = 137.0388 \pm 0.0006, \qquad (3)$$

than that based in part upon a measurement of Robiscoe,[4]

$$\alpha^{-1}(\mathrm{R}) = 137.0370 \pm 0.0006(?). \qquad (4)$$

However, the very accurately measured hyperfine splitting in hydrogen[5,6] gives

$$\alpha^{-1}(\mathrm{HFS}) = 137.0352. \qquad (5)$$

To infer α^{-1} from the measured hyperfine splitting requires knowledge of the proton charge and magnetic-moment distributions, which are known, and its polarizability at all frequencies, which is not known in any detail and has not been included in arriving at the α^{-1} of Eq. (5). Calculations of the contribution of the proton's 3-3 resonance to its polarizability[7] change α^{-1} of Eq. (5) by less than one part per million. Drell and Sullivan[8] have estimated polarizability from other "excited states" of the proton but their total effect does not yet exceed a few ppm.

The magnetic-moment ratio of Eq. (1) is based upon the assumption that the chemical environment of a μ^+ in water is identical to that of a proton, so that the diamagnetic shielding corrections (chemical shift) are the same for both. In water the chemical shift reduces the applied magnetic field on a proton by 26 ppm. Because of its much lighter mass and higher zero-point energy, a μ^+ meson can form a type of bond between water molecules which is considerably stronger than the usual hydrogen bond. Such a μ^+ bonding may be expected to remain unbroken by normal thermal agitation during the microsecond lifetime of the muon so that during the magnetic-moment precession measurement, the μ^+ does not replace a proton in a normal water molecule. The chemical shift of the μ^+ in this state is estimated to be about 15 to 20 ppm less than that of the water proton with which it is compared.

A free proton in water (or aqueous HCl) will attach itself to an H_2O molecule[1] and form hydronium (H_3O^+), where it will generally participate in a hydrogen bond with a neighboring water molecule (Fig. 1). In the Born-Oppenheimer approximate description the proton moves in a fixed potential well similar to the double oscillator potential of Fig. 2. The parameters are consistent with the measured stretching frequency of the OH bond of water and hydronium (10×10^{13} sec^{-1}), the OH separation in H_3O^+ ($1.06 \pm 0.04 \times 10^{-8}$ cm),[9] the O-O distance between such hydrogen-bonded neighbors (2.45 Å), and various experimental facts about activation energies and conductivities of water and heavy water.[9] The potential-well parameters are close to those of Ref. 9 and not critical for the subsequent discussion.

The height V_0 of the potential barrier which separates the two harmonic oscillator wells is about 0.6 eV. The zero-point energy of a proton in such a well, $E_0(p)$, is 0.23 eV. The existence of the second oscillator potential has only a very small effect on the proton zero-point energy because the barrier-penetration probability for a proton almost 0.4 eV below the barrier height is only a few percent.

