

ESR Triplet Exciton Spectrum of Acridine Orange

HARTMUT SCHMIDT

Institut für Physikalische Biochemie und Kolloidchemie der Universität Frankfurt a. M.

(Z. Naturforsch. **26 a**, 763—768 [1971]; received 6 October 1970)

The triplet state of acridine orange dissolved in methanol/water matrix was investigated by ESR. In absence of oxygen a strong temperature dependence of the spectra was observed. At low temperature (100 °K) the zero-field splitting parameters calculated from the triplet spectrum are: $X/hc=0.0050\text{ cm}^{-1}$, $Y/hc=0.0342\text{ cm}^{-1}$, $Z/hc=0.0387\text{ cm}^{-1}$, at higher temperature (140 °K): $X^*/hc=0.0056\text{ cm}^{-1}$, $Y^*/hc=0.0206\text{ cm}^{-1}$, $Z^*/hc=0.0262\text{ cm}^{-1}$. It was assumed that the low temperature spectrum is caused by isolated molecules in the triplet state while the high temperature spectrum must be attributed to the triplet exciton state of the acridine orange dimer. From the theory of the ESR triplet exciton spectra it can be shown that in the dimer state of acridine orange the molecular planes form an angle of 50° or 130°. However, it cannot be excluded that the dimer configuration differs in the ground or excited singlet state from the triplet state.

It is well known since a long time that acridine orange forms dimers and higher aggregates already at room temperature^{1, 2} and even to a higher degree at lower temperature^{3, 4}. The phosphorescence behavior of acridine orange monomers and dimers was investigated by CHAMBERS and KEARNS⁵. They concluded from the change of the phosphorescence emission spectrum accompanying dimerization that "there is a significant change in the intermolecular separation upon excitation of the acridine orange dimer".

The triplet state of the acridine orange dimer represents a first step in the generation of a triplet exciton from the localized excited state of an isolated molecule. Therefore it should be possible to describe it by exciton theory. Theoretical investigations of the ESR spectra which can be expected for triplet excitons were carried out by STERNLICHT and MCCONNEL⁶. Their results were verified by experiments of HAARER and WOLF⁷. SCHWOERER and WOLF⁸ have proven in the case of naphthalene-d₈: naphthalene-h₈ mixed crystals that the theory which had been developed for the explanation of the triplet exciton spectra can also be used — as to be expected — for pairs of molecules. Besides the normal

triplet spectrum the authors found so-called "M-lines" during the excitation of the mixed crystals which were caused by exchange of excitation energy between two neighbouring naphthalene molecules occupying places with two different orientations within the unit cell.

In two preceding papers^{9, 10} the ESR triplet spectrum of acridine orange was investigated. KUBOTA and MIURA¹⁰ found a little change in the D^* -value depending on the concentration of the acridine dye. They suggested that this effect could be explained by the assumption of a delocalization of the triplet electrons over the two halves of the acridine orange dimer. But the change of the D^* -value (between $0.071\text{ cm}^{-1}\cdot hc$ and $0.073\text{ cm}^{-1}\cdot hc$) which was calculated from the half-field signals was very small and is probably within the experimental error.

The purpose of this work is the investigation of the intermolecular interaction and the exchange of excitation energy in the triplet state of the acridine orange dimers using ESR technique. If such an exchange of energy takes place results like those of SCHWOERER and WOLF⁸ are to be expected for the acridine dye as well.

Reprints request to Dr. H. SCHMIDT, Institut für Physikal. Biochemie und Kolloidchemie, D-6000 Frankfurt (Main), Sandhofstraße 1.

¹ V. ZANKER, Z. Phys. Chem. **199**, 225 [1952]; **200**, 250 [1952].

² M. E. LAMM and D. M. NEVILLE, JR., J. Phys. Chem. **69**, 3872 [1965].

³ V. ZANKER, M. HELD, and H. RAMMENSEE, Z. Naturforsch. **14b**, 789 [1959].

⁴ V. ZANKER and J. THIES, Z. Phys. Chem. N.F. **33**, 1 [1962].

⁵ R. W. CHAMBERS and D. R. KEARNS, J. Phys. Chem. **72**, 4718 [1968].

