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^{67}Zn NMR Anomalous Solvent Isotope Effect in Aqueous Solutions

B. W. Epperlein, H. Krüger, O. Lutz,
and A. Schwenk

Physikalisches Institut der Universität Tübingen, Germany

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For ^{67}Zn NMR lines of solutions of $ZnCl_2$, $ZnBr_2$, and ZnI_2 in H_2O and D_2O an anomalous solvent isotope effect is reported. In D_2O solutions the lines are shifted to higher frequencies. The difference between the shieldings in H_2O and D_2O is e. g. $\sigma(H_2O) - \sigma(D_2O) = (13.1 \pm 0.7)$ ppm for a concentration of 0.02 moles zinc bromide per mole solvent.

The frequency of the NMR signal (Larmor frequency) of a nucleus in an ion in aqueous solution can depend on the isotopic composition of the solvent. Such a behaviour has been found for alkali[1–4], halide[1,5,6] and several other nuclei[7–11] in aqueous salt solutions. The largest effect was observed for ^{207}Pb in aqueous lead salt solutions[7]. The difference between the shieldings in H_2O and D_2O is $\sigma(H_2O) - \sigma(D_2O) = -(31 \pm 3)$ ppm for a concentration of 0.004 moles lead nitrate per mole solvent. These shielding differences are presumably due to the different vibronic states of the H_2O and D_2O molecules surrounding the ions[5].

For ^{111}Cd an indication for a shift to higher frequency was found in a cadmium chloride solution[11], whereas in perchlorate and nitrate solutions the usual solvent isotope effect was observed.

During a NMR investigation of II b elements, ^{67}Zn NMR signals were observed in aqueous solutions for a determination of the shielding constant[12]. The ^{67}Zn studies were done at 4.841 MHz in a field of 1.807 Tesla with a Fourier Transform Spectrometer basing on a Bruker pulse spectrometer KR 322 s. For experimental details see for example[2].

The dependence of the Larmor frequency of ^{67}Zn on the concentration of aqueous zinc chloride, bromide, and iodide solutions was measured. The observed linewidths are in the range between 20 Hz for low and 170 Hz for high concentrations. For all these salts an anomalous shift to higher frequencies was found for the solutions in D_2O, compared with those in H_2O. Results are given in the Table 1.

In other zinc salts, like perchlorate, nitrate, and sulfate, contrarily to cadmium salts, no solvent isotope effect was observed within an experimental error of ±1 ppm. But there is also no detectable dependence of the Larmor frequency on the concentration of these salts[12].

Table 1. ^{67}Zn chemical shifts in aqueous zinc salt solutions at (300 ± 2) K using cylindrical samples; no bulk susceptibility correction was made, since this correction is smaller than the given errors (standard deviation).

Salt	Concentration $\frac{\text{moles salt}}{\text{moles solvent}}$	^{67}Zn NMR line shift (to higher frequency in Hz *		^{67}Zn shielding $\sigma(H_2O) - \sigma(D_2O)$ in ppm **
		H_2O	D_2O	
$ZnCl_2$	0.02	341	363	4.6
	0.04	518	531	2.7
	0.06	596	605	1.9
$ZnBr_2$	0.02	125	188	13.1
	0.04	314	356	8.7
	0.06	421	446	5.2
ZnI_2	0.02	48	61	2.7
	0.04	109	125	3.3
	0.06	136	148	2.5

* Relative to vanishing concentration of zinc salts in H_2O.
** The error is smaller than ±1 ppm.

The reason for the difference between the normal and anomalous solvent isotope effect must be looked for in the strong halide complexes which are found in zinc and cadmium solutions. For ^{55}Mn in the MnO_4^--ion, the normal isotope effect is reported[10].

The magnetic shielding of zinc ions by water was evaluated in Ref.[12]: $\sigma^* = -(6.9 \pm 0.1) \cdot 10^{-4}$. With this number the given differences of Table 1 must be compared. The relative solvent isotope effect is therefore for the first bromide solution:

$$\frac{\sigma(H_2O) - \sigma(D_2O)}{\sigma^*(H_2O)} = -1.9 \cdot 10^{-2}.$$

For comparison the following values of ^{133}Cs and ^{87}Rb are reported[6]: $0.35 \cdot 10^{-2}$ and $0.14 \cdot 10^{-2}$.

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Reprint requests to Dr. O. Lutz, Physikalisches Institut der Universität Tübingen, *D-7400 Tübingen*, Morgenstelle 14, Germany.

