Isotope Effect in the Knight Shift of Potassium

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The Knight shifts of the potassium isotopes $^{39}$K and $^{41}$K were determined with high accuracy: $K^{(39)} = 0.274 35(10)\%$ and $K^{(41)} = 0.274 93(12)\%$. The relative isotope effect $\Delta K/K = -0.210 (20)\%$ is in agreement with the hyperfine structure anomaly $^{39}A^{41}$. Isotope effects in the Knight shift are known for three metals: $^{61}$Li/$^{7}$Li$^{1}$, $^{85}$Rb/$^{87}$Rb$^{2}$, and $^{107}$Ag/$^{109}$Ag$^{3}$. Another suitable isotopic pair is $^{39}$K/$^{41}$K. To our knowledge no Knight shift has been measured for $^{3}$Rb/$^{107}$Rb, and $^{87}$Rb/$^{109}$Rb three metals: $^{85}$Ag/$^{87}$Li$^{2}$/$^{109}$K. The reason for this may be the very weak NMR signal of $^{39}$K and $^{41}$K in metallic potassium. The ratio of the Larmor frequencies of $^{39}$K was measured in the metallic sample and the reference sample (31 molal solution of KNO$_3$ in D$_2$O) was $\nu(\nu^{(39)}K_{\text{met}})/\nu(\nu^{(39)}K_{\text{ref}}) = 1.0026413 (4)$. The error given here is three times the r.m.s. error resulting from 22 measurements at different days. The shift between the reference sample and $K^{+}$-ions at infinite dilution is $\delta = -3.0 (2)\,$ppm.$^{5}$

The Knight shift $K^{(39)}_{\text{ion}}$ (referred to the $K^{+}$-ion in aqueous solution at infinite dilution) is therefore $K^{(39)} = 0.26383 (6)\%$. 

With the shielding constant $\sigma = -0.01052 (8)\%$ from,$^{5}$ which describes the shielding of the $K^{+}$-ion by the surrounding water molecules, the Knight shift referred to the free atom is $K_{at}^{(39)} = K_{ion}^{(39)} - \sigma^{*}$: $K^{(39)} = 0.27435 (10)\%$.

The Knight shift of $^{41}$K was not directly determined as the NMR signal of this nucleus is weaker by a factor 82 than that of $^{39}$K. The ratio of the Larmor frequencies of $^{39}$K and $^{41}$K was measured in the metallic sample with high accuracy: $R_{\text{met}}^{(39)} = \nu(\nu^{(39)}K_{\text{met}})/\nu(\nu^{(41)}K_{\text{met}}) = 1.8218626 (5)$.

The error is three times the r.m.s. error of 22 measurements.

Together with the ratio of the Larmor frequencies determined in different aqueous solutions of potassium salts$^{5}$: $R_{sol}^{(39)} = \nu(\nu^{(39)}K_{sol})/\nu(\nu^{(41)}K_{sol}) = 1.8218731 (9)$ the difference of the Knight shifts of $^{39}$K and $^{41}$K may be evaluated:

$$\Delta K = K_{at}^{(39)} - K_{at}^{(41)} = K_{ion}^{(39)} - K_{ion}^{(41)} = (1 - R_{sol}/R_{\text{met}}) (1 + K_{ion}^{(41)}) = -5.8 (6)\,$ppm .

Now the Knight shifts of $^{41}$K are $K^{(41)} = 0.26441 (9)\%$ and $K^{(41)} = 0.27493 (12)\%$. Provided that the factor $(|\psi_F(0)\rangle^2)_{\Lambda V}/|\psi_\Lambda(0)\rangle^2$ in the well known Knight shift formula$^{6}$ is independent of the nuclear properties of different isotopes of the metal, for $s$ electrons any fractional difference in Knight shift for the two isotopes should be equal to their hyperfine structure anomaly (see e.g.$^{5}$): $(K^{(41)} - K^{(2)})/K^{(2)} = 1\Delta^2$. The influence of the inhomogeneity of the field $B_0$ on the shapes and widths of the measured NMR lines is relatively small. The half-widths of the measured absorption curves of metallic potassium were corrected for this effect in a manner described in$^{8}$; the corrected half-widths are $\Delta v_{\text{c}}(39)K = (45 \pm 5)\,$Hz, $\Delta v_{\text{c}}(41)K = (46 \pm 6)\,$Hz.

To our knowledge these are the narrowest NMR lines observed in metallic samples. An anisotropy...
For the potassium isotopes there is the fractional difference
\[ \frac{\Delta K}{K_{41}} = -0.210(20)\% \]
and the hyperfine structure anomaly
\[ ^{39}A_{41} = -0.22934(5)\% \]
from Ref. 5. Within the limits of error there is agreement of these values.

Blumberg et al. 2 have pointed out the agreement of the fractional difference of the Knight shifts and the Hfs-anomaly for the alcali isotopes \(^{85}\text{Rb}\) and \(^{87}\text{Rb}\), whereas there is a striking discrepancy of those quantities for the noble metal isotopic pair \(^{107}\text{Ag}\) and \(^{109}\text{Ag}\). 3.

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4 A. Schwenk, Z. Phys. 213, 482 [1968].