Any hydrogen-bonded proton on the H_3O^+ of

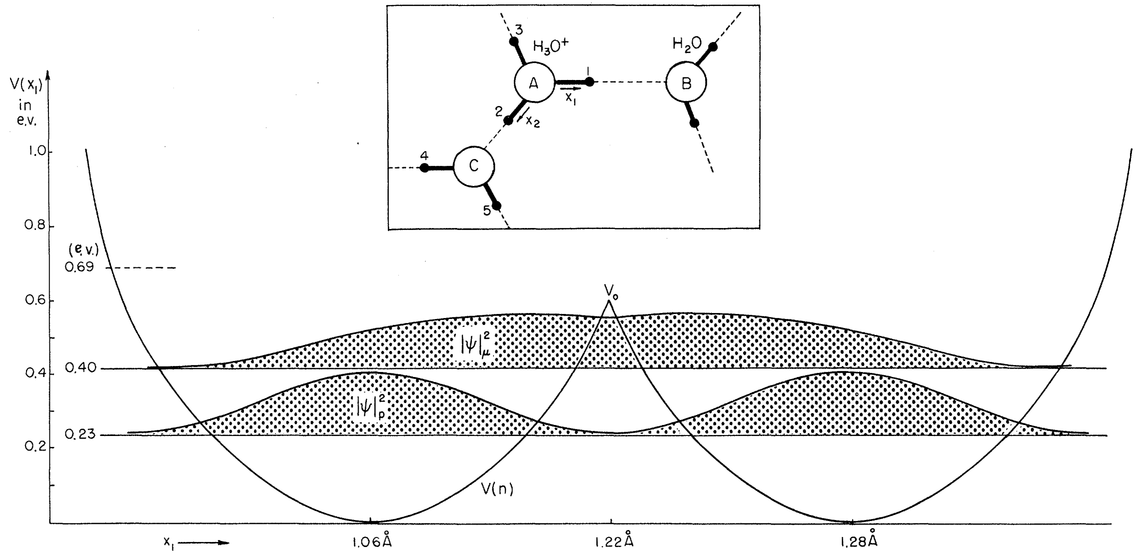

FIG. 1. The potential seen by a proton (or μ^+) attached to a water molecule to form H_3O^+ in water. The lowest energies, $E_0(p)$ and $E_0(\mu)$, of a proton and μ^+ in this potential are shown together with the probability distributions $|\psi|^2$ corresponding to the respective ground states. In the schematic configuration above the black dots are protons, and the open circles are oxygen atoms; the dashed line represents a hydrogen bond.

Fig. 1 can migrate to the equilibrium position near its neighbor in less than 10^{-12} sec. If proton 2 or proton 3 moves away, proton 1 will find itself in the normal potential of a proton in water, hydrogen bonded (i.e., largely electrostatically attracted) to a neighboring water molecule. Its effective potential is similar to that in Fig. 2. Again the secondary potential minimum near its neighbor has an entirely negligible effect on the zero-point proton energy or its wave function.

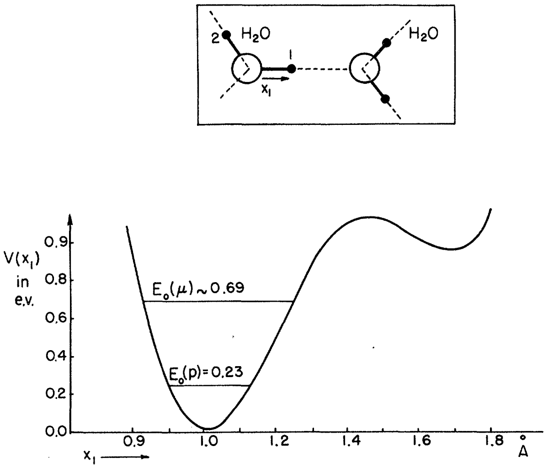

FIG. 2. The potential seen by a proton (or μ^+) in a normal water molecule hydrogen bonded to a neighbor.[10] $E_0(p)$ and $E_0(\mu)$ are the energies of a proton and μ^+ in such a potential.

When a μ^+ meson comes to rest in an aqueous solution, it first forms the analog of hydronium $(H_2O\mu)^+$ with the μ^+ replacing, say, proton 1 in Fig. 1. However, the double oscillator potential greatly changes the value of the μ^+ zero-point energy and wave function relative to what they would be in a single oscillator potential. (Because its mass is one-ninth that of a proton, its zero-point energy in a single oscillator would be 3×0.23 eV = 0.7 eV, greater than the 0.6-eV barrier height.) In the well of Fig. 1 the muon zero-point energy $E_0(\mu)$ is computed to be 0.40 eV. Thus the μ^+ in the configuration of Fig. 1 is bound with only 0.17 eV less energy than the proton. However, if one of the protons of $(H_2O\mu)^+$ were to migrate away and leave behind $H\mu O$, the μ^+ meson then moves in the single oscillator potential of Fig. 2; the muon zero-point energy would rise to almost 0.7 eV, 0.46 eV greater than that of a proton in the same state. Thus the configuration of Fig. 1 with the μ^+ meson shared equally by the two water molecules on each side is stable by $(0.46-0.17) \sim 0.3$ eV against losing proton 2 or proton 3 to one of the neighboring H_2O molecules. (This is twice the energy of a hydrogen bond.)

