

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF BUFFALO]

Absorption and Fluorescence of Styrene Vapor<sup>1</sup>BY JOHN V. MORGAN<sup>2,3</sup>

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The fluorescence bands of styrene vapor have been measured and are given in Table II. The structure of the spectrum undergoes no change when the vapor pressure is varied from 2 to 0.06 mm., nor is any change observed in the presence of an inert gas. Polystyrene was identified as a reaction product. From the vibrational analysis, it is concluded that the fluorescence spectrum has its origin in the zero vibrational level of the excited state. The fluorescence stems from absorption in a discrete banded region. Excitation in a quasi-continuous absorption region at shorter wave lengths gives no observable fluorescence. At low vapor pressures six diffuse bands are observed in this previously continuous portion. A previous vibrational analysis offered by Matsen and co-workers for the discrete absorption bands is elaborated. Nine fundamental frequencies are found active in the excited state, ten in the ground state. This analysis accounts for about half of the observed absorption bands.

**Introduction.**—The fluorescence of styrene vapor has been reported in the literature by several authors<sup>4,5</sup> but the spectrum has not been analyzed with respect to the molecular symmetry and fundamental vibrational frequencies involved in the transition. Likewise, the absorption spectrum has been reported<sup>6-8</sup> with the same lack of interpretation. Matsen and co-workers<sup>9</sup> were the first investigators to assign fundamental frequencies to the upper state. They reported four frequencies as fundamentals and observed close to 400 absorption bands.

Both spectra are re-investigated in this paper and the previous analysis is elaborated.

**Experimental.**—The extensive data of Matsen<sup>9</sup> were chosen for the absorption analysis. In order to check his work, the absorption spectrum was recorded on Eastman Kodak 103-0 spectroscopic plates, using a Bausch and Lomb medium quartz spectrograph. The styrene was obtained 99% pure from Dow Chemical Company and was fractionated under reduced pressure before use. The absorption tube had a side-arm for a liquid reservoir and an absorbing path 25 cm. long. Vapor pressures were varied from 0.1 to 3 mm. The bands were measured on a comparator having a least count of 0.001 mm.; a standard iron arc served as a comparison spectrum. The intensity of the bands was measured on a Bausch and Lomb recording microphotometer.

For the investigation of the fluorescence, a water jacketed quartz tube with a liquid reservoir was employed, the fluorescence being observed end-on through a quartz window. The tube was charged with styrene, evacuated to  $10^{-6}$  mm., the liquid thoroughly degassed, and then re-evacuated to a final pressure of  $10^{-6}$  mm. This tube was placed at one focus of an elliptical reflector, a General Electric UA-2 medium pressure mercury arc was placed at the other. The total length of tube exposed to radiation was 10 cm. The dimensions of the water jacket were such that the inner quartz tube was surrounded by a 1-cm. layer of solution. Solutions could be circulated around the inner tube by means of a centrifugal pump in series with a heat exchanger. These solutions served both to isolate various mercury exciting lines and also as coolant. The vapor temperature was maintained at  $25 \pm 2^\circ$ . The vapor pressures for fluorescence were varied from 0.06 to 2 mm. The

fluorescence bands were measured as mentioned for the absorption spectrum.

In order to study the fluorescence more completely it was necessary to obtain approximately monochromatic excitation. An extensive search for suitable liquid filters in the 2400 to 2900 Å. region yielded very few solutions, none of which isolated one mercury line to the exclusion of all others. The filters found are summarized in Table I.

TABLE I  
LIQUID FILTERS

Note: All these solutions, with the exception of the KNO<sub>3</sub> filter, decomposed rapidly during exposure, making it necessary to replenish them at intervals.

| Solute,<br>grams per liter H <sub>2</sub> O | Spectral characteristics          |
|---|-----------------------------------|
| 1 g. KNO <sub>3</sub>                       | Transmits above 2400 Å.           |
| 1 g. KI                                     | Transmits above 2650 Å.           |
| 1 g. KI and 2 drops<br>pyridine             | Transmits above 2700 Å.           |
| 0.12 g. I <sub>2</sub> and<br>0.155 g. KI   | Part isolation of Hg 2537 Å. line |

