

## Absorption Spectra of Pure Liquid Benzene in the Ultraviolet Region\*

TAKASHI INAGAKI

Department of Physics, Osaka Kyoiku University, Ten-noji, Osaka, Japan

(Received 14 February 1972)

Absorption spectra of pure liquid benzene were measured at several temperatures from room temperature to just below the freezing point of benzene, in the wavelength region 3000–1670 Å. Because of the very large absorption coefficient of benzene in this region, the transmission measurements were made with the samples prepared as thin films. Three absorption bands of quite different intensities were observed, corresponding to the  $\pi\text{-}\pi^*$  singlet transitions well known in the vapor phase spectra. The spectra obtained are compared with those in the vapor and solid phases.

## I. INTRODUCTION

Electronic absorption spectra of benzene have been extensively studied in various states of aggregation. In the vapor phase, it is well known that there exist three absorption bands in the near and far ultraviolet regions.<sup>1</sup> The very weak first band at about 2600 Å (assigned to the  $A_{1g}\rightarrow B_{2u}$  transition) has been completely analyzed by Sponer *et al.*<sup>2</sup> A moderately intense second band near 2100 Å and an extremely intense third band near 1850 Å (assigned to the  $A_{1g}\rightarrow B_{1u}$  and  $A_{1g}\rightarrow E_{1u}$  transitions, respectively) have been observed by a number of investigators.<sup>3–6</sup> It has been established from electronic energy-level calculations for a benzene molecule that these absorption bands are due to  $\pi\text{-}\pi^*$  singlet excitations.

In the solid phase a near ultraviolet study has been performed by Kronenberger<sup>7</sup> with unpolarized light and by Wolf<sup>8</sup> and Broude<sup>9</sup> with polarized light. The far ultraviolet spectrum in solid benzene has been measured by Romand and Vodar<sup>4</sup> and Roncin *et al.*<sup>10</sup> Recently, Brith *et al.*<sup>11</sup> have obtained well-resolved reflection and absorption spectra of solid benzene at low temperatures ( $\sim 4.2^\circ\text{K}$ ) in the region 2700–1700 Å. In addition to these studies of the vapor and solid phases, a number of investigations have been carried out with benzene embedded in various media: fluid solutions,<sup>12</sup> low temperature glasses,<sup>13,14</sup> and rare-gas matrices.<sup>10,15</sup>

So far, however, similar experimental work in the liquid phase has been somewhat neglected and limited to the nearly transparent regions. Lewis and Kasha<sup>16</sup> and Pitts<sup>17</sup> have studied liquid benzene in the region above 2800 Å and found out an exceedingly weak singlet-triplet transition at near 3400 Å. The near ultraviolet spectrum of liquid benzene down to 2330 Å has been measured by Yguerabide,<sup>18</sup> though the absorption coefficient was not determined. In view of the theoretical interest in electronic structures of disordered systems, especially of liquid insulators,<sup>19</sup> it is important to obtain the absorption spectra of liquid benzene in the farther ultraviolet region.

In general, there have been few measurements of electronic absorption spectra of molecular liquids in the near and far ultraviolet regions.<sup>20</sup> This is because of the great difficulties encountered in making samples

thin enough to allow transmission measurements of very intense transitions in these regions. Especially in the vacuum ultraviolet region, the difficulties are increased, since very thin liquid films stable in the evacuated atmosphere must be prepared. In order to avoid such difficulties, recently efforts have been made to obtain the optical constants of molecular liquids from reflection measurements. For liquid benzene such a study has been performed by Williams *et al.*<sup>21</sup> in the 3200–1200 Å region. Recently Sowers *et al.*<sup>22</sup> have repeated their experiments with some technical improvements and obtained somewhat different results. From the energy-loss function of liquid benzene they have ascertained collective oscillations of  $\pi$ -electrons. However, the absorption curve evaluated from their reflection data is quite diffuse. In particular, the absorption band corresponding to the second singlet transition (the  $A_{1g}\rightarrow B_{1u}$  transition) does not appear in it.

