Fourier Transform NMR Studies of ^{95}Mo and ^{97}Mo

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^{95}Mo and ^{97}Mo Fourier transform NMR studies of several alkali molybdate solutions in H_2O and D_2O are reported. The Larmor frequency of the molybdenum nuclides is remarkably dependent on the solute and the solvent.

In potassium molybdate the chemical shifts of ^{39}K were observed. The ratio of the Larmor frequencies of ^{95}Mo and ^{39}K was measured with high accuracy in a 2.6 molal solution of K_2MoO_4 in H_2O. From this value a nuclear magnetic moment of ^{95}Mo and ^{97}Mo in the molybdate ion was derived using the concentration dependencies of the Larmor frequencies of ^{39}K and ^{95}Mo and the ratio of the Larmor frequencies of ^{97}Mo and ^{95}Mo.

In solid Ag_2MoO_4 and metallic molybdenum the ^{95}Mo and ^{97}Mo NMR signals were detected; line widths and shifts are given.

I. Introduction

Systematic NMR investigations of chemical shifts for the elements chromium [1] and tungsten [2] are already known. Shifts of several thousand ppm have been found for these two elements. In this paper systematic investigations of molybdenum, the remaining element of the VIb group, are reported.

The element molybdenum has 7 stable isotopes, but only the isotopes ^{95}Mo and ^{97}Mo have a non-zero spin of $I=5/2$. The natural abundance of ^{95}Mo is 15.8% and that of ^{97}Mo is 9.6%. In a 1 molal solution of K_2MoO_4 in H_2O the relative sensitivity is about $4.6 \cdot 10^{-6}$ and $3.0 \cdot 10^{-6}$ compared with the sensitivity of the proton in the same sample and in the same magnetic field. The magnetic moment of ^{97}Mo is known to be about 2% larger than that of ^{95}Mo [3].

Some NMR investigations indicate that the quadrupole moments of the two isotopes are very different [4–6]. Results of nuclear spin relaxation measurements in molybdenum metal yield an estimate of the quadrupole moment of ^{97}Mo of $Q(^{97}\text{Mo}) = 1.1(0.2) \cdot 10^{-24}\ \text{cm}^2$ (see [7]), whereas an analysis of the ground state hyperfine structure yields $Q(^{95}\text{Mo}) = -0.019(12) \cdot 10^{-24}\ \text{cm}^2$ and $Q(^{97}\text{Mo}) = 0.102(39) \cdot 10^{-24}\ \text{cm}^2$ (see [8]). In spite of these disagreements it seems that ^{95}Mo has a relatively small quadrupole moment, and because of this fact measurements of ^{95}Mo in some less symmetrical complexes should be also successful.

In Ref. [9] a value of the ratio of the Larmor frequencies of ^{95}Mo and ^{97}Mo was determined in order to evaluate the hyperfine structure anomaly of molybdenum with the known ratio of the hyperfine structure constants of the two isotopes in the ground state [8, 10]. The dependence of the relaxation rates of both molybdenum isotopes on the pH value is reported and an analysis of the chemical kinetics in aqueous solutions of Na_2MoO_4 is given in [5]. The indirect spin-spin coupling constant $J(^{17}\text{O}\text{-}^{95}\text{Mo})$ has been measured in a Na_2MoO_4 solution (enriched in ^{17}O) by ^{17}O NMR [11].

Further, a measurement of molybdenum signals in sodium molybdate is known [12], and investigations in metallic samples are reported too [7, 13–15].

In this paper chemical shifts and linewidths mainly of ^{95}Mo in diverse alkali molybdate solutions in H_2O and D_2O are reported. Solutions of Na_2MoO_4 or K_2MoO_4 are proposed as reference standards for other molybdenum NMR investigations. Molybdenum resonances have been observed in solid matter, too. Further the ratio of the Larmor frequencies $\nu(^{95}\text{Mo})/\nu(^{39}\text{K})$ has been measured in a solution of K_2MoO_4 in water. With these results a value of the magnetic moment of ^{95}Mo and, the ratio $\nu(^{97}\text{Mo})/\nu(^{95}\text{Mo})$ being known [9], that of ^{97}Mo can be given in the molybdate ion surrounded only by water molecules.