**Results. A. Absorption.**—Eighty-odd absorption bands were measured precisely in the discrete absorption region, which lies between 2600 and 2900 Å. The results of these measurements checked almost exactly with the data of Matsen and co-workers, both with respect to position and intensity. The gross appearance of this absorption spectrum has been reported previously.<sup>9</sup> At a vapor pressure of 2 mm. there is a strong continuous absorption region starting at about 2570 Å. and extending to shorter wave lengths. At a vapor pressure of 0.1 mm., at which the three strongest bands of the discrete portion can be barely seen, six weak and diffuse bands are observable near the red edge of the previously continuous region. Their frequencies, in cm.<sup>-1</sup>, are 40270, 40060, 39840, 39620 and 39200. The center of gravity of these bands was measured, due to their diffuseness, with a precision of 25 cm.<sup>-1</sup>. Note that the difference between successive bands is constant within the experimental error. It is possible that this separation corresponds to the drop in frequency of a totally symmetrical vibration. For ease of reference, this absorption region will be called continuous in the rest of this paper.

**B. Fluorescence.**—At a vapor pressure of 1 mm., 25 discrete fluorescence bands were observed between 2860 and 3113 Å. all superposed on a strong continuous background. In the region between the 0-0 band and the exciting lines, fluo-

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(2) A.E.C. Predoctoral Fellow, 1951-1953.

(3) Eastman Kodak Company, Navy Ordnance Division, Rochester, N. Y.

(4) J. K. Marsh, *J. Chem. Soc.*, 3315 (1923).

(5) R. Titeica, *Ann. Comb. Liquides*, **11**, 443 (1936).

(6) M. Horio, *Mem. Coll. Eng. Kyoto Imp. Univ.*, **7**, 177 (1933).

(7) A. D. Walsh, *Proc. Roy. Soc. (London)*, **A191**, 35 (1947).

(8) A. Berton, *Ann. chim.*, **19**, 394 (1944).

(9) F. A. Matsen, J. F. Music and W. W. Robertson, *THIS JOURNAL*, **72**, 5260 (1950).

rescence bands coinciding with the absorption bands could be observed but were very weak due to re-absorption. With the various filters described above, the fluorescence retained the same structure, with the exception that the lower the wave length limit of excitation the stronger the continuous background. Excitation with the 2537 Å. Hg line, which lies in the region of continuous absorption, produced an apparently continuous fluorescence in the same spectral region as the fluorescence obtained by excitation in the discrete bands. The long wave length limit of the fluorescence is difficult to define; it can be set at approximately 3600 Å.

Reduction of the vapor pressure in steps to a lower limit of 0.06 mm. revealed no change of structure or position of the bands. The fluorescence observed in the presence of an inert gas ( $N_2$  at 1 atm., styrene vapor pressure 1 mm.) likewise was the same, with the exception that the 0-0 band and the bands in its immediate vicinity were more intense.

Reaction occurred on all exposures, resulting in polymer films, some of which could be removed from the fluorescence tube only by hot fuming nitric acid. In particular, wave lengths below 2400 Å. seemed to produce the largest amount of this insoluble matter. The reaction products soluble in chloroform or benzene were analyzed spectrophotometrically and found to be polystyrene.

In Table II are listed the discrete fluorescence bands and their assignments. Most of the unas-

signed bands could be given several interpretations, but since excitation was not strictly monochromatic it hardly seems justified to list them. The fundamental frequencies of styrene were obtained from the data of Pitzer and co-workers.<sup>10</sup>

**Discussion. A. Absorption.**—From the data given above, it appears that the absorption consists of two separate electronic transitions, the continuous absorption overlapping the discrete region. The 2537 Å. Hg line lies almost at the gross borderline of these two regions. Thus the fluorescence obtained with this excitation is probably due to the discrete bands, while the continuous absorption apparently does not exhibit fluorescence.

Usually with the help of the vibrational structure definite statements about the symmetry of the combining electronic states can be made. Styrene probably has  $C_s$  symmetry, and  $A'-A''$  transitions are allowed only if the electric moment changes perpendicular to the plane of the molecule. Koch<sup>11</sup> has investigated the ultraviolet spectrum of oriented crystals of dicinnamyl, using polarization techniques and found that the moment changed in the ( $xy$ ) plane of the molecule. If, because of the marked similarity of spectra, it is assumed that the moment has the same direction in styrene, then the upper state should have the symmetry  $A'$ . These considerations apply strictly to electronic selection rules only. Transitions to upper states with symmetry  $A''$  are expected to appear through vibrational perturbation although with low intensity.