In this paper we show the absorption spectra of pure liquid benzene in thin films obtained from the transmission measurements in the region 3000–1670 Å. In contrast with the results of the reflection study, remarkably refined spectra have been obtained. The measurements have been performed at several temperatures from room temperature to just below the freezing point of benzene ( $5.45^\circ\text{C}$ ). The spectra obtained are compared with those in the vapor phase and in the solid phase at low temperature and with that from the reflection measurement in the liquid phase.

## II. EXPERIMENTAL

Absorption spectra were obtained with a double-beam Shimadzu SGV-50 vacuum ultraviolet spectrophotometer. It was equipped with a 50 cm radius of curvature concave grating blazed at 1200 Å. With this grating the first-order dispersion of the instrument was 16.6 Å/mm. A toroidal mirror divided into five sections was used as a beam-splitter. The widths of both of entrance and exit slits were set at 200  $\mu$ . The radiation source was a cold cathode-type hydrogen discharge lamp, whose emission spectrum was a continuum in the wavelength region used. Liquid benzene of spectroscopic grade supplied from Nakarai Chemical Co. was used without further purification.

The absorption cell consisted of two fused quartz plates. Between them pieces of very thin films of nickel or glass were inserted as spacers. The quartz plates were tightly clamped together with two cone shaped pressure seals. Such a cell was placed between the beam splitter and the photomultiplier detector. The light path could be evacuated while the cell perimeter was still exposed to the usual atmosphere. A small drop of liquid benzene put on the cell perimeter spread into the small interval between the plates spontaneously. As the sample within a cell was lost by evaporating from the contact perimeter of the cell, it was continuously supplied from the sample reservoir through a glass capillary. With such arrangement, a pure and stable thin film of liquid benzene was successfully obtained.

In order to cool the liquid film, cold air which had passed through liquid nitrogen flowed into a thermally insulated compartment surrounding the absorption cell. The temperature of the film was measured with thermocouples tightly attached to the perimeter and front surface of the quartz plate. Below room temperature these thermocouples showed somewhat different temperatures, so an accurate temperature of the liquid film could not be determined. Hence, the solidification of liquid film was confirmed with direct observation. It was quite easy for the comparatively thick film used in the study above 2250 Å, since upon solidification some small cleavages could be observed in the film. For the very thin films used in the study below 2250 Å, however, the solidification could not be confirmed, as any evidence of it was not observed in the films.

Background incident-light intensity in the 3000–1850 Å region was obtained with a liquid thin film of *n*-hexane which was transparent in this region. As the difference of the reflection loss between the benzene film and the *n*-hexane film was negligibly small in the 3400–2700 Å region, no corrections were performed to the measured background intensity down to 1850 Å. Below 1850 Å the background intensity was measured with an assembled cell without any liquids in it. It was corrected by extrapolating the reflection loss in the region above 1850 Å to the region below 1850 Å.

The thickness of the cell used above 2250 Å was estimated from wavelength intervals between the successive interference fringes of monochromatic lights transmitted through the cell without the sample in it. An interference pattern can be obtained if the empty cell is uniform in its thickness. The monochromatic lights of the same wavelength region as used in the absorption measurement were appropriate for the observation of interference pattern. This method gave 2.490 μ for the thickness of the cell. The absorption cells usable below 2250 Å were, however, too thin to be determined by this method. Therefore, from the approximately constant ratios of optical densities between the 2.490 μ-thick film and the thinner films in their overlapping wavelength regions, the thicknesses

