**Notizen**

**67Zn NMR Anomalous Solvent Isotope Effect in Aqueous Solutions**

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

Physikalisches Institut der Universität Tübingen, Germany

(Z. Naturforsch. 29 a, 660 – 661 [1974]; received February 15, 1974)

For 67Zn NMR lines of solutions of ZnCl₂, ZnBr₂, and ZnI₂ in H₂O and D₂O an anomalous solvent isotope effect is reported. In D₂O solutions the lines are shifted to higher frequencies. The difference between the shieldings in H₂O and D₂O is e.g. \( \sigma(\text{H}_2\text{O}) - \sigma(\text{D}_2\text{O}) \) = (13.1 ± 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 alkali1–4, halide1–5,6 and several other nuclei7–11 in aqueous salt solutions. The largest effect was observed for 207Pb in aqueous lead salt solutions7. The difference between the shieldings in H₂O and D₂O is \( \sigma(\text{H}_2\text{O}) - \sigma(\text{D}_2\text{O}) = -31 \pm 3 \) 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 H₂O and D₂O molecules surrounding the ions5.

For 111Cd an indication for a shift to higher frequency was found in a cadmium chloride solution11, whereas in perchlorate and nitrate solutions the usual solvent isotope effect was observed.

During a NMR investigation of II b elements, 67Zn NMR signals were observed in aqueous solutions for a determination of the shielding constant12. The 67Zn 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 example2.

The dependence of the Larmor frequency of 67Zn 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 D₂O, compared with those in H₂O. 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 salts12.

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 55Mn in the MnO₄⁻-ion, the normal isotope effect is reported9. 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:

\[
\frac{\sigma(\text{H}_2\text{O}) - \sigma(\text{D}_2\text{O})}{\sigma(\text{H}_2\text{O})} = -1.9 \cdot 10^{-2}.
\]

For comparison the following values of 133Cs and 87Rb are reported6: 0.35 \cdot 10^{-2} and 0.14 \cdot 10^{-2}.

**Acknowledgment.** We thank the Deutsche Forschungsgemeinschaft for the financial support.

---

Table 1. 67Zn 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).

<table>
<thead>
<tr>
<th>Salt</th>
<th>Concentration moles salt</th>
<th>67Zn NMR line shift (to higher frequency in Hz *</th>
<th>67Zn shielding ( \sigma(\text{H}_2\text{O}) - \sigma(\text{D}_2\text{O}) ) in ppm **</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCl₂</td>
<td>0.02</td>
<td>341</td>
<td>363</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>318</td>
<td>331</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>596</td>
<td>605</td>
</tr>
<tr>
<td>ZnBr₂</td>
<td>0.02</td>
<td>125</td>
<td>188</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>314</td>
<td>356</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>421</td>
<td>446</td>
</tr>
<tr>
<td>ZnI₂</td>
<td>0.02</td>
<td>48</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>109</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>136</td>
<td>148</td>
</tr>
</tbody>
</table>

* Relative to vanishing concentration of zinc salts in H₂O.

** The error is smaller than ±1 ppm.

---

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
(Z. Naturforsch. 29 a, 661—662 [1974]; received February 2, 1974)

The cross sections for destruction of an alignment in the metastable $6^3P_2$-state of mercury 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 $10^{-16} \text{cm}^2$): $H_2$: 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. 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 ($\nu = 215 \text{ MHz}$) 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. It was necessary to work with a continuously 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. By stimulating rf transitions $Am = \pm 1$ 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 $\lambda = 5461 \text{ Å}$ 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 $\tau_2$. $\tau_2$ is the relaxation time for collisional destruction of the alignment in the metastable state. The transient signals have been detected by means of a sampling technique which was described elsewhere.

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

![Figure 1](image1.png)

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

![Figure 2](image2.png)

Fig. 2. Pressure dependence of the relaxation rate $1/\tau_2$ for $CO_2$. 
Apart from the constant contribution of Hg-Hg collisions (rate $1/\tau_{Hg}$) the measured relaxation rate for the alignment $1/\tau_2$ is made up of two parts due to collisions with the foreign gas molecules:

$$\frac{1}{\tau_2} = \frac{1}{\tau_{Hg}} + \frac{1}{\tau_0} + \frac{1}{\theta_2}.$$  \hspace{1cm} (1)

$1/\tau_0$ is the collisional quenching rate; $1/\theta_2$ describes the contribution of depolarizing collisions. The corresponding cross sections can be obtained from the following relations:

$$\frac{1}{\tau_0} = N \sigma_Q \bar{v}_{rel},$$  \hspace{1cm} (2)

$$\frac{1}{\theta_2} = N \sigma_2 \bar{v}_{rel},$$  \hspace{1cm} (3)

$$\bar{v}_{rel} = \sqrt{\frac{8 \ kT}{\pi \ m_0 \ (M_{Hg} + M)}};$$

$M_{Hg}$ = 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).

In order to obtain $1/\theta_2$ and the cross section for depolarizing collisions $\sigma_2$ which we where interested in, we have measured $\tau_0$ 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 $<10 \mu$s) 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 $\tau_0$. From the transient signal in the absorption of the 5461 Å line $\tau_0$ 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 $\sigma_Q$ for quenching collisions were calculated from Equation (2). The results are (in units of $10^{-16}$ cm$^2$):

$\text{H}_2: \sigma_Q = 10.5 (5)$;

$\text{N}_2: \sigma_Q = 11 (1)$;

$\text{CO}_2: \sigma_Q = 63 (5)$.

Using the experimental values for $1/\tau_0$ and $1/\theta_2$ the cross sections $\sigma_2$ 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 $\sigma_2$ are compared to those for the $6^3P_1$-state of mercury. From similar experiments the ratio of the cross sections $\sigma_2(6^3P_2)/\sigma_2(6^3P_1)$ 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 $\text{H}_2$ compares well with the noble gases there are deviations for $\text{CO}_2$ and $\text{N}_2$. Especially the ratio of the cross sections for $\text{N}_2$ is remarkably small.

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_2(6^3P_2)/10^{-16} \text{ cm}^2$</th>
<th>$\sigma_2(6^3P_2)/\sigma_2(6^3P_1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2$</td>
<td>63 (7)</td>
<td>1.91 (39)</td>
</tr>
<tr>
<td>$\text{N}_2$</td>
<td>104 (13)</td>
<td>0.77 (13)</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>663 (68)</td>
<td>2.67 (44)</td>
</tr>
</tbody>
</table>

We like to thank Professor Dr. H. Krüger for his interest in this work. The financial support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

4. B. Lahaye, Private communication.