

The Infrared Absorption Spectrum of Silane

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used, and Dr. L. T. DeVore of the Department of Physics for densitometer measurements of some of the plates.

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August 18, 1934.

- ¹ Nisi, Jap. J. Phys. **5**, 119 (1929).
² Woodward, Phys. Zeits. **32**, 212 and 788 (1931).
³ Bell and Fredrickson, Phys. Rev. **37**, 1562 (1931).
⁴ Rao, Ind. J. Phys. **8**, 123 (1933).
⁵ Woodward and Horner, Proc. Roy. Soc. **A144**, 129 (1934).
⁶ Average of results obtained by Nisi, Woodward and Rao.
⁷ Kohlrausch, *Der Smekal-Raman Effekt* (1931).

The Infrared Absorption Spectrum of Silane

The infrared spectrum of methane has been very extensively investigated and the normal frequencies are well known. It has been shown that the molecule has the form of a regular tetrahedron. Because of its probable similarity to methane it has seemed of interest to study the absorption in the infrared of silane (SiH_4). With an absorption cell 6 cm long fitted with rocksalt windows the spectrum has been measured to beyond 11.0μ , by using a Wadsworth spectrometer. Four bands enumerated in the order of their intensities have been located at wave-length positions 10.5μ , 4.58μ , 3.187μ and 5.2μ .

The spectrum appears to be entirely similar to that of methane, the three most intense bands definitely showing *P*, *Q* and *R* branches. Two of these regions, at 3.187μ and 4.58μ , have also been examined by means of an echellette grating. The first of these falls just in the water vapor absorption region at 3.16μ , which is quite intense during the summer months because of the high humidity. It has been possible by running transmission curves through the cell with and without gas, and by referring to the work of Plyler and Sleator,¹ quite successfully to separate the two, especially near the center where no intense water vapor lines exist. The *Q* branch is very intense and the lines in the *P* and *R* branches are separated by a spacing of about 5.5 cm^{-1} .

The 4.58μ region resembles the other at 3.187μ a great deal, showing also an extremely intense *Q* branch. The line separation of the *P* and *Q* branches is also about 5.5 cm^{-1} here.

By way of a comparison with the methane spectrum we submit Table I giving the frequency positions of the

TABLE I. A, observed frequencies in SiH_4 in cm^{-1} ; B, intensities; C, corresponding frequencies in CH_4 in cm^{-1} ; D, assignment in Dennison's notation.

A	B	C	D
965	50.	1304	ν_4
1920	0.1	2600	$2\nu_4$
2183.6	20.	3014	ν_3
3155.9	1.0	4217 } 4315 }	$\nu_1 + \nu_4$ } $\nu_3 + \nu_4$ }

observed silane bands, their approximate intensities, and what we deem the corresponding frequencies for methane, using the notation of Dennison.

The band found at 3155.9 cm^{-1} might correspond either with the frequency $\nu_1 + \nu_4$ or with $\nu_3 + \nu_4$, but probably is to be identified with the former. In this case the inactive frequency ν_1 should lie at about 2191. The Raman spectrum of SiH_4 would definitely settle this question since it is to be expected that ν_1 would appear very strongly in that spectrum.

The complete spectrum will be discussed in a later communication when the grating curves have been extended to the other bands and a more exhaustive search for the less intense combination bands which will determine the value of the second inactive frequency ν_2 .

We wish to acknowledge our indebtedness to Professor Warren C. Johnson of the Department of Chemistry at the University of Chicago, who has supplied us with the gas. A grant-in-aid awarded to us by the National Research Council is also acknowledged with appreciation.

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Ohio State University,
August 20, 1934.

¹ E. K. Plyler and W. W. Sleator, Phys. Rev. **37**, 1493 (1931).

Note on Electric Moments and Infrared Spectra. A Correction

In connection with a recent article¹ under the above title, the writer greatly regrets having overlooked an article² by Bartholomé dealing with the above subject as applied to the hydrogen halides. Bartholomé has developed theory, and has made intensity measurements on the $0 \rightarrow 1$ bands of HCl, HBr, HI by a new and apparently improved method; he has made no intensity measurements on other bands, but finds the $0 \rightarrow 2$ band of HI qualitatively very weak. Bartholomé finds the intensity of the $0 \rightarrow 1$ band of HCl to be only about one-fourth as intense as the best previous data (Bourgin) indicated.

Combining Bartholomé's $0 \rightarrow 1$ intensity with Dunham's $0 \rightarrow 2$ intensity (which, however, although supposed to be more accurate than Bourgin's $0 \rightarrow 1$ intensity, was measured by the same method as the latter), one gets instead of Eq. (1) of reference 1 the following:

$$\mu_{\text{HCl}} \times 10^{18} = 1.03 \pm (0.52\xi + [-0.54\xi^2 \text{ or } +1.67\xi^2]).$$

The coefficient of ξ^2 was calculated by means of Dunham's equations.³ Bartholomé's new data also permit writing equations for HBr and HI:

$$\mu_{\text{HBr}} \times 10^{18} = 0.79 \pm 0.51\xi + \dots,$$

$$\mu_{\text{HI}} \times 10^{18} = 0.38 \pm 0.25\xi + \dots.$$

The HI band, although weak, is stronger than previous work of Czerny indicated.