With the measurement of the ^{95}Mo signal in a 5 millimolal K_2MoO_4 solution it has been shown that even in low concentrated solutions of molybdenum, for instance in some less soluble molybdenum complexes, NMR investigations are possible if the lines are not too broad.

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II. Experimental

The NMR measurements were performed with a commercial multinuclei Bruker pulse spectrometer SXP 4 – 100 in a magnetic field of 2.11 T produced by a Bruker high resolution 15″ magnet system. The magnetic field was externally stabilized by the Bruker B-SN 15 NMR stabilizer. The free induction decays[17, 18] of ^{95}Mo, ^{97}Mo and of ^{39}K were accumulated and Fourier transformed by a Bruker BNC 12 computer.

The Larmor frequency of ^{95}Mo was approximately 5.8654 MHz, that one of ^{97}Mo 5.9887 MHz and that of ^{39}K 4.1999 MHz. All these Larmor frequencies can be observed with the described spectrometer merely by retuning.

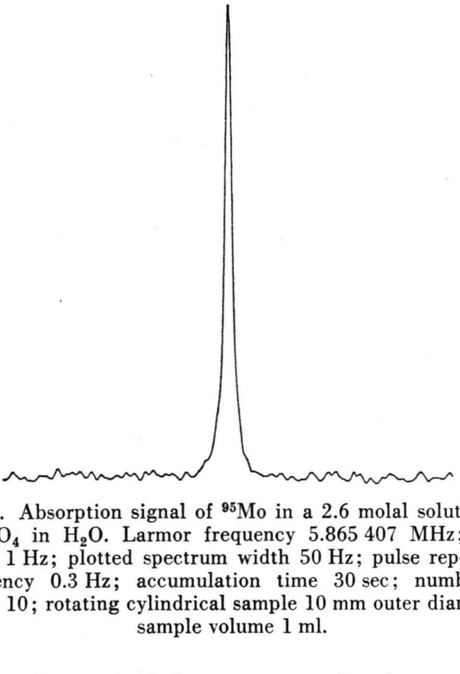

Fig. 1. Absorption signal of ^{95}Mo in a 2.6 molal solution of K_2MoO_4 in H_2O. Larmor frequency 5.865 407 MHz; linewidth 1 Hz; plotted spectrum width 50 Hz; pulse repetition frequency 0.3 Hz; accumulation time 30 sec; number of pulses 10; rotating cylindrical sample 10 mm outer diameter; sample volume 1 ml.

The chemical shifts are given by $\delta = \nu_{\text{sample}} - \nu_{\text{reference}}$. A positive shift means a shift to higher frequency at a constant field. The shifts are measured relative to an external reference by the sample replacement method.

The reference solution was a 2.6 molal solution of K_2MoO_4 in H_2O; the pH value of this solution was adjusted to 10.9 by addition of KOH. In this solution the ratio of the Larmor frequencies $\nu(^{95}\text{Mo})/\nu(^{39}\text{K})$ was measured.

All measurements of liquid samples were performed in rotating cylindrical sample tubes with 10 mm outer diameter. The temperature was (299 ± 2) K.

Unless other values are given, all alkali molybdate solutions had pH values between 10.0 and 13.0. This was achieved by addition of the appropriate base. The pH values were measured with the glass electrode HA 405/M8 of Ingold and a Knick high sensitive voltage meter.

A signal-to-noise ratio of 150 was achieved for ^{95}Mo within 30 sec of measuring time and a signal-to-noise ratio of 120 for ^{39}K within 300 sec; the linewidths were about 1 Hz for ^{95}Mo and 12 Hz for ^{39}K in the reference solution. A typical absorption curve of ^{95}Mo is given in Figure 1.

III. Results and Discussion

a) Chemical Shifts of ^{95}Mo in Solutions of Alkali Molybdates in H_2O

The dependence of the Larmor frequency of ^{95}Mo on the concentration of aqueous solutions of the alkali molybdates Li_2MoO_4, Na_2MoO_4, K_2MoO_4, and of $(NH_4)_2MoO_4$ has been measured. The results are given in Figure 2.

