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# Phosphorescence Bands of Quinones and $\alpha$-Diketones

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Phosphorescence bands, their life times, and the excitation spectra of anthraquinone, $\alpha$-naphthoquinone, phenanthrenequinone, acenaphthenequinone, benzophenone, benzil, furil, and camphorquinone at 77°K in a rigid solution and in the crystalline state have been studied. In a rigid solution the lifetimes of these phosphorescence bands are in the range (10—0.1 msec). The solvent effect on lifetimes shows clear differences between *o*- and *p*-quinones. The behavior of these phosphorescence bands is similar to that of the $n \rightarrow \pi^*$ bands of these compounds. From these facts, these bands are all safely identified as $\pi^* \rightarrow n$ bands. The phosphorescence bands of *p*-quinones in the crystalline state are at far longer wavelengths than those in a rigid solution, and the lifetimes of the former are far longer than those of the latter. The dichroism of excitation spectrum of the phosphorescence band of anthraquinone proved that the phosphorescence band is polarized perpendicularly to the 320 m$\mu$ band and parallel to the 270 m$\mu$ band.

Concerning the phosphorescence bands of quinones, anthraquinone has been stuided by many authors,[1,2] and recently the phosphorescence band of *p*-benzoquinone has been observed.[3,4] These phosphorescence bands have been identified as $\pi^* \rightarrow n$ bands from their positions, lifetimes, and vibrational structures.

However, there seem to be, on the whole, many unknown points about the phosphorescence bands of quinones. In this work the fundamental properties of the phosphorescence bands of quinones in a rigid solution and the crystalline state have been studied. For purposes of comparison, those of benzophenone and $\alpha$-diketones have also been studied.

## Experimental

**Measurements.** The phosphorescence spectra have been measured by an Aminco-Bowman spectrophotofluorometer equipped with a phosphoroscope accessory. This phosphoroscope accessory has a rotating shutter with a maximum speed of 3000 rpm. The grating of the emission monochrometer is of 1200 lines/mm, 500 m$\mu$ blaze, while that of the excitation monochrometer is of 600 lines/mm, 300 m$\mu$ blaze. The photomultiplier used is 1P28. As the light sources, a Hanovia xenon lamp and a Hanovia xenon mercury lamp of 150 W were used. The lifetimes of the phosphorescence bands were obtained by a combination of the rotating shutter and a synchroscope of the Iwasaki Tsusinki Co. (DS-5015). The dichroic excitation spectra were measured with Glan-Thomson prisms.

The solvents used were methylcyclohexane, a methanol-ethanol (1 : 4) mixture, a methylcyclohexane-toluene (2 : 1) mixture, and an ethyl ether - isopentane-ethanol (5 : 5 : 2) mixture.[5] The concentrations used ranged from $10^{-3}$ to $10^{-4}$ M. Measurements were carried out at the liquid nitrogen temperature (77°K) in air. The rigid solutions used were always transparent. As for the measurement in the crystalline state, the phosphorescence bands of crystalline powders were measured using capillary quartz cells as in a rigid solution.

**Materials.** In all the cases commercially-available reagents (except for $\beta$-naphthoquinone) were purified. Anthraquinone, 2-methyl-$\alpha$-naphthoquinone, phenanthrenequinone, benzophenone, benzil and furil were purified by recrystallization from organic solvents. Anthraquinone purified by zone refining was also used. $\alpha$-Naphthoquinone was purified according to Fieser's method.[6] $\beta$-naphthoquinone was prepared according to Fieser's method.[6] 1-Chlor-, 2-chlor- and 2-methyl-anthraquinones and acenaphthenequinone were purified by vacuum sublimation. The melting points of these purified samples all agreed with those reported in the literature.

As for the solvents, spectro-grade methylcyclohexane and methanol of the Tokyo Kasei Kogyo Co. were used without further purification. Toluene and ethyl ether of a special grade were dried over sodium and distilled. Aromatic impurities in commercially-available isopentane were removed with silica gel. After that the isopentane was distilled.

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1) M. Kasha, *Rad. Res. Suppl.*, **2**, 243 (1960); G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944).

2) D. N. Shygorin *et al.*, "Advances in Spectroscopy," Vol. 1 (1957), p. 672.