⁶ H. STERNLICHT and H. M. MCCONNEL, J. Chem. Phys. **35**, 1793 [1961].

⁷ D. HAARER, D. SCHMID, and H. C. WOLF, Phys. Stat. Sol. **23**, 633 [1967]. — D. HAARER and H. C. WOLF, Mol. Cryst. **10**, 359 [1970].

⁸ M. SCHWOERER and H. C. WOLF, Mol. Cryst. **3**, 177 [1967].

⁹ H. SCHMIDT, Photochem. Photobiol. **11**, 17 [1970].

¹⁰ Y. KUBOTA and M. MIURA, Bull. Chem. Soc. Japan **42**, 2763 [1969].

Materials and Methods

Most of the experimental conditions have been described in a preceding paper⁹. The signal to noise ratio of the ESR spectra was improved by using a Computer of Average Transient (TMC: CAT 1000), dark signals of impurities were subtracted electronically from the accumulated spectrum by the Resolver/Integrator 522 A (TMC). Zero-field splitting parameters (ZFS parameters) and g -values were measured with the Varian V-4532 dual cavity using vanadylgelate as the standard which was calibrated by the Varian standard "pitch".

The samples were illuminated with a high pressure xenon lamp (Osram: XBO 150 W/1). A Schott-Kantenfilter (GG 395) cut off light below 395 nm. An aqueous solution of CuSO_4 was used to prevent heating of the sample. For measurements with polarized light a Glan-Thompson prism was used. The purification of acridine orange (Serva) was already described previously⁹. The dye was dissolved in methanol (Merck: p. A.)/water (triple distilled) mixture. The oxygen of the sample was removed by the thaw-freezing technique in vacuum (5×10^{-5} Torr). The ESR tubes were sealed off before measurement.

The samples were cooled using the Varian V-4557 cooling system which was used as adjusted by the factory. The theory of the ESR triplet spectra as far as it is used for the evaluation of the spectra has been reported in a previous paper⁹.

Results

Low temperature spectrum: During the photo-excitation of a rigid solution of acridine orange (10^{-3} M) in methanol/water (molar fraction $x_{\text{MetOH}} = 0.8$) at about 100°K a typical ESR triplet spectrum has been obtained (Figure 1 a). The ZFS parameters calculated from this spectrum coincide with those of a previous paper⁹ within the experimental error:

$$\begin{aligned} \pm |X/hc| &= 0.0050 \pm 0.0006 \text{ cm}^{-1}, \\ \pm |Y/hc| &= 0.0342 \pm 0.0006 \text{ cm}^{-1}, \\ \pm |Z/hc| &= 0.0387 \pm 0.0006 \text{ cm}^{-1}, \\ |D^*/hc| &= 0.0635 \pm 0.0011 \text{ cm}^{-1}. \end{aligned}$$

No influence of oxygen on the spectrum was detected. The assignment of the principal values of the spin-spin coupling tensor X , Y , Z to the molecular axes was made using the magnetophotoselection technique the details of which are described in the

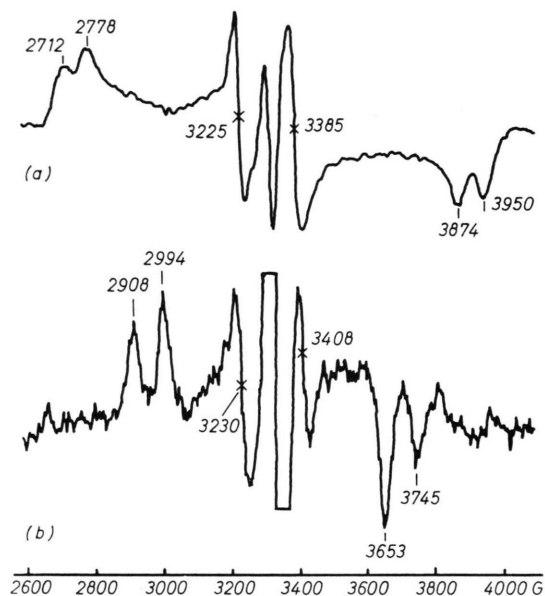


Fig. 1. (a) Low temperature spectrum (100°K) and (b) high temperature spectrum (140°K) of acridine orange (10^{-3} M) in methanol/water ($x_{\text{MetOH}} = 0.8$) in absence of oxygen. Microwave frequency at 100°K : 9.299 GHz, at 140°K : 9.298 GHz. Microwave power: 6 db.