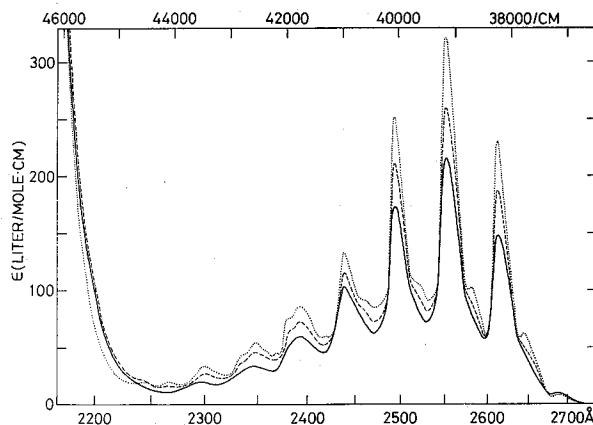


FIG. 1. The absorption spectra of benzene in the pure condensed phase corresponding to the  $A_{1g} \rightarrow B_{2u}$  singlet transition. —: liquid phase at 299°K, ---: liquid phase at just above the freezing point (5.45°C), and ···: solid phase at just below the freezing point. The molar extinction coefficient  $\epsilon$  is exact only for the data of liquid phase at 299°K.

of the latter were estimated. Within the error of approximately 5%, the thicknesses of the films which gave complete spectra below 2250 Å varied between 0.083–0.040 μ. From these values the molar extinction coefficient  $\epsilon$  was determined.

### III. RESULTS

#### A. The Spectral Region 3000–2250 Å

Absorption spectra in the 3000–2250 Å region obtained from the 2.490 μ-thick film are presented in Fig. 1. Measurements were performed at 299°K and at two temperatures just above and just below the freezing of benzene (5.45°C). Three curves at different temperatures were obtained from a same film. Since the thickness of the film might change somewhat with the temperature, the molar extinction coefficient is exact only for the data at 299°K. The measurement at this temperature was repeated using a Shimadzu MPS-50 multipurpose spectrophotometer. The spectrum obtained with this instrument showed a good agreement with one presented here, and they are consistent with the spectrum of Yguerabide.<sup>18</sup>

The very weak absorption system at 2700–2250 Å corresponding to the first singlet  $A_{1g} \rightarrow B_{2u}$  transition (the  $B_{2u}$  band) has some vibrational structures even in the liquid phase. The band interval of main progression at 299°K is  $910 \pm 30 \text{ cm}^{-1}$ . This corresponds to the spacing  $923 \text{ cm}^{-1}$  of  $A^0$  series (in the notation of Sponer *et al.*<sup>2</sup>) in the vapor phase<sup>2</sup> and to the spacing  $925 \text{ cm}^{-1}$  in the solid phase.<sup>9</sup> It is well known that in the solid phase the 0–0 band of the  $B_{2u}$ -transition and the progression built on it (so-called *K* series) are induced by the crystalline field, while they are forbidden in the vapor phase from the symmetry properties of the

TABLE I. Positions of vibronic bands of the  $A_{1g} \rightarrow B_{2u}$  singlet transition of benzene in the vapor,<sup>2</sup> solid,<sup>9</sup> and liquid phases (in  $\text{cm}^{-1}$ ).

Assignment	Vapor	Solid (20°K)	Vapor-solid shift	Liquid (299°K)	Solid-liquid shift
$B_0^0$	37 482	37 200	-282	37 180±70	-20±70
0-0( $K_1$ )	(38 089) <sup>a</sup>	37 835	-254	(37 800±60) <sup>b</sup>	
$A_0^0$	38 609	38 355	-254	38 300±30	-55±30
$K_2$		38 760		(38 760±60) <sup>b</sup>	
$A_1^0$	39 532	39 280	-252	39 200±30	-80±30
$K_3$		39 685		(39 680±60) <sup>b</sup>	
$A_2^0$	40 455	40 205	-250	40 130±30	-75±30
$K_4$		40 610		(40 630±80) <sup>b</sup>	
$A_3^0$	41 378	41 130	-248	41 030±50	-100±50

<sup>a</sup> Theoretical position.