3) M. G. Jayswal and R. S. Singh, *Indian J. Pure & Appl. Phys.*, **2**, 358 (1964); *J. Mol. Spect.*, **17**, 6(1965); *Spectrochim. Acta*, **21**, 1597 (1965).

4) M. Koyanagi and Y. Kanda, Preprints for the 19th Annual Meeting of the Chemical Society of Japan (April, 1966), p. 153.

5) In the following, these four kinds of solvents are denoted as MeCH, alcohol, MeCH-toluene and EPA respectively.

6) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston (1941), pp. 230, 232 and 233.

## Results

The phosphorescence bands of quinones in a rigid solution and the crystalline state were shown in Figs. 1—4. The shapes of the phosphorescence bands of anthraquinone and α-naphthoquinone in MeCH-toluene are similar to those in alcohol. The phosphorescence band and its lifetime in anthraquinone in the crystalline state are identical in both the sample purified by recrystallization and that purified by zone refining. The phosphorescence band of phenanthrenequinone in the crystalline state is too weak to be measured accurately, but it appears that the peak of this phosphorescence band exists near 544 mμ and that its lifetime is *ca.* 5 msec. We have not yet succeeded in observing the phophorescence band of β-naphthoquinone. The phosphorescence bands of benzophenone and α-diketones are

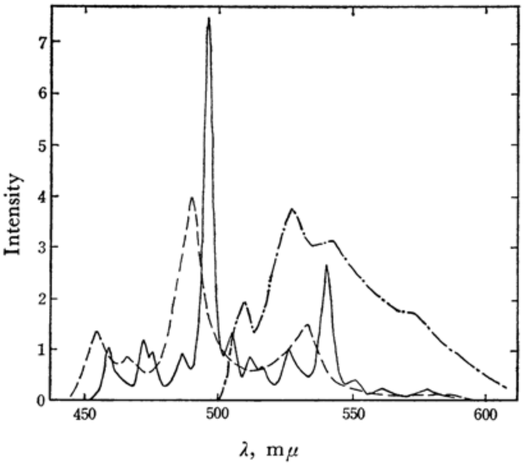

Fig. 1. Anthraquinone.
——— MeCH —·— Alcohol
— — — Cryst. state

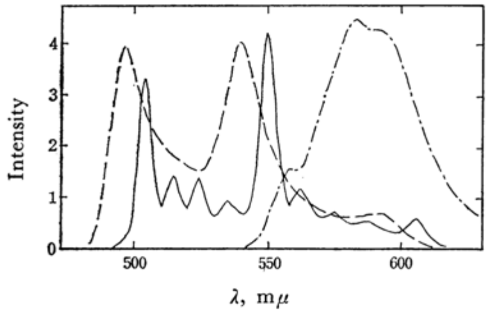

Fig. 2. α-Naphthoquinone.
——— MeCH —·— MeCH-tol.
— — — Cryst. state

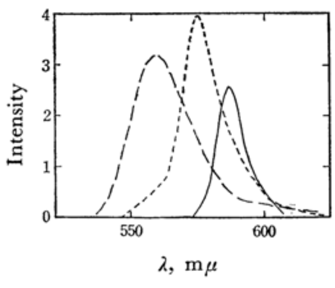

Fig. 3. Phenanthrenequinone.
——— MeCH —·— Alcohol
------ MeCH-tol.

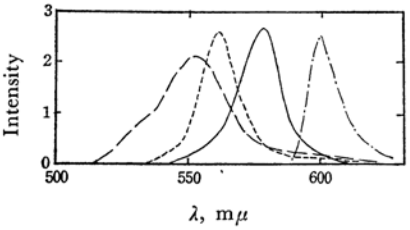

Fig. 4. Acenaphthenequinone.
——— MeCH —·— Alcohol
------ MeCH-tol. — — — Cryst. state