literature¹¹⁻¹³. The transition moment of the longest wavelength absorption band of acridine orange is assumed to be along the long axis of the molecule^{4, 14}. Assuming no depolarization during an excitation with light polarized (E -vector) perpendicular to the external magnetic field H only those peaks of the $\Delta m = 1$ spectrum should be detected which are caused by molecules whose principal axes perpendicular to the molecular plane are parallel to H . The other peaks should appear during an excitation with light polarized parallel to the external field. The experimental results show (Figure 2) that the Z -axis is perpendicular to the molecular plane.

High temperature spectrum: If the temperature is increased the low temperature spectrum disappears gradually. At about 140°K a new triplet spectrum can be detected in absence of oxygen differing clearly from the low temperature spectrum (Figure 1 b). In the presence of oxygen no spectrum could be obtained. The ZFS parameters which

¹¹ P. KOTTIS and R. LEFEBVRE, J. Chem. Phys. **41**, 3660 [1964].

¹² S. P. MCGLYNN, T. AZUMI, and M. KINOSHITA, Mol. Spectroscopy of the Triplet State, Prentice-Hall, Englewood Cliffs, N. J. 1969.

¹³ M. A. EL-SAYED and S. SIEGEL, J. Chem. Phys. **44**, 1416 [1966].

¹⁴ H. ITO and Y. J. PHAYA, Int. J. Quant. Chem. **2**, 5 [1968].

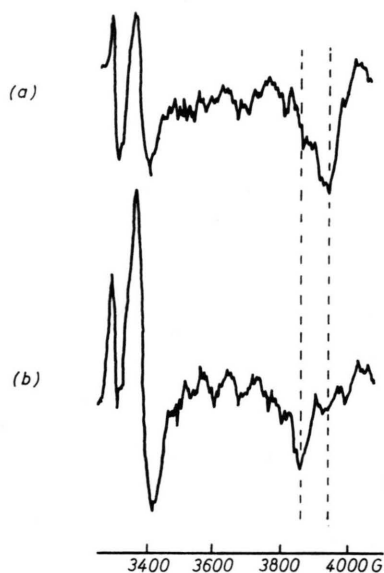


Fig. 2. Effect of illumination with polarized light. (a) E -vector perpendicular to the external magnetic field H ; (b) E parallel to H . Only the high-field part of the spectrum is presented. The signal at the lowest field is the two-quantum signal which is independent of the direction of the polarized light. Temperature: 100 °K.

were calculated from the $\Delta m = 1$ transitions are the following:

$$\begin{aligned} \pm |X^*/hc| &= 0.0056 \pm 0.0006 \text{ cm}^{-1}, \\ \pm |Y^*/hc| &= 0.0206 \pm 0.0006 \text{ cm}^{-1}, \\ \pm |Z^*/hc| &= 0.0262 \pm 0.0006 \text{ cm}^{-1}. \end{aligned}$$

Therefrom the other parameters are calculated:

$$\begin{aligned} |D/hc| &= 0.0393 \pm 0.0009 \text{ cm}^{-1}, \\ |E/hc| &= 0.0075 \pm 0.0006 \text{ cm}^{-1}, \\ |D^*/hc| &= 0.0414 \pm 0.0011 \text{ cm}^{-1}. \end{aligned}$$

The temperature dependence of the half-field signal is presented in Figure 3. The ZFS parameter D^* calculated from the $\Delta m = 2$ spectrum for the low temperature range (100 °K) has the value:

$$|D^*/hc| = 0.062 \text{ cm}^{-1},$$

for the high temperature range (140 °K)

$$|D^*/hc| = 0.041 \text{ cm}^{-1}.$$

These values are in very good agreement with those calculated from the $\Delta m = 1$ spectra.