Bartholomé's data appear to be consistent with either of the two types of curves (Figs. 1a, 1b) shown in reference 1. Bartholomé gives a figure similar to Fig. 1b, with reasons for preferring this to the Fig. 1a or other types. Bartholomé shows theoretically that μ should increase as r^3 for r near zero. His argument that the $\mu(r)$ curve should rise, near

$r=0$, most rapidly for HI, least rapidly for HCl, causing the HI curve to have its maximum at smaller r than HBr or HCl, does not, however, seem convincing. As Bartholomé points out, quantitative intensity data on the various $0 \rightarrow 2$ bands, together with good frequency data on HI, might help greatly in determining the true form of the $\mu(r)$ curves.

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University of Chicago,
August 20, 1934.

¹ R. S. Mulliken, J. Chem. Phys. **2**, 400 (1934). In Eq. (1) and the text, the possible values of the coefficient of ξ^2 in Eq. (1) should have been given as 0.035, 2.28 instead of 0.07, 4.56; the change is, however, unessential. In Figs. 1a and 1b, the μ scale should read 1.0 instead of 0.8, and other values in proportion; this, however, has no effect on the forms of the curves or on the discussion.

² E. Bartholomé, Zeits. f. physik. Chemie **B23**, 131 (1933).

³ J. L. Dunham, Phys. Rev. **35**, 1347 (1930), Eq. (19). This paper seems to have been overlooked by Bartholomé.

Solutions Containing Zwitterions: Erratum

(J. Chem. Phys. **2**, 351, 1934).

Eq. (18) on page 355 should read

$$Q_n = \int \int \{ \rho_0(r, \vartheta, \varphi) \rho_0(r', \vartheta', \varphi') r^n r'^n P_n(\cos \gamma) \} dv' dv$$

$$\cos \gamma = \cos \vartheta \cos \vartheta' + \sin \vartheta \sin \vartheta' \cos(\varphi - \varphi').$$

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August 24, 1934.

On a Test for Free Radicals of Short Life

In the chemical investigation of free radicals of short life two major difficulties are encountered, first, their high rate of reaction, excluding all methods in which a gas is pumped out of the reaction vessel and analyzed afterwards, and secondly, closely connected with it, their small concentration. Actually, no characteristic chemical tests are known for free radicals as OH, NH, CH.

In the experiments to be described, the concentration of OH radicals present in the electric discharge through water vapor was observed by the intensity of their absorption spectrum. After interrupting the discharge, their gradual disappearance was traced by snapshots indicating the decay of their absorption spectrum with time.

The absorption spectrum of OH radicals has been observed in *thermally dissociated water vapor* at temperatures up to 1600°C by Bonhoeffer and Reichardt.¹ Various failures, however, to observe the same spectrum in *electric discharges* or *chemical reactions* have been reported in particular by Bonhoeffer and Pearson,² investigating the electric discharge through water vapor, and by Geib and Harteck³ investigating various chemical reactions. It seems probable that the failures have in common the application of medium sized spectrographs. Actually, extremely high resolving power is required to observe a

faint and sharp *absorption* line—contrary to the corresponding problem in *emission*. Hence in the present experiment the absorption spectrum was investigated in the second order of a 21-foot grating. This method is so sensitive that any carbon arc in air, without an absorption tube, shows the absorption spectrum of OH. Therefore the carbon arc has to be operated in dry nitrogen in order to provide the continuous background for the absorption experiment.

The electric discharge through water vapor was operated in series with a mechanical switch, turned by a synchronous motor, letting through one-half period of 60 cycle a.c. and interrupting through the following three halves, or, in other experiments, letting through one full period and interrupting the following 9 periods. A sector disk fixed on the same axis with the switch, rotating immediately in front of the slit of the spectrograph, screened off the inevitable emission spectrum of the discharge through water vapor and let through the continuous light from the carbon arc with the absorption spectrum for a brief snapshot after interrupting the discharge. The time interval between the breaking of the discharge and the snapshot could be varied by adjusting the phase of the sector disk on the axis with respect to the switch. This process of discharge and following snapshot went on periodically until an adequate total time of exposure was secured.

With the 21-foot grating the absorption spectrum of OH in the uninterrupted electric discharge through water vapor can be observed, provided that the continuous background is strong as compared with the emission of the discharge. It can be observed without this restriction after interrupting the discharge. These absorption bands of OH radicals show an intensity far above the minimum intensity observable with the present apparatus.

Their aspect, based on their intensity distribution, is different from the well-known OH emission bands. The strong heads, characteristic in emission, disappear in absorption. The reason is that in absorption the rotation of the OH molecules is low, determined by the temperature, whereas in emission much higher rotational quanta come out with great intensity. This difference has been interpreted in a recent paper.⁴

After interrupting the discharge a marked decay of the intensity of absorption was observed. The rate of reaction is such that after 1/8 sec. some absorption is left. This time limit was given by the present construction of the switch; it does not indicate the limit of the absorption spectrum observable.

The persistence of the absorption spectrum of OH radicals does not necessarily indicate a correspondingly long life of *OH radicals* after the interruption of the discharge. Instead, it might be that the average life of OH radicals is much shorter and that a new supply of OH is permanently reproduced by combination of O and H atoms so that actually the lifetime of *these atoms* is being observed.⁵ It is hoped to decide this alternative by other experiments.

In order to study the kinetics of the OH radicals⁶ a quantitative determination of their concentration will be attempted by photographic photometry.