An examination of the values of σ_r and σ_d for XeO_4 shows that they are almost half as much as their respective counterparts in [1] XeF_4. This is indeed interesting if one remembers that the force constants of both molecules bear the inverse relationship [12].

The author wishes to extend his sincere gratitude to Professor SVEN J. CYVIN of the Institute of Theoretical Chemistry of the Technical University of Norway whose timely articles on mean amplitudes of vibration have been a constant source of inspiration to him.

[12] Preliminary results of the 27 tetrahedral molecules studied previously [13] suggests a linear relationship between the percent ionic character with the reciprocal of the mean amplitude quantities σ_r. The complete study shall be submitted to this Journal as soon as available.

[13] W. A. YERANOS and J. D. GRAHAM, Spectrochim. Acta **23 A**, 732 [1966].

A Level-Crossing Investigation of the hfs in the 3 $^2P_{3/2}$-State of Sodium

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The first studies of the hyperfine structure (hfs) in the 3 $^2P_{3/2}$ state of ^{23}Na atoms [1, 2] had yielded an ambiguity, concerning the sign and magnitude of the nuclear electric quadrupole moment of ^{23}Na $(I=3/2)$, which could be removed by some recent double-resonance experiments [3–5]. In view of the difficulties in interpreting double resonance spectra in a case where the hfs level separations are comparable with the level-widths [6], it seemed worth-while to seek for a confirmation of the results in a level-crossing experiment [7, 8] by observing the field-dependence of the polarization of fluorescence radiation in a magnetic field. Such an experiment had been previously undertaken [9] but the authors were not able to deduce the hfs coupling constants from their measurements.

According to BREIT [10] the intensity, $R(\boldsymbol{f},\boldsymbol{g})$, of laterally scattered fluorescence radiation is given by the formula

$$R(\boldsymbol{f},\boldsymbol{g}) = C \sum_{m,m',\mu,\mu'} \frac{f_{m\mu}\, f_{\mu m'}\, g_{m'\mu'}\, g_{\mu' m}}{1 - 2\pi i \tau \nu(m,m')} . \qquad (1)$$

Here $f_{m\mu} = \langle m \mid \boldsymbol{f}\cdot\boldsymbol{r} \mid \mu \rangle$, etc., where $\boldsymbol{f}$ and $\boldsymbol{g}$ are the polarization vectors of the exciting light and the observed fluorescent light, respectively. The eigenvectors of the excited state and of the ground state are $\mid m\rangle$ and $\mid \mu\rangle$, respectively. τ is the radiative lifetime of the excited atoms. $\nu(m,m') = (E_m - E_{m'})/h$ is the difference of term values in the excited state. In (1) it is assumed that the power density of the exciting light is constant over the hfs components of the atomic resonance line and that no multiple scattering takes place. The first assumption is not exactly satisfied for the lamp in the present experiment.

The eigenvectors of the Na atoms were determined by diagonalizing the Hamiltonian for the atoms in a magnetic field with the aid of a computer. $R(\boldsymbol{f},\boldsymbol{g})$ was calculated as a function of the magnetic field for different values of the magnetic hfs splitting constant A

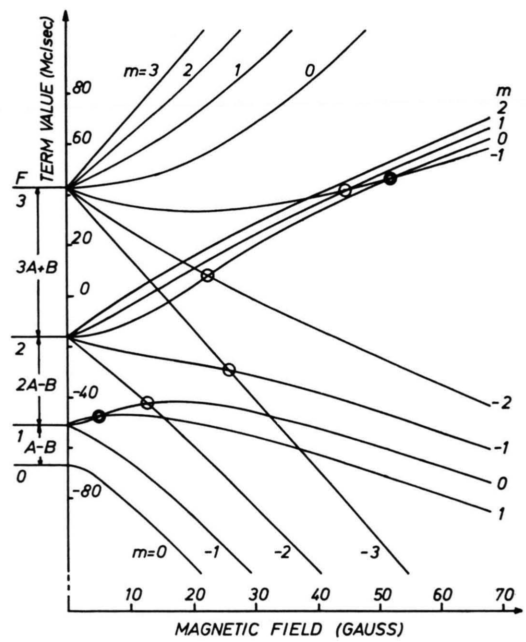

Fig. 1. Splitting of the 3 $^2P_{3/2}$ hfs levels of ^{23}Na in a magnetic field: $A=18{,}8$ Mc/sec; $B=2{,}9$ Mc/sec; $g_J=1{,}3344$ [4]; the $\Delta m=1$ crossings are marked by single and double circles, respectively.

