Chemical shift correction to the Knight shift in beryllium

Wayne M. Itano
Time and Frequency Division, National Bureau of Standards, Boulder, Colorado 80303
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The Knight shift in beryllium has previously been measured to be small and negative, when referred to an aqueous solution of $BeCl_2$. Theoretical calculations assume a reference consisting of a bare nucleus shielded by the core electrons. With the use of a recent measurement of the shielded nuclear magnetic moment in free Be^+ ions and published Hartree-Fock wave functions of Be and Be^+, it is shown that 20(4) ppm should be added to the experimental shifts in order to compare them with theory. This correction is of about the same magnitude as the measured Knight shift.

The Knight shift K is defined to be the fractional increase in the spin precession frequency of a nucleus in a metal relative to its value in a nonmetallic reference environment in the same magnetic field. This definition can be written as

$$\nu_{\text{metal}} = (1+K)\nu_{\text{ref}} \ , \tag{1}$$

where ν_{metal} is the frequency observed in the metal and ν_{ref} is the frequency observed in the reference. For definiteness, a standard reference should be chosen because of the different diamagnetic shielding factors (chemical shifts) in different possible reference compounds. Typically, K is positive and on the order of 10^{-3} to 10^{-2}, while the range of chemical shifts is on the order of 10^{-5} to 10^{-4}, so that a careful definition of the reference is not necessary.

However, K is very small in beryllium, as was first reported by Townes, Herring, and Knight.[1] Later measurements of K were made (which were not mutually consistent), yielding the values $-25(6)$ ppm (Ref. 2) and $-10(3)$ ppm (Ref. 3) referred to an aqueous solution of $BeCl_2$ and $-27(6)$ ppm referred to BeO.[4] These shifts are not small compared to possible chemical shifts.

A large number of theoretical papers have been written to try to explain the anomalous sign and magnitude of K in beryllium.[5–13] The more recent papers take into account contributions to K from the Fermi contact interaction between the nucleus and the conduction electrons[1] (the dominant effect in typical metals), the Fermi contact interaction with the core electrons due to the exchange-core-polarization effect,[7] and the orbital diamagnetic shielding due to the conduction electrons.[14,15] The diamagnetic shielding due to the 1s core electrons is not included, since this is essentially the same as in the reference. Thus the theoretical convention is that

$$\nu_{\text{ref}} = (1-\sigma_{\text{core}})\nu_0 \ , \tag{2}$$

where σ_{core} is the diamagnetic shielding due to the core electrons in the metal and ν_0 is the spin precession frequency of a bare nucleus in the same magnetic field. Since contributions to K on the order of 10 ppm and smaller are considered significant, the theoretical ν_{ref} should be related to the experimental ν_{ref}. Calculation of the chemical shift in a solid or liquid is difficult, but is relatively simple for a free atom or atomic ion. Nuclear magnetic resonance measurements of free Be atoms have been made by a spin-exchange optical pumping technique,[16] but the accuracy of 760 ppm is not good enough to be useful in this context.

Recently, a measurement of the nuclear moment in free Be^+ ions was made,[17] by optical pumping techniques previously applied to Mg^+.[18] Ground-state hyperfine-Zeeman transitions were observed at several magnetic fields and the frequencies were fitted to the Breit-Rabi formula. The magnetic field was calibrated by detecting the cyclotron resonance of electrons at the same position as the ions, so the nuclear moment was obtained in Bohr magnetons. The moment is obtained in nuclear magnetons by multiplying by m_p/m_e, the proton-to-electron mass ratio.[19] The result is

$$\mu(\text{Be}^+) = (1-\sigma_{\text{Be}^+})\mu^0_{\text{Be}} = -1.177\,265(3)\mu_N \ , \tag{3}$$

where σ_{Be^+} is the diamagnetic shielding factor for Be^+ and μ^0_{Be} is the unshielded moment. Published Roothaan-Hartree-Fock wave functions[20] were used to evaluate Lamb's formula[21] for the diamagnetic shielding, with the result

$$\sigma_{\text{Be}^+} = 141.5 \text{ ppm} \ , \tag{4}$$

from which it can be shown that μ^0_{Be} is equal to $-1.177\,432(3)\mu_N$.

The two previous Knight-shift measurements which used aqueous solutions of $BeCl_2$ as references[2,3] agree that the ratio of the Be resonance frequency in this environment to that of the deuteron in D_2O is

$$\nu(\text{Be}_{\text{aq}})/\nu(\text{D}) = 0.915\,387(3) \ . \tag{5}$$

The shielded nuclear moment is obtained in nuclear magnetons by the following formula:

$$\mu(\mathrm{Be_{aq}}) = (1-\sigma_{aq})\mu^0_{\mathrm{Be}} = -\tfrac{3}{2}[\nu(\mathrm{Be_{aq}})/\nu(\mathrm{D})](\mu_{\mathrm{D}}/\mu_{\mathrm{H}})(\mu'_p/\mu_B)(m_p/m_e) = -1.177\,302(3)\mu_N \; . \quad (6)$$

The factor of $\frac{3}{2}$ comes from the ratio of the nuclear spins of beryllium and deuterium, $\mu_{\mathrm{D}}/\mu_{\mathrm{H}}$ is the deuteron-to-proton nuclear moment ratio, measured in a D_2O-H_2O mixture,[22] and μ'_p/μ_B is the ratio of the proton nuclear moment in H_2O to the Bohr magneton.[23] The diamagnetic shielding factor of Be in an aqueous solution of $BeCl_2$, σ_{aq} is found from Eqs. (3), (4), and (6) to be

$$\sigma_{aq} = 111(4)\ \mathrm{ppm} \; . \quad (7)$$

No corrections for bulk diamagnetism have been made because the experimental works do not specify the sample shapes. In any case, such corrections should not be larger than 2 ppm. The measurement of K which was referred to BeO[4] did not report a frequency ratio against a standard reference, such as D_2O.

The $1s$ wave functions in beryllium metal are known to be very close to those in the free Be atom.[24] Roothaan-Hartree-Fock wave functions for the free Be atom[20] were used to calculate σ_{core}, with the result that

$$\sigma_{\mathrm{core}} = 130.7\ \mathrm{ppm} \; . \quad (8)$$

The final result is that

$$\sigma_{aq} - \sigma_{\mathrm{core}} = -20(4)\ \mathrm{ppm} \; , \quad (9)$$

which means that the experimental measurements of K which use an aqueous solution of $BeCl_2$ as a reference must be corrected by adding 20(4) ppm to them if they are to be compared with the theoretical calculations. The corrected values of K are $-5(7)$ ppm (Ref. 2) and $+10(5)$ ppm (Ref. 3). The situation with regard to the comparison of experiment and theory for K is not clear, since there is disagreement among the experiments and among the calculations.

It should be noted that the measurement of Mehring and Raber,[3] which disagrees with that of Barnaal *et al.*,[2] has been questioned because of possible systematic errors related to the rf skin effect (see Ref. 12 and references therein). Measurements of the Be Knight shift in BeNi alloys, which were referred to an aqueous solution of $BeCl_2$, appear to support the measurement of Barnaal *et al.* when extrapolated to zero Ni concentration.[12] More experimental work is required to resolve the experimental discrepancy. The measurement of Anderson *et al.*[4] used BeO as a reference, so it cannot be compared directly to the others without knowing the chemical shift between BeO and aqueous $BeCl_2$.

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