

The Ultraviolet Absorption of Methane

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Citation: *The Journal of Chemical Physics* **2**, 851 (1934); doi: 10.1063/1.1749407

View online: <http://dx.doi.org/10.1063/1.1749407>

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The crystal structure of cyclohexane is not known. Hassel and Kringstad²⁵ have, however, shown it to be cubic ($a_0=8.41\text{\AA}$, four molecules in the unit cell) and have shown its space group to be probably T_h^2 or O_h^4 . This is of some interest in view of the general belief that the liquid structure is characterized by parallel orientation of the rings, the thickness of the ring being, from the position of the strong band, about 5.1\AA . Since the arrangement cannot be of such a type in the crystal, since it is cubic, it is very probable that there is no great tendency for parallel orientation in the liquid either.

THE SOLUTION OF CYCLOHEXANE AND BENZENE

Ward²⁶ has found that in the x-ray scattering from a solution of cyclohexane and benzene, the two main peaks for the pure components were both present. The simplest explanation, which he presented, is that we have here, not a random distribution of the two kinds of molecules, but

²⁵ O. Hassel and H. Kringstad, *Tidsskrift f. Kjemi og Bergvesen* **10**, 128 (1930); *C. A.* **25**, 1500 (1931).

²⁶ H. K. Ward, *J. Chem. Phys.* **2**, 153 (1934).

an emulsion of one liquid in the other. It may be pointed out that, even if we accept an explanation of this nature, it is unnecessary to assume the existence of aggregates so large that "emulsion" is more applicable than "association." If we should assume the existence in the solution of aggregates of only a few (hardly more than ten) cyclohexane molecules, arranged as in pure cyclohexane, calculations such as have been presented in this paper would undoubtedly be in accord with the experimental observation. The carbon atoms in the interior of the group would be surrounded very nearly as in the pure liquid; the atoms at the surface of the group would be less nearly so surrounded; it appears not at all unreasonable to suppose that the average ρ -function for the carbon atoms of such a small aggregate would sufficiently resemble the ρ -function for pure cyclohexane to account for the appearance of an intensity maximum in approximately the same position as the strong band of the pure liquid.

The author acknowledges with pleasure his debt of gratitude to Dr. Emil Ott for suggesting this work and for his aid during its progress.

The Ultraviolet Absorption of Methane

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(Received October 1, 1934)

The absorption spectrum of methane from 1450\AA to 850\AA is found to be entirely continuous and all excited states up to the first ionization potential are repulsive.

THE absorption spectrum of methane in the Schumann region was photographed first by Leifson¹ using a small vacuum grating spectrograph and an uncondensed discharge in hydrogen as a continuous source. He found six bands at low pressures all below 1558\AA . Rose,² using the same source and a small prism instru-

ment, was unable to find these bands, and suggested that Leifson's bands were merely gaps in the band spectrum of hydrogen, which appears with great intensity in such a source. The object of the present work was to photograph the spectrum under greater dispersion and resolving power, using a source which gave a true continuum in the region in question and to extend the spectrum to shorter wave-lengths, below the Schumann region.

¹ S. Leifson, *Astrophys. J.* **63**, 87 (1926).

² A. Rose, *Zeits. f. Physik* **81**, 758 (1933).

EXPERIMENTAL PROCEDURE

The methane was prepared by the Grignard reaction, from purified methyl iodide, especial precautions being used to free the gas from ether vapor. The methane was fractionated in vacuum, the middle fraction only being used. It was admitted to the spectrograph from a storage bulb through small calibrated volumes.

The one meter focus glass grating had 125,000 lines, ruled 30,000 to the inch. The dispersion was 8.52Å/mm in the first order and the resolving power unusually high for a small instrument, since care was taken to cover all the ruled surface with light. The spectrograph was evacuated with a single Cenco Hypervac pump, which proved entirely adequate down to about 1000Å. Below this, absorption by hydrogen diffusing through the slit from the discharge became troublesome, and below 850Å absorption by this gas became complete.

The light source was a condensed discharge in hydrogen, used by many workers in this region. An 8 mf. condenser, charged to 3000 volts, was discharged twice a second through a one millimeter capillary tube. A strong continuum was obtained, with lines of Si, C, O and B superimposed. Exposure times were four to ten minutes.

RESULTS

Exposures were made at methane pressures from 0.002 mm up to 1.0 mm. The absorbing column was about two meters. At the lowest pressure the methane absorption was barely perceptible, extending from about 1300 to 1200Å. As the pressure was increased the absorption widened rapidly on the short wave side and slowly on the red side. At our highest pressure the absorption extended to about 1450Å but no significance was attached to any of these limits. It is quite possible that we could have observed absorption up to 1800Å (as reported by Leifson at atmospheric pressure) by going to still higher pressures.

In no case was any indication of vibrational structure in the absorption obtained. With our

spectrograph, any vibrational structure should be clearly resolved, and the rotational structure partially resolved or at least indicated. So we believe that it may be safely concluded that in this region of the spectrum, methane shows only true continuous absorption.

The ionization potential of methane is 14.5–15.2 volts³ (855–810Å). Most of the continuous absorption observed by us cannot thus be due to the usual continuum following a Rydberg series, but must be due to repulsive electron states. Furthermore we must conclude that all of these excited states are repulsive up to ionization.

Without a detailed examination of the wave functions for the excited states, we can only speculate on the reasons for the instability of methane on electronic excitation. According to Mulliken,⁴ the lack of discrete absorption in methane is to be explained by the high value of its ionization potential, as compared with that of ammonia, which shows discrete absorption at considerably longer wave-lengths. It is the opinion of the present writers that the value of the ionization potential is not so important as the value of the lowest excitation potential. This is much higher in methane than in ammonia, if the absorption at the lowest pressure in each case comes from molecules in the $n''=0$ level of the normal state of the molecule. The larger excitation energy required in methane might remove an electron (probably an a_1 electron) so far that its bonding power would be entirely lost. It would then be impossible to form four bonds (without the promotion of one of the inner electrons) and dissociation would occur.

Several examples of continuous ultraviolet spectra of molecules having tetrahedral symmetry are known and the phenomenon may be a general one. Lead tetramethyl, observed by one of us,⁵ carbon tetrachloride¹ and germane, GeH_4 ⁶ are examples.

³ G. Glockler, J. A. C. S. **48**, 2021 (1926).

⁴ R. S. Mulliken, J. Chem. Phys. **1**, 501 (1933).

⁵ Duncan and Murray, J. Chem. Phys. **2**, 636 (1934).

⁶ Observations by Mr. H. E. Mahncke in this laboratory.