<sup>b</sup> Solid at just below the freezing point (5.45°C).

benzene molecule.<sup>2</sup> Actually, in the spectrum recorded just below the freezing point (Fig. 1) this series can be found between each band of main progression, though they are somewhat weaker than the similar series of the solid phase at low temperature.<sup>7</sup> It is noticeable, however, that even in the liquid spectrum at 299°K there exist appreciable inflections from which the  $K$  series will originate. With the decrease of temperature to just above the freezing point, the bands in main progression become considerably sharper, and at the same time these inflections become slightly more apparent. Thus, it is the solidification that makes some bands of the  $K$  series distinguishable. A similar spectral feature has been observed in the spectra of solutions.<sup>23</sup> The weak first vibronic band at near 2690 Å seems to be the first member of  $B^0$  series (in the notation of Sponer *et al.*<sup>2</sup>), that is one of the hot bands. Reasonably decreasing temperature causes a relative damping of this band. No significant shifts of the positions of vibronic bands with the temperature were observed. The oscillator strength for the  $B_{2u}$  band at 299°K was estimated to be 0.0020. This estimate is somewhat larger than the corresponding strengths 0.0016 in the vapor phase<sup>24</sup> and in a hydrocarbon solution.<sup>25</sup>

The comparison of some band positions among vapor,<sup>2</sup> solid<sup>9</sup> and liquid phases is shown in Table I. The solid-liquid shifts are considerably small compared with the vapor-solid shifts and seem to be slightly to the red. This is consistent with Broude's<sup>9</sup> finding that the vapor-solid shift of entire series increases with increasing temperature, that is,  $-254 \text{ cm}^{-1}$  at 20°K and  $-287 \text{ cm}^{-1}$  at 77°K.

### B. The Spectral Region 2250–1670 Å

The room temperature spectrum in the 2250–1670 Å region is shown in Fig. 2. This is one of several spectra obtained from the very thin films (between 0.083–

0.040  $\mu$  in thickness), but is not the mean value among them. The molar extinction coefficients agreed with each other within the error of 3% in the vicinity of the absorption maximum. In the other regions the variation among them was smaller.

In Fig. 2 two strong absorptions can be found. A moderately intense band supposed to correspond to the  $A_{1g} \rightarrow B_{1u}$  singlet transition (the  $B_{1u}$  band) starts at about 2150 Å and has a quite diffuse structure, in which only three components spaced about  $900 \text{ cm}^{-1}$  apart can be identified. This band interval is in agreement with that observed in vapor<sup>3-6</sup> and solid phases.<sup>11</sup> The short wavelength tail of the  $B_{1u}$  band merges into the very intense consecutive band corresponding to the  $A_{1g} \rightarrow E_{1u}$  singlet transition (the  $E_{1u}$  band). The absorption maximum of the  $E_{1u}$  band is located at about 1895 Å, and no structures are found in it. The Rydberg bands which have been observed in the vapor phase

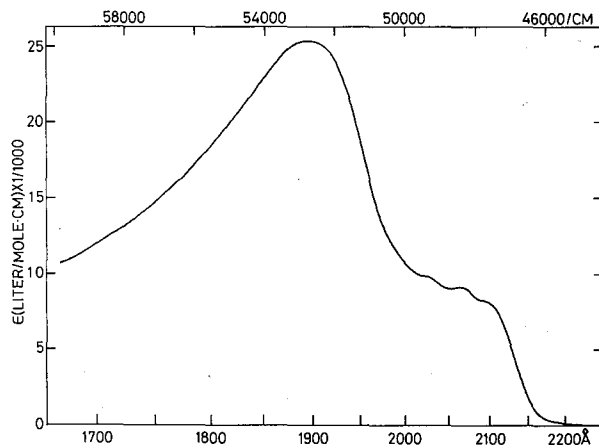


FIG. 2. The absorption spectrum of pure liquid benzene at room temperature corresponding to the  $A_{1g} \rightarrow B_{1u}$  and  $E_{1u}$  singlet transitions.

spectra<sup>3-6,26</sup> at the region of the  $E_{1u}$  band were not detected. From the band resolution technique, the oscillator strength for the  $B_{1u}$  band was estimated to be 0.095. This estimate is in good agreement with one of benzene in the vapor phase<sup>6</sup> 0.094, in the hydrocarbon solution<sup>12</sup> 0.10 and in the solid phase<sup>11</sup> 0.10. For the  $E_{1u}$  band, the oscillator strength was estimated down to the short wavelength limit 1670 Å to be 0.77. In the vapor phase<sup>6</sup> and in a hydrocarbon solution,<sup>12</sup> the corresponding strengths are 0.88 and 0.69, respectively.

