

deutlich schwächer als in c. Gleichzeitig treten neue Banden bei 471, 481 und 505 m μ auf, die der Phosphoreszenz des Naphthalins zugeordnet werden müssen. Zum Vergleich ist in e das Phosphoreszenzspektrum von Naphthalin in EPA bei 77 °K wiedergegeben.

Analoge Verhältnisse werden beobachtet, wenn im obigen System Naphthalin durch Phenanthren ersetzt wird. Die Verstärkung der verzögerten Fluoreszenz des Methylcoronens bei 295 °K beim Übergang vom 2- zum 3-Stoffsystem (b und c in Abb. 1) tritt hingegen nicht auf, wenn Chrysen, 2,3-Benzfluoren oder Anthracen an Stelle von Naphthalin treten. — Ersetzt man im System Benzophenon — Phenanthren — Methylcoronen das letztere durch 1,2; 6,7-Dibenzpyren, 1,2; 7,8-Dibenzanthracen oder 1,2; 3,4-Dibenzanthracen, so wird die verzögerte Fluoreszenz der zweiten Gastkomponente (1,2; 6,7-Dibenzpyren etc.) ebenfalls nicht beobachtet. Es ist offensichtlich, daß das Phänomen einer intensiven verzögerten Fluoreszenz bei Raumtemperatur in den von uns untersuchten 3-Stoffsystemen zumindest an zwei Be-

dingungen gebunden ist:

$$\begin{aligned} T_{1W} - T_{1GI} &< \text{ca. } 4000 \text{ cm}^{-1} \\ \text{und} \quad T_{1W} &> S_{1GII}, \end{aligned}$$

wobei T_{1GI} der niedrigste Triplettzustand der 1. Gastkomponente (Naphthalin etc.) und S_{1GII} der niedrigste Singletanregungszustand der 2. Gastkomponente (Methylcoronen etc.) ist. — Die Arbeiten werden im Hinblick auf den Mechanismus dieses Typs von verzögerter Fluoreszenz fortgesetzt.

Experimentelles

Alle verwendeten Substanzen wurden bis zur Konstanz der Lumineszenzspektren gereinigt, Benzophenon durch Zonenschmelzen.

Für die Messungen verwendete man ein Aminco-Keirs-Spektrophosphorimeter.

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Hyperfine Structure Anomalies of ^{115}Sn , ^{117}Sn and ^{119}Sn

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The hyperfine structure anomaly of two isotopes 1 and 2 is defined by $^1\Delta^2 = A_1 g_{12}/A_2 g_{11} - 1$; A_1 , A_2 are the hyperfine interaction constants of the atomic state in question, g_{11} , g_{12} are the nuclear g -factors. The value of Δ is usually given in %.

The hyperfine interaction constants for the 3P_1 and 3P_2 states of the ground state configuration $5p^2$ of the tin isotopes 115, 117 and 119 are known with an uncertainty of $1 \cdot 10^{-5}$ or better ^{1, 1a}. The ratios of the g_I -factors are only known with an accuracy ² of $1 \cdot 10^{-4}$. Further, there is an inconsistency in the ratios $g_I(^{115}\text{Sn})/g_I(^{117}\text{Sn})$ and $g_I(^{117}\text{Sn})/g_I(^{119}\text{Sn})$ in the work of PROCTOR ², which leads to different values for the hyperfine structure anomalies in the paper of CHILDS and GOODMAN ¹ and the recent table of hyperfine structure anomalies, published by COHEN and FULLER ³: The sign of the anomalies seems to reverse, going from $^{115}\Delta^{117}$ to $^{117}\Delta^{119}$. This would be a surprising property.

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Therefore we have measured the ratios of the Larmor-frequencies of ^{115}Sn and ^{117}Sn and of ^{117}Sn and ^{119}Sn with higher accuracy. Because the natural abundance of ^{115}Sn is only 0.33%, the NMR signal is very small. This is the reason for the failure of an accurate measurement of $\nu(^{115}\text{Sn})/\nu(^{117}\text{Sn})$.