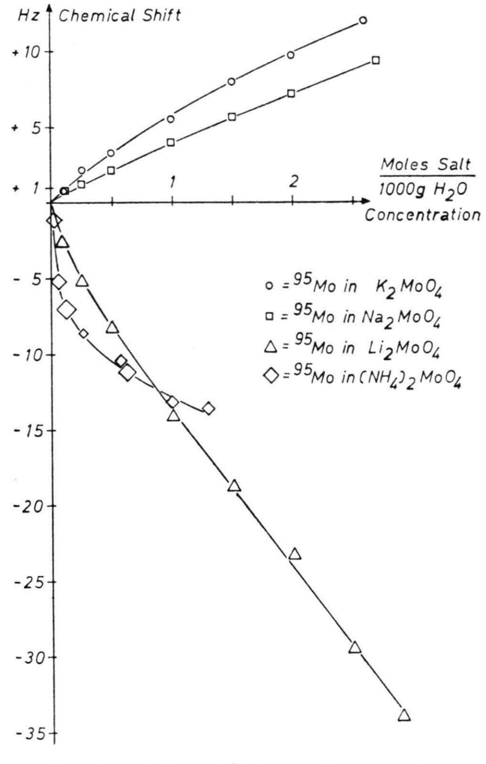

Fig. 2. Chemical shifts of ^{95}Mo in diverse molybdate solutions in H_2O as a function of concentration. Cylindrical samples of 10 mm outer diameter were used. The shifts are referred to the Larmor frequency of ^{95}Mo in the molybdate ion surrounded only by H_2O molecules. The *p*H value of all solutions was between 10.0 and 13.0. No bulk susceptibility corrections were made. The size of the symbols is adjusted to the measuring errors.

For solutions of Li_2MoO_4 and $(NH_4)_2MoO_4$ one gets a shift to lower frequency if the concentration of the solutions is increased, whereas for solutions of Na_2MoO_4 and K_2MoO_4 one gets a shift to higher frequency. Further the amount of the shift is greater for Li_2MoO_4 and $(NH_4)_2MoO_4$ solutions than for the corresponding Na_2MoO_4 or K_2MoO_4 solutions. Because of this fact Na_2MoO_4 or K_2MoO_4 solutions can be used as reference standards for other NMR investigations of molybdenum.

This behaviour of the molybdenum signals in alkali molybdate solutions is quite different from the concentration dependence found for ^{53}Cr in alkali chromate solutions, where the Larmor frequency decreases for all solutions if the concentration is increased[1]. Further the amount of the shift of ^{53}Cr in chromate solutions is increasing in the sequence of the cations: Na^+, K^+, Rb^+, NH_4^+ and Cs^+. In alkali permanganate solutions in water one finds similar results for ^{55}Mn[19] as for ^{53}Cr.

In Fig. 3 the dependence of the chemical shift of ^{95}Mo on the p_H value is given for $(NH_4)_2MoO_4$ solutions in H_2O. For p_H values between 6.4 and 10.4 only small dependencies of the Larmor frequencies of about 2 ppm are observed. For $p_H = 5.4$ one gets a shift of 179 Hz and the line is growing broader, as it is shown in Fig. 3, too.

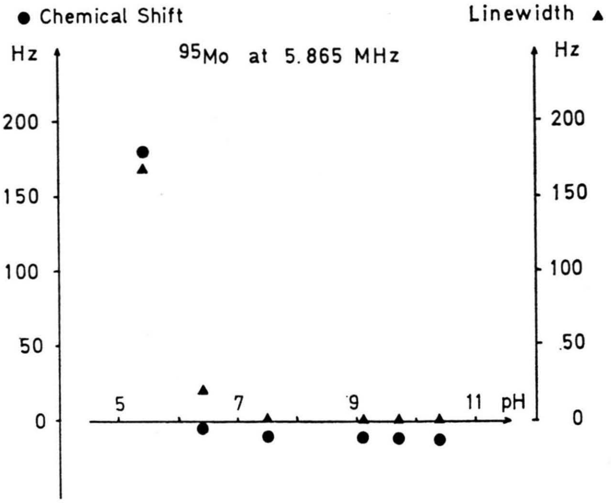

Fig. 3. Chemical shifts (circles) and linewidths (triangles) of ^{95}Mo in 1.3 molal solutions of $(NH_4)_2MoO_4$ in H_2O as a function of the p_H value. The shifts are referenced to the extrapolated frequency of the infinite dilution resonance of ^{95}Mo in the molybdate ion in H_2O.