Because of thermal fluctuations, this lowest energy configuration (H_2O-μ^+-H_2O) will ultimately be destroyed by the migration of one of the water protons leaving behind HμO in which the μ^+ replaces a proton and has a wave function similar to that of a typical proton in water. However, at room temperatures a rough estimate[11] suggests that this may take much longer than the μ^+ lifetime. If the μ^+ remains in the shared (H_2O-μ^+-H_2O) configuration for a few microseconds, its probability distribution during the magnetic-moment measurement is that of Fig. 1. The characteristic separation of the μ^+ from the nearest O^- is about 0.1 Å greater than that of the proton in H_3O^+.

In proton magnetic-moment resonance experiments on various compounds, the diamagnetic chemical shift δ relative to that of a free proton tends to decrease in magnitude as the proton–negative-ion distance R increases. (For example, both $\Delta\delta$ and ΔR are proportional to the change in stretching vibration frequency of hydrogen-bonded protons.[12,13]) The quantitative effect upon δ of stretching R may be estimated for specific models of hydronium. The extreme electronegativity of O suggests a simple picture of H_3O^+:H_2O plus a proton resonating among the three configurations in which a single one of the three equidistant protons, in turn, does not have a full covalent bonding to the core O. Such a model for H_3O^+ implies that each OH bond should be one-third ionic and two-thirds the usual covalent bond.[15] When averaged over orientations in a magnetic field, δ for a proton not enveloped by covalent-bond electrons is expected to be much smaller than that for a proton in a water molecule, and we shall neglect it. Then the expected proton δ in H_3O^+ is about two thirds that in normal water except for the effect of the "ionic" proton on the electrons of its neighbors, which has been estimated[16] to change δ by $+7.4\times10^{-19}\times E^2$ or about 2 ppm when E is the electric field of the "ionic" proton. Instead of the -26 ppm of of water, the estimated δ for H_3O^+ is $-(\frac{2}{3})(26-2) = -16$ ppm, in agreement with the experimental value of Table I. The stretching of a single one of the proton-O separations when that proton is replaced by a μ^+ meson causes a reduction in the fraction of covalent bond between μ^+ and O from $\frac{2}{3}$ and also a change in the electron distribution associated with this bond.

A simple approximation for $\Delta\delta$ when a covalent bond is stretched follows from the "average energy approximation"[17] for the chemical shift of a proton in a molecule with axial symmetry:

$$\delta = \frac{-e^2}{3mc^2}\sum_k \left[\left\langle \frac{1}{r_k}\right\rangle - \left\langle \frac{\vec{r}_k}{r_k{}^3}\right\rangle \cdot \langle \vec{r}_k\rangle\right]. \tag{6}$$

Here $\vec{r}_k$ is the vector distance between the proton and the kth electron, m is the electron mass, and the expectation value is taken with respect to the ground-state electron wave function. When the Coulomb repulsion between electrons is neglected, the dependence of δ upon R for identical atoms can be expressed in terms of derivatives of the interatomic potential $V(R)$:

$$\frac{d}{dR}\delta = +\frac{1}{6mc^2}[RV''(R) + 2V'(R)]. \tag{7}$$

In the absence of a satisfactory quantitative theory, we apply Eq. (7) to the potential of Fig. 1 when a proton is replaced by a μ^+. For $\Delta R \sim 0.1$ Å, $\Delta\delta \sim +2\times10^{-6}$.