In addition to the triplet signals of the high temperature spectrum a strong signal in the range of $g = 2$ can be detected. Because the kinetics are

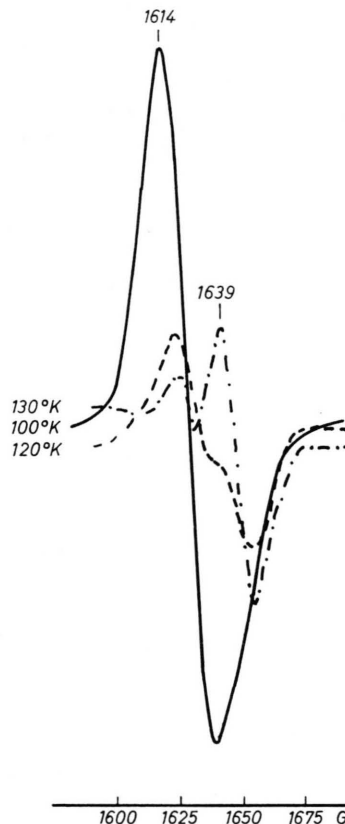


Fig. 3. Temperature dependence of the half-field signal in absence of oxygen. The amplification at 120 °K is half of that at 130 °K. Microwave frequency: 9.299 GHz.

of first order and the rise and decay constants agree approximately with those of the half-field signal in this temperature range, it is reasonable to assume that this signal should be a two-quantum signal¹⁵. No proof for this could be given by measuring the amplitude of the signal in dependence of the microwave power because the signal showed saturation above 20 db. But the analysis of the resonance field shows that this signal cannot be a triplet signal. Its g -value is

$$g = 1.9955,$$

the line width 26 Gauss. The signal was quenched completely by oxygen. No hyperfine structure could be obtained. Therefore this signal cannot be attributed to a solvent radical. (Such a solvent radical signal has been detected in presence of oxygen after irradiation of acridine orange in methanol/

¹⁵ M. S. DE GROOT and J. H. VAN DER WAALS, *Physica* **29**, 1128 [1963].

water at 100 °K with light > 320 nm and the typical hyperfine structure for the $\cdot\text{CH}_2\text{OH}$ radical¹⁶ can be resolved.) The nature of this radical signal cannot be explained without further investigations. Perhaps it could be the primary product of acridine orange.

The transitions between the high and low temperature spectrum can be reproduced repeatedly with the same sample by variation of temperature.

The monomer : dimer ratio of acridine orange is changed at the same concentration of the dye by variation of the methanol : water ratio of the solvent mixture. With a molar fraction of $x_{\text{MeOH}} = 0.1$ much more acridine orange dimers are formed than at a molar fraction of $x_{\text{MeOH}} = 0.8$. While the $\Delta m = 1$ spectrum of the solvent mixture with higher water content could be detected in the high temperature range without difficulties the signal disappeared at 100 °K because of its low intensity.

Discussion

The magnitude of the ZFS parameters indicates that the observed triplet states of the low temperature spectrum as well as the high temperature spectrum are $\pi\pi^*$ transitions¹⁷. The only substance which can be excited to a $\pi\pi^*$ triplet state under the conditions of the experiments is acridine orange. Therefore both the high and low temperature spectra must be attributed to the acridine dye. (After measuring the high temperature ESR spectra no photoproducts could be detected neither by chromatographic methods nor by absorption spectroscopy.) From the value of the ZFS parameter D of the high temperature spectrum it can be deduced that the delocalization of the triplet electrons is considerably larger in the high temperature range than at 100 °K. Therefore it seems reasonable to assign the low temperature spectrum to an isolated acridine orange molecule while the high temperature must be attributed to the dimer species. The last spectrum can be explained by the theory of triplet excitons the simplest case of which are dimers.

The problem concerning the temperature dependence of the spectra cannot be exactly solved so

far. Cooling the methanol the dielectric constant of the alcohol passes through a maximum which is located within the range of existence of the triplet excitation spectrum¹⁸. A high dielectric constant will favour the tendency of aggregation of the dye cation even in the ground state but also in the excited state. (The temperature dependence of the fluorescence quenching curves of some acridine dyes have been explained similarly¹⁹.) There is also quite an amount of acridine orange aggregates at 77 °K³. No explanation can be given for the fact that this kind of aggregates doesn't show triplet spectra as in the case of the high temperature range.