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Cross Sections for the Destruction of an Alignment in the Metastable 6 $^3P_2$-State of Hg by Collisions with H_2, N_2 and CO_2

M. Baumann, E. Jacobson and W. Koch

Physikalisches Institut der Universität Tübingen

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The cross sections for destruction of an alignment in the metastable 6 $^3P_2$-state of mercury atoms by collisions with H_2, N_2 and CO_2 molecules have been determined from the observation of transient signals. The results were (in units of 10^{-16} cm²) H_2: 63(7); N_2: 104(13); CO_2: 663(68).

The cross sections for depolarization of aligned Hg atoms in the metastable 6 $^3P_2$-state by collisions with noble gases have been studied by several authors [1–4]. It seemed to be of some interest to extend these measurements to collisions with other molecules. In this paper we report on an investigation of relaxation processes caused by collisions with H_2, N_2 and CO_2 molecules.

The experimental arrangement was as follows: The Hg atoms (even isotopes) were excited to the metastable 6 $^3P_2$-state in a vhf. discharge (ν = 215 MHz) which was driven by the electric field (about 150 V/cm) between the two plates of a capacitor outside the resonance vessel which contained the mercury vapour and the foreign gas. The direction of the electric field vector was chosen parallel to an external static magnetic field H_0 ($\approx 2.6 \cdot 10^{-4}$ Tesla). With these conditions a longitudinal component of an alignment in the excited state could be produced [5]. It was necessary to work with a continously pumped system instead of the usual sealed-off resonance cell in order to avoid variations of the foreign gas pressure by clean-up effects in the gas discharge [6]. By stimulating rf transitions $\Delta m = \pm 1$ between the Zeeman sublevels of the metastable state by a magnetic rf field H_1 perpendicular to H_0 the alignment will be disturbed. The change of the alignment can be monitored by the absorption of linearly polarized radiation at $\lambda = 5461$ Å corresponding to the transition $6\,^3P_2 \rightarrow 7\,^3S_1$. After switching off the disturbing rf field the alignment will be restored according to an exponential time law, which leads to transient signals in the absorption with a time constant τ_2. τ_2 is the relaxation time for collisional destruction of the alignment in the metastable state [7]. The transient signals have been detected by means of a sampling technique which was described elsewhere [7, 8].

Figure 1 and Fig. 2 show the pressure dependence of the relaxation rate $1/\tau_2$ for H_2, N_2 and CO_2.

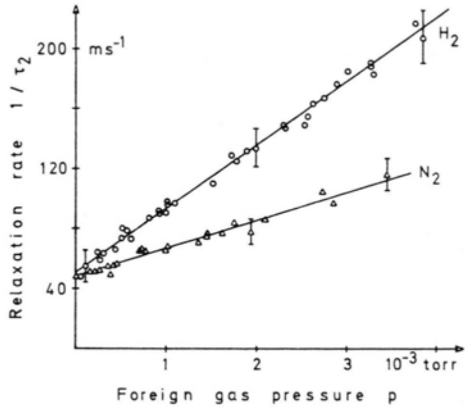

Fig. 1. Pressure dependence of the relaxation rate $1/\tau_2$ for H_2 and N_2.

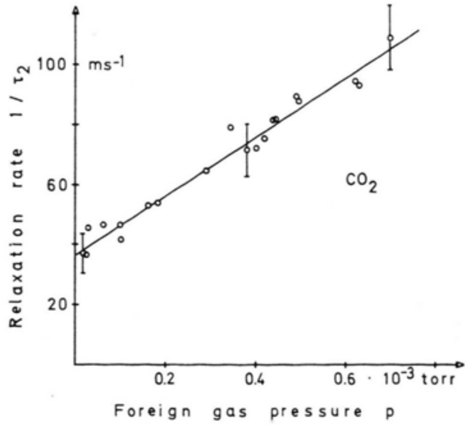

Fig. 2. Pressure dependence of the relaxation rate $1/\tau_2$ for CO_2.

Reprint requests to Prof. Dr. M. Baumann, Physikalisches Institut der Universität Tübingen, *D-7400 Tübingen,* Morgenstelle 14.

