

Raman Spectrum and Fluorescence of Dioxane

Hugh W. Hunter

Citation: *J. Chem. Phys.* **6**, 544 (1938); doi: 10.1063/1.1750310

View online: <http://dx.doi.org/10.1063/1.1750310>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v6/i9>

Published by the AIP Publishing LLC.

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



Explore the **Most Cited**
Collection in Applied Physics

AIP
Publishing

Raman Spectrum and Fluorescence of Dioxane

HUGH W. HUNTER

Department of Physics, Indiana University, Bloomington, Indiana

(Received June 13, 1938)

A. The Raman spectrum of dioxane is shown to include eleven lines, some of which have been reported by one or both of two previous investigators. B. Dioxane, when irradiated by the ultraviolet light from a mercury arc, gives scattered light whose spectrum shows a broad continuous band in the visible region. Intensity of the scattered band diminishes rapidly with increasing temperature of the dioxane. Shortened time exposures bring out two maxima at about 5800Å and 4500Å. A similar phenomenon has been observed in work on cyclohexane.

A. RAMAN SPECTRUM OF DIOXANE

DURING an investigation on the conductance of solutions of certain organic salts, it became desirable to know something as to the Raman frequencies of the solvent dioxane, 1-4 diethylene oxide. Dioxane has been studied previously by two independent experimenters, Villars¹ and Wolkenstein and Syrkin,² but their results were not completely in agreement, even though both used the same region of the mercury spectrum for their work. The former reported ten frequencies, the latter eleven, with agreement on only six values. Since the frequency shifts measured in the first work were duplicated almost identically in the second, the disagreement obviously arose from doubtful assignment of shifted lines to proper "parent" mercury frequencies.

The values reported here rest upon measurements, made in the near ultraviolet, of frequency shifts from the pair of mercury lines 3125.6Å and 3131.6Å. These two lines, being almost equal in intensity, gave modified lines that were paired in characteristic fashion, and it was possible to relate each shifted line with its unmodified "parent" without ambiguity.

Dioxane was prepared by Dasher.³ The commercial product was frozen (freezing point 11.7–11.8°C) to remove the major part of the water, melted and refluxed with sodium hydroxide to remove methylene acetal, and then repeatedly refluxed, first with quick-lime and then with sodium, until the resultant solvent did not

tarnish bright sodium. The final product had a specific conductivity of $1-2 \times 10^{-16}$ ohm⁻¹, and a density of 1.02766 (25°C).

The spectrograph employed was a Hilger E-3 quartz spectrograph, having a dispersion in the region of the spectrum used (3000–4000Å) of about twenty angstroms per millimeter. Exposure time varied from one to eight hours. The light source was a quartz mercury arc with a luminous column ten centimeters long. Both glass and quartz containing tubes were used, and their shape and arrangement were according to that described by Wood.⁴ The temperature of the dioxane was controlled by a smooth sheet of water that flowed over the tube and was carried away by an aluminum reflector below.

Results are indicated in Table I. Eleven frequency shifts were measured, the modified

TABLE I. *Raman frequency shifts for dioxane in wave numbers per centimeter. Numbers in parentheses indicate relative intensities.*

I	II	III	IV
VILLARS	WOLKENSTEIN, SYRKIN	THIS DETERMINATION	AVERAGE
291 (0)		288 (0)	290
434 (00)?	427 (3)		
	487 (3)	493 (1)	490
519 (00)?			
837 (4)	836 (10)	837 (5)	837
	940 (2)		
	1017 (5)	1018 (4)	1018
1117 (1)	1115 (5)	1113 (3)	1115
1214 (1)	1213 (3)	1211 (2)	1213
	1306 (5)	1303 (4)	1304
1442 (2)	1450 (6)	1450 (5)	1450
2720 (00)		2724 (2)	2722
2864 (3)	2862 (10)	2858 (10)	2861
2967 (3)	2971 (10)	2976 (10)	2972

¹ Villars, J. Am. Chem. Soc. **52**, 4612 (1930).

² Wolkenstein, Syrkin, J. Chem. Phys. **3**, 594 (1935).

³ Paul J. Dasher, thesis, Indiana University (1937).

⁴ R. W. Wood, Phil. Mag. **6**, 729 (1928); Phys. Rev. **36**, 1421 (1930).

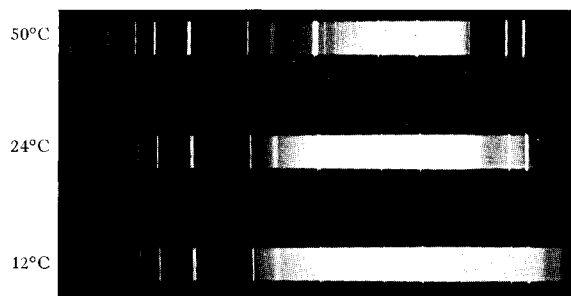


FIG. 1.

lines in every case appearing in pairs having the configuration of the originating mercury lines, 3125.6 and 3131.6Å. Measurements were accurate to ± 6 wave numbers per centimeter. The six values previously reported both by Villars¹ and by Wolkenstein and Syrkin² were confirmed closely; of the remaining five, two agreed with Villars' original report, and three agreed with the values given by Wolkenstein and Syrkin.

In Table I, the first two columns list final values taken from the two earlier reports. The results of the present determination appear in the third column, and shifts verified definitely by two independent determinations are given in column four. The six frequency shifts confirmed in all three cases are italicized.

B. FLUORESCENCE

In the course of the determination of the Raman spectrum of dioxane, it was observed that the spectrum of the scattered light exhibited a strong continuous band in the visible region when a quartz mercury arc and a quartz containing tube were used. Reduced time exposures brought out distinct bands, with maxima at about 5800Å and 4500Å. The band of shorter wave-length was the broader of the two, extending well below 4000Å.

When a glass containing tube of the same dimensions was substituted for the quartz tube, the continuous background disappeared. A thin glass filter produced the same result, an indication that the fluorescence was due to the irradiation of the dioxane by ultraviolet light below 2900Å.

The intensity of the fluorescence was found to diminish rapidly with increasing temperature of the dioxane. At 12°C (freezing point 11.8°C) there resulted a strong continuous spectrum extending from 3400Å entirely through the visible range. With higher temperatures of the dioxane, and with all other conditions unchanged, the two maxima were evident, and the extent of the spectrum was reduced at both ends. At temperatures as high as 50°C the long wavelength component disappeared, and the remaining band was limited to a region between about 4000Å and 5000Å. These results are shown in Fig. 1 which represents three exposures made consecutively on the same plate. The only factor changed during the series was the temperature of the dioxane, as indicated. Exposure was for three hours.

Continued irradiation of the dioxane with ultraviolet light did not affect the transparency of the liquid. Dioxane exposed for a period of three days showed the same fluorescence as that exhibited by a fresh sample.

A phenomenon similar to that just described was found by Karl Haberl⁵ during an investigation on the intensity of the Raman lines of cyclohexane, C₆H₁₂. He reported that the intensity of the fluorescence from cyclohexane was negligible for temperatures above 20°C, increasing rapidly with diminishing temperatures to 8°C, the liquid freezing at 5°C. He also found two maxima, at 4000Å and 2900Å.

⁵ Karl Haberl, *Ann. d. Physik* **21**, 301 (1934).