At $p_H = 4.1$ the signal is hardly observable after 100000 scans. The chemical shift and the broad lines at p_H values less than 7 are due to polymerization of the molybdates, which occurs at a p_H value of about 6 (see [20]).

b) Solvent Isotope Effect

The Larmor frequency of a nucleus depends on its chemical environment; the Larmor frequency therefore also depends on the isotopic composition of the solvent. Measurements in solutions of Li_2MoO_4 and Na_2MoO_4 in H_2O and D_2O are given in Figure 4.

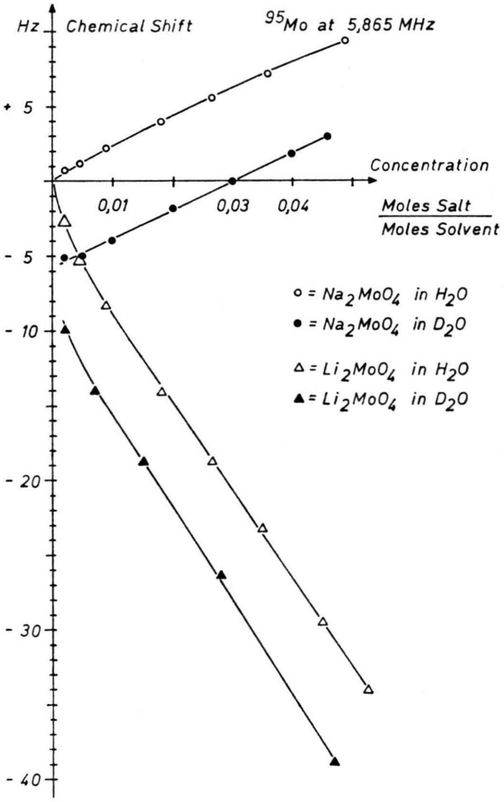

Fig. 4. Solvent isotope effect of the ^{95}Mo resonance in aqueous solutions of Li_2MoO_4 and Na_2MoO_4 as a function of concentration. For the Li_2MoO_4 solutions the p_H value was adjusted to 11.3 ± 0.3 and for the Na_2MoO_4 solutions to 12.8 ± 0.3. No bulk susceptibility corrections were made. The shifts are referenced to the extrapolated frequency of the infinite dilution resonance of ^{95}Mo in the molybdate ion in H_2O.

The Larmor frequency in the solvent D_2O is lower than in the solvent H_2O. This is the effect which is normally observed[21]. The difference of the Larmor frequency depends only a little on the concentrations of the solutions and on the cations. One gets for infinitely diluted solutions:

$$[\nu(^{95}\mathrm{Mo\ in\ D_2O})/\nu(^{95}\mathrm{Mo\ in\ H_2O})] - 1 = -(1.0 \pm 0.2)\ \mathrm{ppm}.$$

The solvent isotope effect of ^{53}Cr in the CrO_4^{2-} ion is $-(1.3 \pm 0.3)$ ppm[1].

One has almost the same value for ^{53}Cr and ^{95}Mo. The solvent isotope effect of ^{55}Mn in the MnO_4^- ion is only a little bit smaller[19].

c) ^{95}*Mo NMR Signal at low Concentration*

In biological systems only concentrations of some millimoles solute/kg solvent are usually achievable. From the signal-to-noise ratio at higher concentrations one can conclude that measurements of millimolal solutions must be possible for ^{95}Mo. We obtained in a 5 millimolal solution of K_2MoO_4 within a measuring time of 6000 sec the absorption signal, which is given in Figure 5. The signal to noise ratio is about 5.