[1] P. L. SAGALYN, Phys. Rev. **94**, 885 [1954].
[2] M. L. PERL, I. I. RABI u. B. SENITZKI, Phys. Rev. **98**, 611 [1955].
[3] J. N. DODD and R. W. N. KINNEAR, Proc. Phys. Soc. London **75**, 51 [1960].
[4] H. ACKERMANN, Z. Phys. **194**, 253 [1966].
[5] M. BAUMANN, W. HARTMANN, H. KRÜGER, and A. OED, Z. Phys. **194**, 270 [1966].
[6] G. W. SERIES, Rep. Progr. Phys. **22**, 280 [1959].
[7] F. D. COLEGROVE, P. A. FRANKEN, R. R. LEWIS, and R. H. SANDS, Phys. Rev. Lett. **3**, 420 [1959].
[8] P. A. FRANKEN, Phys. Rev. **121**, 508 [1961].
[9] G. V. MARKOVA and M. P. CHAIKA, Opt. i Spektroskopiya **17**, 319 [1964] (Engl. transl.: Opt. Spectroscopy USSR) **17**, 170 [1964].
[10] G. BREIT, Rev. Mod. Phys. **5**, 91 [1933].

and the electric quadrupole interaction constant B in order to fit the experimental results. The term-value diagram for the $3\,^2P_{3/2}$ state of ^{23}Na is shown in Fig. 1. Several level-crossings $\Delta m=2$ and $\Delta m=1$ occur in the region where I and J are increasingly decoupled by the magnetic field.

The experimental arrangement for detecting these crossings was as follows: Sodium atoms in a sealed glass cell (vapour pressure $2\cdot10^{-6}$ torr) were irradiated by a microwave excited Na lamp. By absorption of the D_2-line ($\lambda=5890$ Å) the atoms were raised from their $3\,^2S_{1/2}$ ground state to the $3\,^2P_{3/2}$ excited state. The resonance fluorescence could be observed through suitable analyzers and a lucite light pipe by means of a μ-metal shielded multiplier. The magnetic field was generated by Helmholtz coils and calibrated by EPR. The earth's field was compensated.

$\Delta m=2$ crossings

In a coordinate system with the basic vectors $\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$, the exciting light was directed along the $\boldsymbol{j}$ axis with its electric vector parallel to $\boldsymbol{i}$. The magnetic field and the direction of observation were along the $\boldsymbol{k}$ axis. The scattered light was observed through a rotating linear analyzer. Thus the intensity of the coherent part in the scattered radiation was modulated at twice the rotation frequency of the analyzer, because the light coherently scattered in the $\boldsymbol{k}$ direction is linearly polarized perpendicular to the magnetic field. The incoherently scattered light (σ^+ and σ^- radiation) will not be modulated. By lock-in detection it was possible to observe only the coherently scattered radiation. This modulation technique offers the advantage that the influence of the lamp profile on the crossing signals will be considerably reduced. By appropriate phase adjusting of the lock-in detector, the intensity difference $I(\boldsymbol{i})-I(\boldsymbol{j})$ could be measured as a function of the magnetic field, where $I(\boldsymbol{i})$ and $I(\boldsymbol{j})$ denote the intensity seen by the multiplier when the analyzer transmits light with the electric vector parallel to $\boldsymbol{i}$ and $\boldsymbol{j}$, respectively. Under these conditions an isolated crossing signal has a Lorentzian line shape (apart from the field dependence of the matrix elements $f_{m\mu}$ etc.). Fig. 2 shows the experimental results and a calculated signal curve which is fitted at $H=0$ Gauss. The influence of the line profile of the exciting radiation was approximately accounted for by introducing a parameter $r=I_1/I_2$ which gives the intensity ratio of the incident light that can be absorbed by the two ground state hfs terms $F=1$ and $F=2$, respectively. The parameter r exerted only a weak influence on the position of maxima and minima in the signal curve; its chief influence was to alter the height of the maximum at ≈ 12 Gauss.