In addition to the upper state fundamental frequencies chosen by Matsen, we have found what may be fundamental frequencies of 148, 478, 1024, 1300 and 1486  $cm^{-1}$ . If the sum is taken of the number of frequencies found to the red of the 0-0 band and the number found in fluorescence, there are ten frequencies active in the ground state. From the absorption data, nine frequencies are found active in the upper state. These are listed in Table III.

TABLE II  
FLUORESCENCE BANDS OF STYRENE VAPOR

Note: s, strong; m, medium; w, weak; vw, very weak. Because of the diffuse nature of some of the bands, coupled with the continuous background, the assignments were considered correct if they agreed within  $\pm 15 cm^{-1}$ .

| Wave length, Å | $cm^{-1}$ | In-<br>tensity | Separation<br>from<br>0-0 band | Assignment                        |
|----------------|-----------|----------------|--------------------------------|-----------------------------------|
| 2860.1         | 34963     | w              | 207                            |                                   |
| 2864.2         | 34901     | m              | 145                            | 148 + 0                           |
| 2868.3         | 34854     | m              | 98                             | 105 + 0                           |
| 2872.4         | 34816     | m              | 59                             | 59 + 0                            |
| 2876.3         | 34756     | s              | 0                              | 0-0                               |
| 2882.8         | 34678     | m              | 78                             | 0 - 86                            |
| 2888.9         | 34651     | m              | 105                            | 0 - 102                           |
| 2897.7         | 34500     | w              | 256                            | 0 - 240(?)                        |
| 2928.5         | 34137     | ms             | 619                            | 0 - 622                           |
| 2934.4         | 34069     | m              | 687                            |                                   |
| 2942.2         | 33978     | m              | 778                            | 0 - 777                           |
| 2947.4         | 33918     | w              | 838                            | 0 - 2 × 416                       |
| 2952.6         | 33859     | w              | 897                            | 0 - 2 × 442                       |
| 2957.1         | 33808     | w              | 948                            |                                   |
| 2962.0         | 33751     | s              | 1005                           | 0 - 999                           |
| 2971.5         | 33640     | w              | 1116                           |                                   |
| 2975.1         | 33603     | w              | 1153                           | 0 - 1155                          |
| 2979.6         | 33552     | w              | 1204                           | 0 - 1204                          |
| 2987.7         | 33477     | s              | 1279                           | 0 - 1280                          |
| 2998.7         | 33338     | w              | 1418                           | 0 - 1415                          |
| 3018.1         | 33123     | w              | 1633                           | 0 - 1636                          |
| 3051.5         | 32761     | vw             | 1995                           | 0 - 2 × 999                       |
| 3071.7         | 32546     | vw             | 2210                           | 0 - 999 + 1204                    |
| 3090.5         | 32348     | vw             | 2408                           | 0 - 999 + 1415 or<br>0 - 2 × 1204 |
| 3113.4         | 32110     | vw             | 2646                           | 0 - 999 + 1636                    |

TABLE III  
ACTIVE VIBRATIONAL FREQUENCIES

| Ground state | Excited state | Ground state | Excited state |
|--------------|---------------|--------------|---------------|
| 240          | 148           | 1155         | 1024          |
| 510          | 478           | 1204         | 1209          |
| 622          | 746           | 1280         | 1300          |
| 777          | 948           | 1415         | 1486          |
| 999          | 959           | 1636         |               |

Matsen and co-workers reported five difference frequencies displayed by the fundamentals. By further investigation it was found that not only the fundamentals but the entire  $0 - \nu'$  spectrum is shifted, and repeated five times. The frequency differences are 0 - 43, 0 - 86, 0 - 102, 0 + 59, 0 + 107. The minus frequencies have their origin in strong bands to the red of the 0-0 band; it is suggestive to interpret these bands as 1-1 transitions of relatively low frequency antisymmetrical vibrations. It would be tempting to consider the 0 - 43 band as a 1-1 transition and the 0 - 86 band as a 2-2 transition of the same vibration. But this

(10) K. S. Pitzer, E. F. Westrum and L. Guttman, *THIS JOURNAL*, **68**, 2209 (1946).