In the present spectral region, the temperature change over the same range as in the study above 2250 Å did not produce any significant shifts in the spectra. From the thickest film usable below 2250 Å (the 0.083  $\mu$ -thick film) we could obtain not only the complete spectrum of the  $B_{1u}$  and  $E_{1u}$  bands, but that of the  $B_{2u}$  band, though the latter was extremely weak (the maximum optical density of this band was about 0.02). Decreasing the temperature of this film made several of the bands of the  $B_{2u}$ -absorption system considerably sharper, but did not cause any detectable changes in the  $B_{1u}$  and  $E_{1u}$  bands. As previously mentioned, there was no way to confirm the solidification for liquid films thin enough to be usable below 2250 Å, including the 0.083  $\mu$ -thick film. However, it was ascertained from the direct observation of the solidification of the thick film used above 2250 Å that the measured temperatures of the absorption cell were completely reproducible, though the temperatures of the film itself could not be determined with sufficient accuracy. Therefore, it is probable that at the temperature measured when the thick film solidified, the true temperature of the very thin film also was just below the freezing point of benzene. The fact that the spectra hardly change with the temperature would occur if the sample were in the liquid phase even at just below the freezing point. A similar observation has been reported by Verrall and Senior<sup>20</sup> for a thin film of heavy water. They have speculated that heavy water prepared as a thin liquid film has supercooled at just below the freezing point. As can be seen in Fig. 1, the long wavelength edge of the  $B_{1u}$  band became somewhat steeper upon solidification. It would be difficult to detect this change if it occurs in the very thin film, since the absorption at this wavelength region was exceedingly weak.

The comparison of the absorption spectra in liquid phase with those in vapor<sup>5</sup> and solid at low temperature<sup>11</sup> is presented in Fig. 3 in a logarithmic plot. In Fig. 3 the curve of the liquid (film) is a complete reproduction of the spectrum shown in Fig. 2. It is remarkable that the whole shape of the absorption curve of liquid (film) is very similar to the one of the solid at low temperature, though the former is considerably diffuse compared with the latter. The absorption peak at 1947 Å of solid benzene has been identified as the second component of vibrational series in the  $E_{1u}$  band. The solid-liquid (film) shift is about 480  $\text{cm}^{-1}$  for the

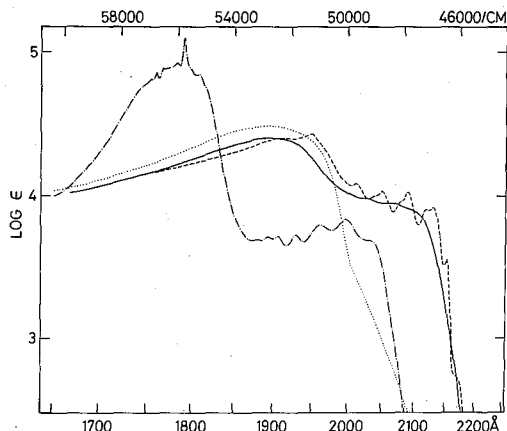


FIG. 3. The comparison of the absorption spectra of benzene among the vapor, solid and liquid phases in a logarithmic plot. —: liquid (film) at room temperature, ---: solid<sup>11</sup> at near 4.2°K, - · - ·: vapor<sup>5</sup>, and · · ·: liquid<sup>22</sup> (evaluated from the data of reflection measurement).

$B_{1u}$  band and about 800  $\text{cm}^{-1}$  for the  $E_{1u}$  band. These shifts are decisively smaller than the vapor-solid shifts, -3000 and -4900  $\text{cm}^{-1}$ , respectively.<sup>11</sup> It is to be noted that the solid-liquid shift is to the blue for both of these bands, while that is slightly to the red for the  $B_{2u}$  band.