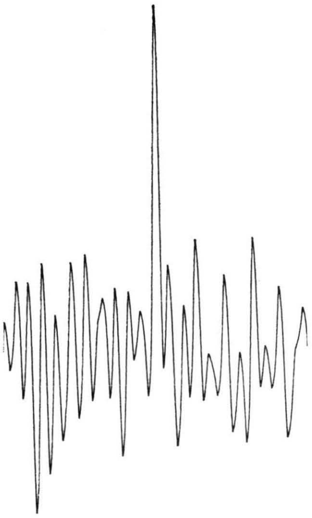

Fig. 5. Absorption signal of ^{95}Mo in a 0.005 molal K_2MoO_4 solution in water. Larmor frequency 5.865 395 MHz; linewidth 2.7 Hz; plotted spectrum width 175 Hz; pulse repetition rate 1.7 Hz; accumulation time 6000 sec; number of pulses 10000; rotating cylindrical sample tube 10 mm outer diameter; sample volume 1 ml. 1 K data points were accumulated. The linewidth results from a trapezoidal multiplication of the free induction decay.

d) *Linewidths*

Because the NMR linewidth of ^{95}Mo in aqueous solutions of alkali molybdates is very small, it is easier to study the linewidths of ^{97}Mo, which are about a factor 130 broader in aqueous solutions[4–6]. The linewidth of ^{97}Mo increases from about 35 Hz for low concentrations to 65 Hz for the 2.6 molal solution of K_2MoO_4 in water. In Fig. 3 not only the dependence of the chemical shift of ^{95}Mo on the p_H value in a 1.3 molal ammonium molybdate solution is given, but also the dependence of the linewidth of ^{95}Mo. In the p_H range from 7.5 to 10.4 no dependence of the linewidth is observable; this linewidth is partly due to the inhomogeneity of the magnetic field. For lower p_H values, however, one obtains linewidths growing synchronously to the chemical shifts.

Vold and Vold[5] have measured the relaxation rates in a solution of Na_2MoO_4 and NaCl. They found strongly growing linewidths, too, but in the p_H range from 7 to 8.

e) *Molybdenum Signals in Solid Samples*

The NMR signals of ^{95}Mo and ^{97}Mo have been measured in silver molybdate powder. The results are given in Table 1. The NMR signals of both molybdenum isotopes have already been measured in Na_2MoO_4 powder by Lynch and Segel[12]. They got much broader lines. It seems that Na_2MoO_4 is not a perfectly cubic crystal.

Nucleus	Sample *	Measuring time	Signal-to-noise ratio	Chemical shift	Line-width
^{95}Mo	Ag_2MoO_4 powder	8 min	15	82 (2) ppm	80 Hz
^{97}Mo	Ag_2MoO_4 powder	2 min	15	83 (2) ppm	100 Hz
^{95}Mo	metallic powder	20 min	30	0.5848 (5) %	500 Hz
^{97}Mo	metallic powder	180 min	10	0.5835 (20) %	700 Hz

Table 1. Results of the NMR investigations of ^{95}Mo and ^{97}Mo in solid samples. The chemical shifts are given relative to the corresponding molybdenum signal in the MoO_4^{2-} ion at infinite dilution in H_2O.

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* We like to thank Dr. J. Kaufmann for the solid state samples.

It is obvious that in solid molybdate the linewidths of the two isotopes are no longer as much different as in molybdate solutions. The different measuring times of the two isotopes are due to the different relaxation times T_1, which have been estimated to be about 1 sec for ^{95}Mo and 40 msec for ^{97}Mo.

The results of measurements in metallic molybdenum at room temperature are given in Table 1.

Because of the limited precision of the value of the Knight shift of ^{97}Mo one cannot decide whether there is an isotopic effect on the Knight shift for the two molybdenum isotopes or not, as it has been found at other isotopes e. g. for silver [22].