It is also possible, however, that the temperature dependence of the ESR triplet spectra can be explained by the rise of the rate of the triplet excitation transfer with higher temperature which was obtained in the case of tribenzotriptycene by other authors^{20, 21}.

Quantitative considerations: The theory for the description of the high temperature spectrum was developed by SCHWOERER and WOLF⁸: The spin-Hamiltonian for the magnetic interaction of the unpaired electrons of the isolated acridine orange molecule is:

$$\mathcal{H}_s = g\beta \mathbf{S} \cdot \mathbf{H} + X S_x^2 + Y S_y^2 + Z S_z^2.$$

The spin-Hamiltonian of the acridine orange dimer system is the average over the spin-Hamiltonians of the two monomer triplet states:

$$\begin{aligned} \mathcal{H}_s^* &= \frac{1}{2} (\mathcal{H}_{s1} + \mathcal{H}_{s2}) \\ &= \frac{1}{2} [(g\beta \mathbf{S} \cdot \mathbf{H} + X S_x^2 + Y S_y^2 + Z S_z^2)_1 \\ &\quad + (g\beta \mathbf{S} \cdot \mathbf{H} + X S_x^2 + Y^* S_y^2 + Z^* S_z^2)_2]. \end{aligned}$$

The subscripts 1 and 2 indicate that the x, y, z axes coincide with the molecular axes of the acridine orange molecules 1 and 2 respectively. In the principal axes system of the dimer \mathcal{H}_s^* can be written:

$$\mathcal{H}_s^* = g^* \beta \mathbf{S} \cdot \mathbf{H} + X^* S_{x^*}^2 + Y^* S_{y^*}^2 + Z^* S_{z^*}^2.$$

The parameters X, Y, Z can be calculated from the low temperature spectrum, the parameters X^*, Y^*, Z^* from the high temperature spectrum. By this transformation it was possible⁸ to calculate the ZFS parameters of the naphthalene "M-spectrum"

¹⁶ H. J. BIELSKI and J. M. GEBICKI, Atlas of Electron Spin Resonance Spectra, Acad. Press, New York 1967.

¹⁷ H. STERNLICHT, J. Chem. Phys. **38**, 2316 [1963].

¹⁸ H. STAUDE, Phys. Chem. Taschenbuch, Bd. II, Akad. Verlagsgesellschaft, Leipzig 1949.

¹⁹ V. ZANKER and H. RAMMENSEE, Z. Phys. Chem. N.F. **26**, 168 [1960].

²⁰ M. S. DE GROOT and J. H. VAN DER WAALS, Mol. Phys. **6**, 545 [1963].

²¹ P. KOTTIS, J. Chem. Phys. **47**, 509 [1967].

from the triplet spectrum of the isolated molecules and the X-ray data of the single crystal. No X-ray data for acridine orange are known. Therefore the attempt is made to get informations about the structure of the acridine orange dimer (in the triplet state) from the ESR data.

It is a simple matter to show^{6,8} that a change of the ZFS parameters at the transition from an isolated triplet state to the triplet exciton state can only be expected if an exchange of energy takes place between differently oriented molecules. Systems with parallel oriented molecules give essentially the same resonance spectra as the isolated molecules except for the absence of a nuclear hyperfine structure (a sufficiently high exchange frequency is presumed). Naturally in samples of randomly oriented molecules the latter effect is not detectable.

Thus the large differences between the ZFS parameters in the high and low temperature spectrum of acridine orange can only be explained if there is a considerable deviation of the dimer configuration (at the triplet state) from a parallel structure.

The coordinate transformations consist of rotations of the Eulerian angles about the coordinate axes. (For definition of the Eulerian angles see²².) For all calculations an isotropic g -value ($g = g^* = 2.0023$, the g -value of the free electron) is assumed.