For comparison, the absorption curve from the reflection study of liquid benzene<sup>22</sup> is added to Fig. 3. This is evaluated from the imaginary part  $k$  of the complex index of refraction of liquid benzene using the relationships  $\alpha = (4\pi k/\lambda) \times 10^8$  and  $\epsilon = (\alpha \log_{10} e)/c$ , where  $\alpha$  is the absorption coefficient in  $\text{cm}^{-1}$ ,  $\lambda$  is the wavelength in angstroms and  $c$  is the concentration of liquid benzene, i.e., 11.28 moles/liter. As can be found in the figure, the  $B_{1u}$  band is not observed in the reflection study. This has been explained as due to the large experimental error in the wavelength region where this band is expected to occur. In good agreement with the present transmission measurement, the absorption maximum of the  $E_{1u}$  band is found at about 1890 Å.

#### IV. DISCUSSION

The liquid films used in the study below 2250 Å were quite thin by normal macroscopic standards. This may raise the question whether the nature of the liquid benzene prepared as thin films is the same as that of bulk liquid benzene or not. Unfortunately, we do not have any decisive information about this problem. It has been observed, however, that in the wide range of film thickness between 2.490–0.040  $\mu$ , the ratios of optical densities between the films of different thickness were approximately constant in the regions of overlap within the error of 5%. This fact seems to suggest that if there is any *thin film effect* of liquid benzene on its optical properties, it is insignificant in the present

study. Furthermore, this suggestion seems to be supported by the good agreement between the present transmission measurement and the reflection measurement of the absorption curves in the region of the  $E_{1u}$  band.

One possible interpretation of electronic absorption spectra of molecular liquids is in terms of the same absorption processes as occur in the isolated molecules. In the vapor and liquid phases, absorptions occur at different energies, because in the liquid phase each molecule is perturbed by their neighboring identical molecules. It has been shown from our study, however, that the absorption spectra of liquid benzene hardly changes with temperature from room temperature to just below the freezing point apart from the behavior of the  $K$  series in the first band, and, moreover, that the spectra are very similar even to those of the solid phase at low temperature. These facts seem to make it preferable that the spectra of liquid benzene are interpreted in connection with those of solid benzene. The disappearance of the distinguishable  $K$  series in the liquid phase may be ascribed to supposition that the distortion of benzene molecule is very small in this phase compared with that in the solid phase. In general, the liquid state is characterized by the absence of any long-range order in it. Then, the results obtained here may be regarded as showing how critically the inherent features of absorption spectra of solid benzene depend on the periodic structure in it. Electronic spectra of crystalline benzene have been usually interpreted by mean of molecular exciton theory using the Frenkel model.<sup>27-30</sup> Most of the investigations based on this theoretical framework have pertained only to the first  $B_{2u}$  band. Recently, Brith *et al.*<sup>11</sup> have carried out a calculation on the intensity distribution of the third  $E_{1u}$  band employing this formalism. Their result accounts well for the shape of this absorption band which is very different from the one of vapor (Fig. 3). Although the band shape alone does not permit to identify the absorption process, the remarkable similarity of absorption spectra between the liquid and solid over a wide range of transition energies may suggest the occurrence of similar processes in the liquid to that in the solid. The observed small shifts of the absorption bands in the liquid phase with respect to those in the solid phase may be interpreted as due to the decrease in effective intermolecular interaction arising from the orientational averaging in the liquid.

## ACKNOWLEDGMENTS

We wish to thank Dr. Thomas Ebrey of Columbia University for reading the manuscript. We are also grateful to members of L. Jishuken which is an originative and creative study group of Department of Physics, Kyoto University and Dr. Buhang Yamada of Department of Biology, Kyushu University for many helpful discussions and for encouragement in the course of this investigation.

\* The experiments reported were performed at the Department of Physics, Kyoto University, Kyoto.