Apart from the constant contribution of Hg-Hg collisions (rate $1/\tau_{\mathrm{Hg}}$) the measured relaxation rate for the alignment $1/\tau_2$ is made up of two parts due to collisions with the foreign gas molecules:

$$\frac{1}{\tau_2} = \frac{1}{\tau_{\mathrm{Hg}}} + \frac{1}{\tau_0} + \frac{1}{\vartheta_2} \,. \tag{1}$$

$1/\tau_0$ is the collisional quenching rate; $1/\vartheta_2$ describes the contribution of depolarizing collisions. The corresponding cross sections can be obtained from the following relations [9]:

$$1/\tau_0 = N\,\sigma_{\mathrm{Q}}\,\bar{v}_{\mathrm{rel}} \tag{2}$$

$$1/\vartheta_2 = N\,\sigma_2\,\bar{v}_{\mathrm{rel}} \tag{3}$$

$$\bar{v}_{\mathrm{rel}} = \sqrt{\frac{8}{\pi}\,\frac{k\,T}{m_0}\left(\frac{1}{M_{\mathrm{Hg}}} + \frac{1}{M}\right)}\,;$$

M_{Hg} = molecular weight of Hg,
M = molecular weight of the foreign gas,
N = density of the foreign gas,
m_0 = atomic mass unit,
k = Boltzmann factor,
T = temperature of the gas (303 K).

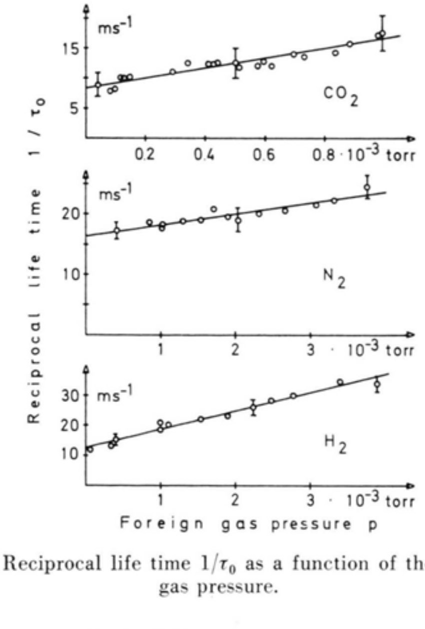

Fig. 3. Reciprocal life time $1/\tau_0$ as a function of the foreign gas pressure.

In order to obtain $1/\vartheta_2$ and the cross section for depolarizing collisions σ_2 which we where interested in, we have measured τ_0 as a function of the foreign gas pressure separately by means of the following method: The driving voltage of the gas discharge was square wave modulated (rise time $< 10\ \mu$sec) with a frequency of 1 kHz and a modulation level of about 10%. Consequently there is a periodical change in the excitation rate of the mercury atoms. The corresponding variation in the stationary number of metastable atoms is governed by the time constant τ_0. From the transient signal in the absorption of the 5461 Å line τ_0 can be determined. Figure 3 shows the reciprocal life time $1/\tau_0$ of the metastable Hg atoms as a function of the foreign gas pressure. The corresponding cross sections σ_{Q} for quenching collisions were calculated from Equation (2). The results are (in units of $10^{-16}\ \mathrm{cm}^2$): $\mathrm{H}_2{:}\sigma_{\mathrm{Q}} = 10.5(5)$; $\mathrm{N}_2{:}\sigma_{\mathrm{Q}} = 11(1)$; $\mathrm{CO}_2{:}\sigma_{\mathrm{Q}} = 63(5)$.

Using the experimental values for $1/\tau_2$ and $1/\tau_0$ the cross sections σ_2 for depolarizing collisions have been calculated from Equation (3). The results are indicated in the first column of Table 1. In the second column the cross sections σ_2 are compared to those for the $6\,^3\mathrm{P}_1$-state of mercury [10]. From similar experiments [1–4, 10] the ratio of the cross sections $\sigma_2(6\,^3\mathrm{P}_2)/\sigma_2(6\,^3\mathrm{P}_1)$ for collisions with noble gases can be determined. One obtains values in the range from about 1.5 to 2.0. While the result for H_2 compares well with the noble gases there are deviations for CO_2 and N_2. Especially the ratio of the cross sections for N_2 is remarkably small.

Table 1. Cross sections σ_2 for depolarizing collisions.

	$\sigma_2(6\,^3\mathrm{P}_2)/10^{-16}\ \mathrm{cm}^2$	$\sigma_2(6\,^3\mathrm{P}_2)/\sigma_2(6\,^3\mathrm{P}_1)$
H_2	63 (7)	1.91 (39)
N_2	104 (13)	0.77 (13)
CO_2	663 (68)	2.67 (44)

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