From the equations of the principal axis transformation the Eulerian angles have to be calculated. But for our purpose they must not be solved for the general case (rotation about the three axes). The ZFS parameters of the high and low temperature spectrum reveal that the X - and X^* -axis have to be oriented parallel to each other within the experimental error. One has to consider only rotations by φ about the X -axis and $\vartheta = 0^\circ$ or $\vartheta = 180^\circ$ about one of the other axes to get a parallel oriented X^* -axis with respect to the X -axis. A simple calculation gives two values for φ : $\pm\varphi_{1,2} = 25 \pm 2^\circ$ and $\pm\varphi_{1,2} = 65 \pm 2^\circ$. $+\varphi_1$ and $-\varphi_2$ represent the angles between the Y_1 - or the Y_2 -axis and the Y^* -axis. Therefore the angles between the Y_1 and the Y_2 -axis are 50° or 130°

respectively. Obviously these are supplementary angles. As it cannot be concluded from the magneto-photoselection experiments whether the X -axis is oriented along the short or long molecular axis there are some possibilities for the configuration of the acridine orange dimer which are shown in Figure 4. The ESR spectra do not allow any distinction between these possibilities.

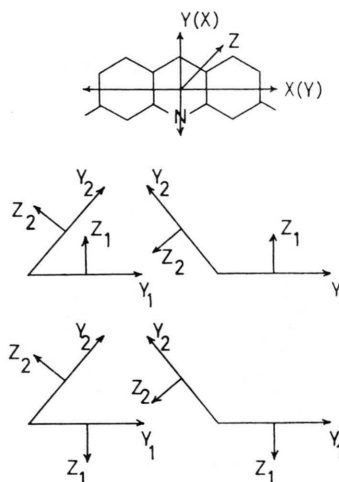


Fig. 4. Possible conformations of the acridine orange dimer based on the ESR spectra.

As a proof of the calculated results the Z^* -value was calculated from the experimental Y - and Z -value and the angle φ (which was determined from the experimental Z -, Y - and Y^* -values):

$$|Z^*/hc| = 0.0251 \pm 0.0038 \text{ cm}^{-1} \text{ (calculated),}$$

$$|Z^*/hc| = 0.0262 \pm 0.0006 \text{ cm}^{-1} \text{ (experimental).}$$

BLEARS and DANYLUK²³ concluded from their NMR measurements that the molecular planes of acridine orange are oriented nearly parallel to each other with the centers of the adjacent rings slightly out of line. A parallel arrangement of acridine orange¹⁴ and analogous dyes²⁴ is also assumed by some other authors. But if the interpretation of the ESR spectra is correct this assumption must be wrong for acridine orange, at least in the triplet state under the experimental conditions of this work (rigid solutions with methanol). However, it cannot be excluded that the dimer configuration

²² C. J. BALLHAUSEN, *Ligand Field Theory*, McGraw-Hill, New York 1962.

²³ D. J. BLEARS and S. S. DANYLUK, *J. Amer. Chem. Soc.* **89**, 21 [1967].

²⁴ TH. FÖRSTER, *Naturwiss.* **33**, 166 [1946].

differs in the triplet state from that of the ground or electronically excited singlet state^{4, 5}.

As it was pointed out previously, the low temperature spectrum could also originate from acridine orange aggregates the molecular planes of which are oriented parallel to each other^{6, 8}.

The calculations are applicable as well for the energy transfer between molecules within a higher

acridine orange aggregate assuming not more than two different orientations of molecules.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft. The author wishes to thank Dr. G. VIERKE for helpful discussions and Professor J. STAUFF for the continuous support of this work.

Schwingungs- und Kernresonanzspektren von Trijodsilan und gemischten Trihalogensilanen

E. HENGGE und F. HÖFLER

Institut für Anorganische Chemie der Technischen Hochschule in Graz

(Z. Naturforsch. **26 a**, 768—772 [1971]; eingegangen am 31. Dezember 1970)