<sup>1</sup> For a complete survey see G. Herzberg, *Electronic Spectra of Polyatomic Molecules* (Van Nostrand, Princeton, N.J., 1966), p. 555.

<sup>2</sup> H. Sponer, G. Nordheim, A. L. Sklar, and E. Teller, *J. Chem. Phys.* **7**, 207 (1939).

<sup>3</sup> W. C. Price and A. D. Walsh, *Proc. Roy. Soc. (London)* **A191**, 22 (1947).

<sup>4</sup> J. Romand and B. Vodar, *Compt. Rend.* **223**, 930 (1951).

<sup>5</sup> L. W. Pickett, M. Muntz, and E. M. McPherson, *J. Am. Chem. Soc.* **73**, 4862 (1951).

<sup>6</sup> V. J. Hammond and W. C. Price, *Trans. Faraday Soc.* **51**, 605 (1955).

<sup>7</sup> A. Kronenberger, *Z. Physik* **63**, 494 (1930).

<sup>8</sup> H. C. Wolf, *Solid State Phys.* **9**, 1 (1959).

<sup>9</sup> V. L. Broude, *Usp. Fiz. Nauk* **74**, 577 (1971) [*Sov. Phys. Usp.* **4**, 584 (1962)].

<sup>10</sup> J. Y. Roncin, S. Y. Ch'en, J. Granier, and N. Damany-Astin, *Spectrochim. Acta* **18**, 907 (1962).

<sup>11</sup> M. Brith, R. Lubart, and I. T. Steinberger, *J. Chem. Phys.* **54**, 5104 (1971).

<sup>12</sup> J. R. Platt and H. B. Klevens, *Chem. Rev.* **41**, 301 (1947).

<sup>13</sup> E. Clar, *Spectrochim. Acta* **4**, 116 (1950).

<sup>14</sup> W. J. Potts, *J. Chem. Phys.* **23**, 73 (1955).

<sup>15</sup> B. Katz, M. Brith, B. Sharf, and J. Jortner, *J. Chem. Phys.* **52**, 88 (1970).

<sup>16</sup> G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.* **67**, 994 (1947).

<sup>17</sup> A. C. Pitts, *J. Chem. Phys.* **18**, 1416 (1950).

<sup>18</sup> J. Yguerabide, *J. Chem. Phys.* **49**, 1018 (1968).

<sup>19</sup> For example, S. A. Rice and J. Jortner, *J. Chem. Phys.* **44**, 4470 (1966).

<sup>20</sup> The author knows only the data of liquid water: R. E. Verrall and W. A. Senior, *J. Chem. Phys.* **50**, 2746 (1969); R. Onaka and T. Takahashi, *J. Phys. Soc. Japan* **24**, 548 (1968).

<sup>21</sup> M. W. Williams, R. A. MacRae, R. N. Hamm, and E. T. Arakawa, *Phys. Rev. Letters* **22**, 1088 (1969).

<sup>22</sup> B. L. Sowers, E. T. Arakawa, and R. D. Birkhoff, *J. Chem. Phys.* **54**, 2319 (1971).

<sup>23</sup> For example, M. Koyanagi, *J. Mol. Spectry.* **25**, 273 (1968).

<sup>24</sup> H. Sponer, *J. Chem. Phys.* **22**, 234 (1956).

<sup>25</sup> F. A. Matsen, W. E. Robertson, and R. L. Chuoke, *Chem. Rev.* **41**, 263 (1947).

<sup>26</sup> P. G. Wilkinson, *Can. J. Phys.* **34**, 596 (1956).

<sup>27</sup> J. Frenkel, *Phys. Rev.* **37**, 17, 1276 (1931).

<sup>28</sup> A. Davydov, *Theory of Molecular Excitons* (McGraw-Hill, New York, 1962).

<sup>29</sup> D. Fox and O. Schnepp, *J. Chem. Phys.* **23**, 767 (1955).

<sup>30</sup> D. P. Craig and S. H. Walmsley, *Mol. Phys.* **4**, 113 (1961).