# 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 $^{39}\Delta^{41}$.

Isotope effects in the Knight shift are known for three metals: $^6Li/^7Li$ [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 $^{41}K$. The reason for this may be the very weak NMR signal of $^{41}K$.

With a Fourier pulse spectrometer, described in [4], the NMR signals of $^{39}K$ and $^{41}K$ in metallic potassium were determined in our constant magnetic field $B_0 = 1.807$ Tesla. The potassium was manufactured by Merck AG, Darmstadt (No. 804815). The sample was a small-particle dispersion of potassium metal in paraffin. The size of the K-particles was about 10 μm. The sample was contained in a glass sphere of 18 mm internal diameter. The reference sample, which was the same as used in Ref. [5], had the same size and shape and was measured in the same probe assembly. The measurements of the frequency ratio $\nu(^{39}K)/\nu(^{41}K)$ were done with a cylinder of 20 mm internal diameter and 40 mm length. All measurements were performed at a temperature of $(300 \pm 1)$ K. 90°-pulses were applied with a repetition rate of 12.5 Hz; the free induction NMR signal following such a pulse decayed completely before the next rf-pulse. Moreover the equilibrium magnetization was built up completely within this time interval. A signal/noise-ratio of better than 100 was achieved by applying $2^8$ pulses and $2^{12}$ pulses in the case of $^{39}K$ and $^{41}K$ respectively.

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 [5]; the corrected half-widths are

$$\Delta\nu_{1/2}(^{39}K) = (45 \pm 5)\,\text{Hz},$$
$$\Delta\nu_{1/2}(^{41}K) = (46 \pm 6)\,\text{Hz}.$$

To our knowledge these are the narrowest NMR lines observed in metallic samples. An anisotropy of the line shape was not to be detected; however it must be mentioned that the line shapes were affected slightly by the inhomogeneity of $B_0$.

The ratio of the Larmor frequencies of $^{39}K$ in the metallic sample and the reference sample (31 molal solution of $KNO_2$ in $D_2O$) was

$$\nu(^{39}K_{met})/\nu(^{39}K_{ref}) = 1.0026413(4).$$

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 $K^{(39)}_{ion}$ (referred to the $K^+$-ion in aqueous solution at infinite dilution) is therefore

$$K^{(39)}_{ion} = 0.26383(6)\%.$$

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 $K_{at} = K_{ion} - \sigma^*$:

$$K^{(39)}_{at} = 0.27435(10)\%.$$

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:

$$R_{met} = \nu(^{39}K_{met})/\nu(^{41}K_{met}) = 1.8218626(5).$$

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]:

$$R_{sol} = \nu(^{39}K_{sol})/\nu(^{41}K_{sol}) = 1.8218731(9)$$

the difference of the Knight shifts of $^{39}K$ and $^{41}K$ may be evaluated:

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

Now the Knight shifts of $^{41}K$ are

$$K^{(41)}_{ion} = 0.26441(9)\% \quad \text{and} \quad K^{(41)}_{at} = 0.27493(12)\%.$$

Provided that the factor $\langle|\psi_F(0)|^2\rangle_{Av}/|\psi_a(0)|^2$ 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. [3]): $(K^{(1)} - K^{(2)})/K^{(2)} = {}^1\Delta^2$.

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For the potassium isotopes there is the fractional difference

$$\Delta K / K_{\mathrm{at}}^{(41)} = -0.210(20)\,\%$$

and the hyperfine structure anomaly

$$^{39}\Delta^{41} = -0.22934(5)\,\% \qquad \text{from Ref. } ^5.$$

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 $^{85}$Rb and $^{87}$Rb, whereas there is a striking discrepancy of those quantities for the noble metal isotopic pair $^{107}$Ag and $^{109}$Ag [3].

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