The NMR signals of the three tin isotopes have been observed with a Bruker B-KR 322 s pulse spectrometer (for the use of a pulse spectrometer for measuring Larmor frequencies see for example by SCHWENK ⁴) in a magnetic field of 18.07 kOe, which is held constant with the aid of a ^7Li NMR probe ⁵.

Because all these tin isotopes have the nuclear spin $I=1/2$, they have long relaxation times. Therefore a special technique, the so-called quadrature fourier transform spectroscopy of SCHWENK ⁶ was used. The signals were enhanced by a Hewlett-Packard signal analyzer 5480 A and the Fourier transformation was computed on the CDC 3300 of the Rechenzentrum der Universität Tübingen. The Larmor frequencies of each pair, ^{115}Sn , ^{117}Sn and ^{119}Sn , were measured alternately in the same probe only by varying the radio-frequency. Table 1 shows the Larmor frequencies, the line widths, measuring times and the probe, which was used. For the weak NMR signal of ^{115}Sn a signal to noise ratio of 20 was achieved. The line widths of the tin resonance in a sample of 7 mm inner diameter are partly due to the inhomogeneity of the magnetic field and partly due to the special technique which was used ⁶. More



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Table 1. Experimental conditions employed for recording the tin resonances at a field of 18.07 kOe and (28 ± 3) °C.

nucleus	Larmor frequency MHz	line width Hz	measuring time min	probe
^{115}Sn	25.161	100	11.0	aqueous solution of tin-dichlorid *
^{117}Sn	27.401	100	5.2	
^{119}Sn	28.677	100	5.2	

* 14.1 mol-% SnCl_2 , 3.7 mol-% HCl , 82.2 mol-% H_2O .

than 40 measurements of the ratios have been done at different days.

The results are

$$\nu(^{115}\text{Sn})/\nu(^{117}\text{Sn}) = 0.918\,2341(6),$$

$$\nu(^{117}\text{Sn})/\nu(^{119}\text{Sn}) = 0.955\,5287(6).$$

All the measured ratios lie within the given limits of error. From the work of PROCTOR² the following ratios are derivable:

$$\nu(^{117}\text{Sn})/\nu(^{119}\text{Sn}) = 0.95557(10),$$

$$\nu(^{117}\text{Sn})/\nu(^{119}\text{Sn}) = 0.95586(10)$$

and $\nu(^{115}\text{Sn})/\nu(^{117}\text{Sn}) = 0.91794(9).$

Only the first is in agreement within the limits of error. From MCFARLANE⁷, $\nu(^{117}\text{Sn})/\nu(^{119}\text{Sn}) = 0.955\,5285$

can be calculated. This value is in good agreement with ours; McFarlane gives no error.

Using the A -factors of CHILDS and GOODMAN^{1, 1a}, the hyperfine structure anomalies in the $^3\text{P}_1$ and $^3\text{P}_2$ states have been calculated. Table 2 shows the results. The absolute size is about ten times smaller than in the work of CHILDS and GOODMAN¹, who have used the values of PROCTOR². There is no reversal of sign, going from ^{115}Sn to ^{117}Sn to ^{119}Sn .

Table 2. Hyperfine structure anomalies of tin isotopes using the A -factors quoted.

isotopic pair state	Δ in % *	A_1/A_2	Ref.
$^{115}\text{Sn}, ^{117}\text{Sn} \quad ^3\text{P}_1$	0.0034(10)	0.918 2652 (92)	1, 1a
$^{115}\text{Sn}, ^{117}\text{Sn} \quad ^3\text{P}_2$	-0.0003(10)	0.918 2315 (92)	1, 1a
$^{117}\text{Sn}, ^{119}\text{Sn} \quad ^3\text{P}_1$	0.0049(10)	0.955 5753 (96)	1, 1a
$^{117}\text{Sn}, ^{119}\text{Sn} \quad ^3\text{P}_2$	-0.0009(10)	0.955 5205 (96)	1, 1a

* The uncertainties of Δ are obtained by taking the square root of the sum of the squares of the uncertainties quoted for the parameters entering into the calculation.

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