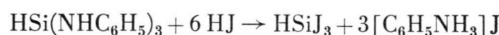
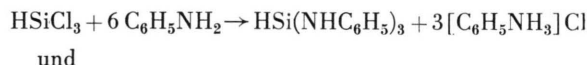
Die aus den Raman-Spektren erhaltenen Grundschnwingungen von HSiJ_3 , HSiClJ_2 (I), HSiCl_2J (II), HSiBr_2J (III) und HSiBr_2J (IV) sowie von SiBr_2J_2 und SiBr_3J werden mitgeteilt. Die Zuordnung erfolgt nach spektralen Übergängen und wird durch Kraftfelder gesichert. Die bisher unbekannt Mischhalogenide I—IV entstehen durch Äquilibrierung von HSiJ_3 und HSiCl_3 bzw. HSiJ_3 und SiBr_4 ; sie werden auch über ihre $^1\text{H-NMR-Parameter } \tau(\text{SiH})$ und $J(^{29}\text{SiH})$ charakterisiert.

1. Einleitung

Während die Molekülspektren der leichteren Trihalogensilane bereits mehrfach und auch in ihrer Feinstruktur untersucht worden sind^{1–3}, existieren bei Trijodsilan nur die Daten aus dem $^1\text{H-NMR-Spektrum}^4$. Für eine vergleichende Diskussion des Substituenteneinflusses auf die SiH- und SiSi-Bindung⁵ benötigten wir die Frequenz der SiH-Valenzschwingung des Trijodsilans. Zugleich interessierten uns Äquilibrierungsreaktionen in den Systemen $\text{HSiJ}_3/\text{HSiCl}_3$ und $\text{HSiJ}_3/\text{SiBr}_4$, wobei sich entstehende Mischhalogenide in idealer Weise im Raman- und $^1\text{H-NMR-Spektrum}$ nachweisen lassen⁶.

2. Trijodsilan

Trijodsilan wurde nach einer modifizierten Vorschrift von RUFF⁷ über die Reaktionsschritte



als farblose, sehr hydrolysenempfindliche Flüssigkeit dargestellt.

Alle 6 Grundschnwingungen dieses C_{3v} -Moleküls sind IR- und Raman-aktiv. Da wir in den Raman-Spektren bessere Aufnahmebedingungen erzielen konnten, erfolgte die Vermessung der langwelligen Banden ausschließlich mit dem Raman-Effekt, $\nu(\text{SiH})$ und $\delta(\text{HSiJ})$ wurden auch im IR-Spektrum registriert. Tabelle 1 enthält die gemessenen Frequenzen einschließlich Zuordnung. Aus Mikrowellenspektren ist die Molekülstruktur von HSiF_3 ⁸, HSiCl_3 ⁹ und HSiBr_3 ¹⁰ bekannt. Nach diesen Untersuchungen an den gasförmigen Substanzen bedingt der wachsende Platzbedarf der Halogenatome eine Aufweitung des XSiX-Winkels von $108,5^\circ$ über $110,6^\circ$ zu $111,4^\circ$,

Sonderdruckanforderungen an Prof. Dr. E. HENGGE, Institut für Anorganische Chemie der Technischen Hochschule Graz, A-8010 Graz, Österreich, Rechbauerstraße 12.

¹ H. BÜRGER u. A. RUOFF, Spectrochim. Acta, im Druck.

² H. BÜRGER u. A. RUOFF, Spectrochim. Acta **26 A**, 1449 [1970].

³ H. BÜRGER u. J. CICHON, Spectrochim. Acta, im Druck.

⁴ H. J. CAMPBELL-FERGUSON, E. A. V. EBSWORTH, A. G. MACDIARMID u. T. YOSHIOKA, J. Phys. Chem. **71**, 723 [1967].

⁵ E. HENGGE, Monatsh. Chem., im Druck.

⁶ E. A. V. EBSWORTH, A. G. LEE u. G. M. SHELDRIK, J. Chem. Soc. (A) **1968**, 2294.

⁷ O. RUFF, Ber. Dt. Chem. Ges. **41**, 3738 [1908].

⁸ J. SHERIDAN u. W. GORDY, J. Chem. Phys. **19**, 965 [1951].

⁹ M. MITZLAFF, R. HOLM u. H. HARTMANN, Z. Naturforsch. **22 a**, 1415 [1967].

¹⁰ M. MITZLAFF, R. HOLM u. H. HARTMANN, Z. Naturforsch. **23 a**, 65 [1968].