Isotope Effect in the Knight Shift of Potassium

W. Sahm and A. Schwenk

Physikalisches Institut der Universität Tübingen, West Germany

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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: ^{6}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 ^{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 $\nu(^{39}\mathrm{K})/\nu(^{41}\mathrm{K})$ were done with a cylinder of 20 mm internal diameter and 40 mm length. All measurements were performed at a temperature of (300 ± 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

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

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

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

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

$$K_{\mathrm{ion}}^{(39)} = 0.26383\,(6)\,\%.$$

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

$$K_{\mathrm{at}}^{(39)} = 0.27435\,(10)\,\%.$$

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:

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

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]:

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

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

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

Now the Knight shifts of ^{41}K are

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

Provided that the factor $\langle|\psi_{\mathrm{F}}(0)|^2\rangle_{\mathrm{Av}}/|\psi_{\mathrm{a}}(0)|^2$ 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]): $(K^{(1)} - K^{(2)})/K^{(2)} = {}^{1}\Delta^{2}$.

Reprint requests to Dr. A. Schwenk, Physikalisches Institut der Universität Tübingen, *D-7400 Tübingen*, Auf der Morgenstelle.

For the potassium isotopes there is the fractional difference

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

and the hyperfine structure anomaly

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

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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