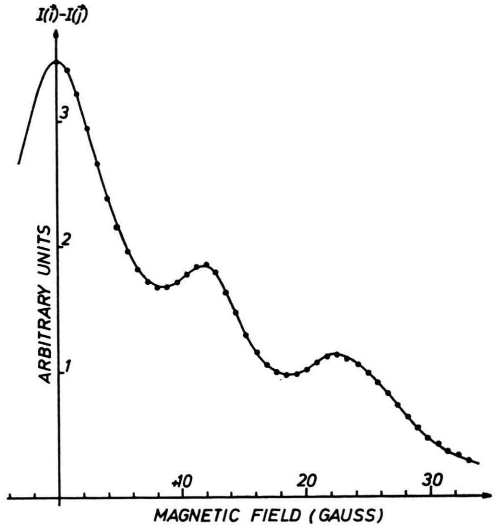

Fig. 2. Theoretical signal curve for level-crossings $\Delta m=2$ with $A=18{,}8$ Mc/sec; $B=2{,}9$ Mc/sec; $g_J=1{,}3344$; $\tau=1{,}59\cdot10^{-8}$ sec [11]; $r=1{,}44$. The dots are mean values of experimental curves; the individual runs differ less than the diameter of the dots.

$\Delta m=1$ crossings

The incident light was directed along the $\boldsymbol{j}$ axis through a rotating polarizer. The fluorescence radiation was observed in the $\boldsymbol{i}$ direction through a fixed analyzer with the electric vector of the transmitted light parallel to $(\boldsymbol{j}+\boldsymbol{k})$. The phase of the lock-in detector was suitably adjusted to observe the signal difference between the two directions $(\boldsymbol{i}+\boldsymbol{k})$ and $(\boldsymbol{i}-\boldsymbol{k})$ of the

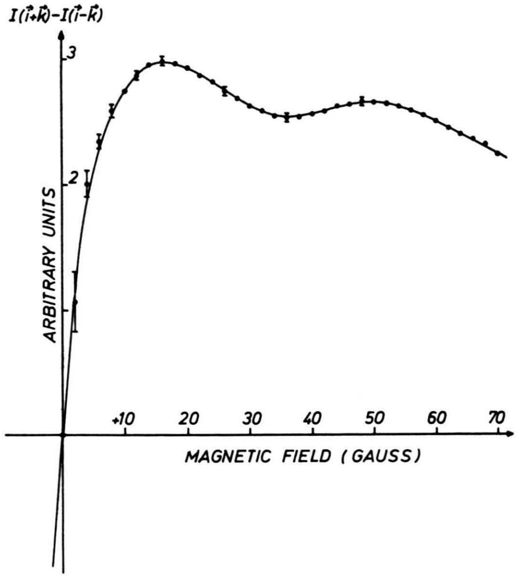

Fig. 3. Theoretical signal curve for level-crossings $\Delta m=1$. Parameters are the same as in Fig. 2, but $r=1{,}28$. The experimental dots (mean values of 5 runs) and the calculated curve are fitted at 24 Gauss. The error bars indicate three times the standard deviation of the mean. There was a slight difference in the excitation of the Na lamp between the $\Delta m=1$ and $\Delta m=2$ measurements, which causes the difference in the lamp parameter r.

[11] E. HULPKE, E. PAUL, and W. PAUL, Z. Phys. **177**, 257 [1964].

polarization in the exciting light. It can be shown that under these conditions the coherently scattered light with $|m-m'|=1$ gives the only contribution to the signal which is neither disturbed by $\Delta m=2$ crossings nor masked by incoherently scattered radiation. An isolated crossing signal $\Delta m=1$ should have the shape of a dispersion curve. Fig. 3 shows the experimental results together with a theoretical signal curve.

hfs coupling constants

The experimental results of the observation of $\Delta m=2$ and $\Delta m=1$ crossings could be fitted by calculated curves with the hfs coupling constants (preliminary values):

$$A=(18.8\pm0.3)\ \text{Mc/sec}; \quad B=(2.9\pm0.4)\ \text{Mc/sec}.$$

These values are in agreement with the results of the double resonance experiments within the error bars. From the ratio B/A the nuclear electric quadrupole moment of ^{23}Na can be derived [12]:

$$Q(^{23}\text{Na})=(0.124\pm0.02)\cdot10^{-24}\ \text{cm}^2$$

(without Sternheimer correction).