(11) H. P. Koch, *J. Chem. Soc.*, 1123 (1948).

doesn't seem likely, since the intensities of these two bands are almost equal. The frequency differences on the blue side of the 0-0 band are at first sight more difficult to resolve as to their origin. But note that  $148 - 43 = 105$ , and  $148 - 86 = 62$ , which, within the limits of error of measurement, agree with the frequency differences  $0 + 107$  and  $0 + 59$ . These can then be interpreted as having their origin in a superposition of the  $0 + 148$  band on the 1-1 transitions. If this is true, there is no reason why we should not expect the frequency difference of  $148 - 102 = 46$ . Such a frequency difference was subsequently noted, although rather weak.

It is obvious that no vibrational selection rules are violated in the above scheme. It is difficult to determine the higher members of the various frequency difference series unambiguously, but this is not necessarily a fault of the analysis.

This scheme accounts for the assignment of about 190 of the bands reported by Matsen and co-workers. A breakdown of the bands reported and those given assignments is given in Table IV. A complete table is available from the Chemistry Department, University of Buffalo, on request.

TABLE IV  
BREAKDOWN OF ABSORPTION ASSIGNMENTS

| Intensity | Number of bands reported | Number of bands assigned |
|-----------|--------------------------|--------------------------|
| 10        | 2                        | 1 <sup>a</sup>           |
| 9         | 1                        | 0 <sup>a</sup>           |
| 8         | ...                      | ..                       |
| 7         | ...                      | ..                       |
| 6         | 2                        | 2                        |
| 5         | 5                        | 5                        |
| 4         | 50                       | 31                       |
| 3         | 70                       | 48                       |
| 2         | 95                       | 60                       |
| 1         | 164                      | 39                       |
| Totals    | 389                      | 186                      |

<sup>a</sup> The two bands not assigned with such high intensity are reported by Matsen to be 7 and 13  $\text{cm}^{-1}$  to the red of the 0-0 band. These bands were not seen on any of our plates, possibly because of the poorer resolving power of our instrument. This could be a serious weakness of our analysis.

From the intensity of the 1-1 bands, it is suggestive to interpret the  $0 - 43$  band as a 1-1 transition of the  $212 \text{ cm}^{-1} a''$  vibration. A band at  $0 - 421$  may possibly be interpreted as a 2-0 transition of this vibration. Since the intensities of the  $0 - 86$  and  $0 - 102$  bands are almost equal, they could be interpreted as arising from 1-1 transitions of the  $416$  and  $442 \text{ cm}^{-1} a''$  vibrations. Note that in the fluorescence the bands  $0 - 838$  and  $0 - 897$  can be

interpreted as  $0 - 2 \times 416$  and  $0 - 2 \times 442$ , respectively.

It must be emphasized that these inferences concerning the vibrational frequencies responsible for the 1-1 transitions are tentative. They could possibly be verified or refuted by temperature dependence measurements of the bands in question.

**B. Fluorescence.**—The obvious feature of the assignment is that the bands appear to have their origin in the zero vibrational level of the upper electronic state. But in all instances this is not the vibrational level directly excited, the lowest possible directly excited level being  $958 \text{ cm}^{-1}$  above the 0-0 band. This means that vibrational energy is lost before the molecule re-emits the absorbed radiation. Using essentially  $2798-2804 \text{ \AA}$ . excitation, which gives the least amount of continuous background, no change was observed in either the position or number of the bands even at the lower limit of  $0.06 \text{ mm}$ . vapor pressure. Calculations indicated that to further reduce the vapor pressure would be useless, since the dimensions of the fluorescence tube were such that below this vapor pressure collisions with the walls of the tube would predominate.

If we assume that collisions alone are responsible for the loss of the excess vibrational energy, we may calculate a lower limit for the lifetime of the excited state from the kinetic theory of gases, based on the mean free path and root mean square velocity. Making the assumptions that the vapor behaves as an ideal gas, that the molecule is approximately spherical, and that every collision results in loss of vibrational energy, we can calculate that the order of magnitude of the lower limit of the lifetime is  $10^{-6}$  second. This is a rather long lifetime for an excited electronic state and would suggest that this may be a forbidden transition. Assuming a  $C_{2v}$  symmetry for the styrene molecule, electronic selection rules based on group theory indicate that the forbidden electronic transitions should be of the type  $A'-A''$ .

Simpson<sup>12</sup> has suggested that the presence of positive and negative terms of the same order of magnitude in a transition moment integral could result in a small value of a transition probability, even though according to selection rules the transition is allowed. If the long lifetime is real, theory is inadequate to explain this further at present.

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BUFFALO, NEW YORK

(12) W. T. Simpson, *J. Chem. Phys.*, **16**, 1124 (1948).