Other measurements of the Knight shift of both molybdenum isotopes are known, too [7, 13–15]. Aksenov [13] found 0.582(5)% for ^{95}Mo and 0.586(5)% for ^{97}Mo. As in the measurements which are reported in this paper, Aksenov got a much better signal for the ^{95}Mo than for the ^{97}Mo isotope. Rowland [14] gives the same value of 0.584% without any error limitations for both isotopes; he found linewidths of 220 Hz and 250 Hz for ^{95}Mo and ^{97}Mo. Narath and Alderman [7] have measured relaxation times of both molybdenum isotopes in the temperature range 1 – 4 K and the Knight shift between 4 and 300 K. At 300 K they obtained the same value as Aksenov and at 4 K they got a value of 0.57%. In a later work Narath et al. [15] gave another value of the Knight shift at 4 K of 0.610(5)% for both molybdenum isotopes.

f) Nuclear Magnetic Moment of ^{95}Mo and ^{97}Mo

In a 2.6 molal solution of K_2MoO_4 in H_2O 60 measurements of the ratio of the Larmor frequencies $\nu(^{95}\mathrm{Mo})/\nu(^{39}\mathrm{K})$ were carried out on 4 different days.

The result is:

$$\nu(^{95}\mathrm{Mo})/\nu(^{39}\mathrm{K}) = 1.396\,572\,9(3).$$

The error is two times the standard deviation. With the chemical shift $\delta = \nu$ (^{95}Mo in 2.6 molal K_2MoO_4 in H_2O) $-$ ν (^{95}Mo in infinitely diluted K_2MoO_4 solution in H_2O) = 12(1) Hz, given in Fig. 2, and the corresponding chemical shift ν(^{39}K in 2.6 molal K_2MoO_4 solution in H_2O) $-$ ν (^{39}K in infinitely diluted K_2MoO_4 solution in H_2O) = 1.8(1.0) Hz, which has been determined, too, the above ratio can be extrapolated to an infinitely diluted K_2MoO_4 solution in H_2O:

$$[\nu(^{95}\mathrm{Mo})/\nu(^{39}\mathrm{K})]_{\mathrm{extrapol.}} = 1.396\,570\,6(6).$$

The additional error is due to the extrapolation to zero concentration.

With the ratio

$$[\nu(^{39}\mathrm{K})/\nu(^{2}\mathrm{H})]_{\mathrm{extrapol.}} = 0.303\,984\,85(9),$$

given in [23] and the ratio of Smaller [24] $\nu(^{2}\mathrm{H})/\nu(^{1}\mathrm{H}) = 0.153\,506\,083(60)$ one gets the ratio:

$$[\nu(^{95}\mathrm{Mo})/\nu(^{1}\mathrm{H})]_{\mathrm{extrapol.}} = 0.065\,168\,904(43).$$

With the value of the magnetic moment of the proton in H_2O: $\mu_p = 2.792\,774\,0(11)\ \mu_N$ of [25] and the value of the spin $5/2\,\hbar$ one can derive a magnetic moment of ^{95}Mo in the MoO_4^{2-} ion of:

$$|\mu(^{95}\mathrm{Mo\ in\ MoO_4^{2-}\ in\ H_2O})| = 0.910\,010\,1(7)\ \mu_N.$$

As ^{97}Mo has the same spin as ^{95}Mo, one gets the corresponding value of the magnetic moment of ^{97}Mo by multiplying the above value with the ratio of the Larmor frequencies:

$$\nu(^{97}\mathrm{Mo})/\nu(^{95}\mathrm{Mo}) = 1.020\,986(1),$$

which has been given in [9]:

$$|\mu(^{97}\mathrm{Mo\ in\ MoO_4^{2-}\ in\ H_2O})| = 0.929\,107\,6(10)\ \mu_N.$$

These magnetic moments are not corrected for the diamagnetism due to the electrons.

The only known value of the magnetic moments of ^{95}Mo and ^{97}Mo has been reported by Proctor and Yu [3]. The relative accuracy of these magnetic moments is about $2 \cdot 10^{-4}$. But nevertheless these values do not agree with those given in this work. This is perhaps caused by the fact that Proctor and Yu did not take into account the chemical shift of ^{14}N in the HNO_3 which they used as reference solution.

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