The decrease in the covalent character of the μ^+-O bond has been estimated for a model of three fixed positive charges surrounding a positive ion with enough valence electrons to form only two covalent bonds. Electron-electron interactions and electron exchange directly between the protons is ignored. In a Heitler-London approximation for the core-proton bonds, the relative decrease in the covalent-bond probability when one of the "protons" (μ^+ meson) is moved slightly further away from the core than its two companions is $(\frac{4}{3})\Delta U/U$, where U is the exchange energy. For U proportional to that of the hydrogen molecule or $H_2{}^+$,

$$U \sim C(1 + R/a_0)\exp(-Ra_0) \tag{8}$$

with C a constant, a_0 the Bohr radius, and R, in this case, the O-H separation. Then $\Delta U/U \sim -0.9\,\Delta R/a_0$, and the covalent bond probably in H_2O-μ^+ is reduced from $\frac{2}{3}$ by $\frac{2}{3}(0.2)$. When

Table I. The O-H distance R and chemical shift δ for various forms of water.

Molecule	R (Å)	$-\delta$ (ppm)
H_2O (vap.)	0.965	31
H_2O (liq.)	1.00	26
H_3O^+	1.06 ± 0.04	15[a]
H_2O-μ^+-H_2O	1.13 ± 0.04	11,5 (?)

[a] See Ref. 14.

this reduction is combined with the change in δ predicted from Eq. (7), the total reduction in screening compared with that in H_3O^+ is estimated to be $+\frac{2}{3}(0.2)21+\frac{2}{3}(2)$ ppm, which leads to the first entry of the last column of Table I. The second entry is a linear extrapolation based upon the unsupported presumption that the $(\Delta\delta)/(\Delta R)$ measured for the stretching between H_2O vapor and liquid is also appropriate to the stretching from H_3O^+ to $H_2O\mu^+$. (The uncertainty in R for H_3O^+ does not reflect a comparable uncertainty in ΔR between H_3O^+ and $H_2O\mu^+$.) Although there is no definitive model for hydronium,[16] it appears that a δ of, say, −10 ppm is perhaps even more plausible than the usually assumed −26 ppm. Then instead of Eq. (2) we would have

$$\alpha^{-1}(\mathrm{H}) = 137.0377 \pm 0.0013, \tag{2'}$$

in somewhat closer agreement with Eq. (4), which disagrees with the hydrogen hyperfine structure value by 18 instead of 36 ppm.

It is a pleasure to thank Professor S. Drell for his helpful comments.

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*Research supported in part by the National Science Foundation.

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[11] If, in Fig. 1, particle 1 is a μ^+ meson, then proton 2 effectively (i.e., in the Born-Oppenheimer approximation which neglects the muon mass relative to the proton's) moves in a potential qualitatively similar to that of Fig. 2 except that the higher minimum is raised by only about 0.3 eV above the lower one. The transition rate for a proton jumping from the lower potential to the higher, corresponding to proton 2 moving from the neighborhood of A to that of C, is $\exp(-0.3\ \mathrm{eV}/kT)$ times the inverse de-excitation rate R, $10^{-5}R$ at room temperature. The rate R is not known; the transition energy does not fall on any strong ir absorption band of water and the transition is presumably nonresonant. In water vapor at 490°K a measured [P. W. Huber and A. Kantrowitz, J. Chem. Phys. 15, 275 (1947)] vibrational de-excitation rate is 3×10^{-3} per collision[7] and decreases with decreasing temperature. (But this very fast rate may be for the bending mode; the stretching vibration de-excitation rate could be faster.) When the assumed two-body excitation rate is scaled to the density of (liquid) water, $R \sim 10^{11}\ \mathrm{sec}^{-1}$. However, the de-excitation which results in the shift of proton is expected to have a much smaller matrix element than that for usual vibrational transitions since there is such a reduced overlap between the initial and final proton wave functions. This suggests a plausible excitation rate $\ll 10^{-5}\times10^{11} = 10^6\ \mathrm{sec}^{-1}$ insufficient to break up the H_2O-μ^+-H_2O complex during the μ^+ lifetime of 10^{-6} sec. At considerably higher temperatures the H_2O-μ^+-H_2O complex should have a very much shorter lifetime.

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