I like to thank Prof. Dr. H. Krüger for the continuous support of this work. Thanks are due to Dipl.-Math. W. Sautter of the Rechenzentrum der Universität Tübingen for programming, for the CDC 3200 computer, the calculated crossing signals. The financial support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

[12] H. Kopfermann, Kernmomente, 2. Aufl., Frankfurt a. M., Akademische Verlagsgesellschaft 1956.

ESR-Nachweis eines aliphatischen zinnorganischen Radikals mit Zinn-Hyperfeinstruktur

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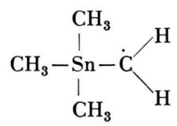
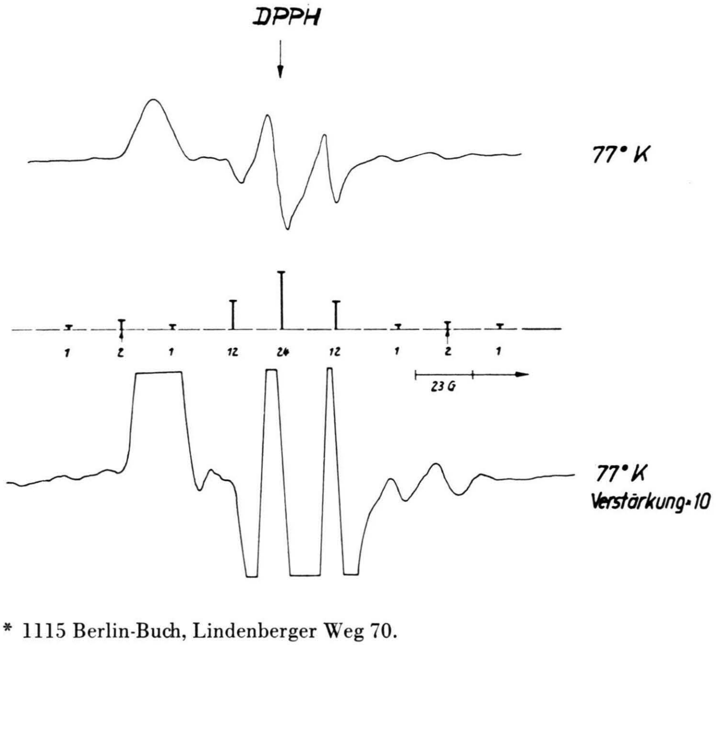
By γ-radiolysis of tetramethyltin at 77 °K a tin-organic free radical with Sn-hyperfine structure is formed with the following parameters g, a_H and a_{Sn}:



$g=2.0067$, $a_H=21$ G, $a_{Sn}=132$ G.

The observed Sn-coupling represents a tin 5s spin population of 2.3%.

Im Rahmen strahlenchemischer Untersuchungen zur Radikalbildung in röntgenbestrahlten zinnorganischen Verbindungen (1) wurde in bestrahltem, erstarrtem Tetramethylzinn bei 77 °K ein ESR-Spektrum gefunden, aus dem auf eine Beteiligung des Zinnatoms an der Hyperfeinstruktur (Hfs)-Wechselwirkung geschlossen wird.



Das in der Abb. 1 gezeigte ESR-Spektrum von bei 77 °K bestrahltem und gemessenem Tetramethylzinn ist stark asymmetrisch und hat eine Gesamtbreite von etwa 170 Gauß. Im Zentrum sind zwei starke Linien mit dem Intensitätsverhältnis 1 : 2 im Abstand von 21 ± 1 Gauß voneinander erkennbar. Die dritte dazugehörige Linie mit der relativen Intensität 1 ist von einer extrem asymmetrischen breiten Linie bei $g=2{,}023$ teilweise verdeckt. Beiderseits des starken Tripletts mit $g=2{,}0067$ sind um etwa eine Größenordnung schwächere Satellitenlinien, ebenfalls als 1 : 2 : 1-Triplett erkennbar, die auf der Seite niedrigeren Feldes von der breiten Linie teilweise überlagert werden und nur angedeutet sind. Die Aufspaltung der Satellitenlinien beträgt 20 ± 1 Gauß und stimmt innerhalb der Fehlergrenze mit der des Haupttripletts überein.

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