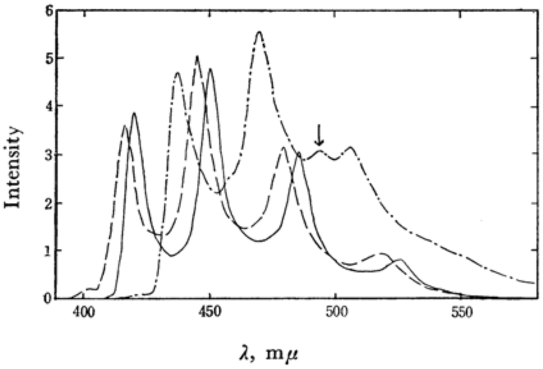

Fig. 5. Benzophenone.
——— MeCH —·— Alcohol
— — — Cryst. state

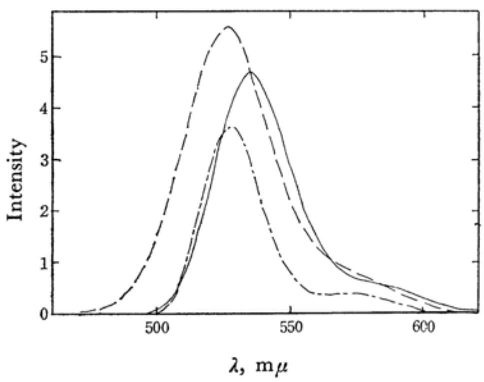

Fig. 6. Benzil.
——— MeCH —·— Alcohol
— — — Cryst. state

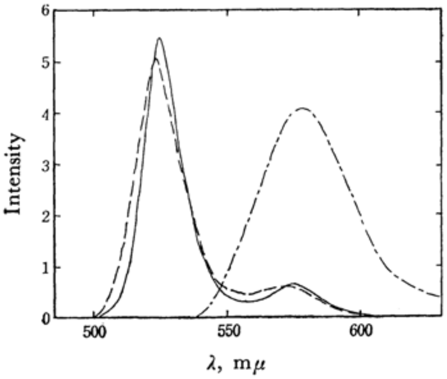

Fig. 7. Furil.

—— MeCH　　——— Alcohol

— — — Cryst. state

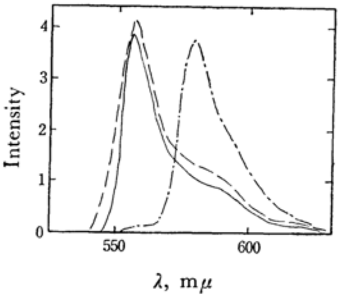

Fig. 8. Camphorquinone.

—— MeCH　　——— Alcohol

— — — Cryst. state

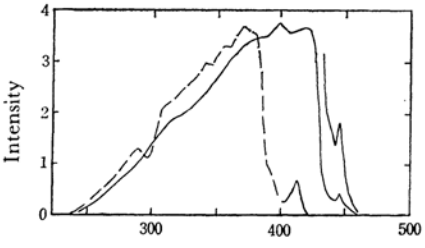

Fig. 9. Excitation spectra in cryst. state.

—— Anthraquinone

——— Benzophenone

shown in Figs. 5—8. The excitation spectra of the phosphorescence bands of anthraquinone and benzophenone in the crystalline state are shown in Fig. 9. The spectra are all uncorrected for the response of the photomultiplier and the energy distribution of the xenon lamp.[7] In all the figures the scales of the ordinates are arbitrary. The peak wavelengths of the phosphorescence bands are shown in Table 1. The wavelengths of the main peaks are described with Gothic letters, while the wavelengths in brackets are those of shoulders. The accuracy of these wavelengths is within 1 m$\mu$.

The obtained lifetimes of the phosphorescence bands are shown in Table 2. The reproducibility of the lifetimes is within 20 percent. The lifetime, in Table 2, of benzophenone in EPA agrees with that reported by Gilmore *et al.*[8] The lifetime, in Table 2, of benzophenone in the crystalline state is that at the shorter wavelength peak (434.5 m$\mu$), and the decay curves at the longer wavelength peaks show that two phosphorescence bands overlap, one of them with a short lifetime similar to that at the above shorter wavelength peak, and the other one with a far longer lifetime.

The dichroism of the excitation spectrum of the phosphorescence band of anthraquinone in alcohol was also measured. The degrees of polarization at the excitation peaks (at 333 m$\mu$ and 280 m$\mu$) for the phosphorescence peak were $-0.24$ and 0.33 respectively. These values were obtained using Azumi-McGlynn's formula.[9]

## Discussion

From the obtained results in a rigid solution, the following distinct facts are found.

1) The lifetimes of phosphorescence bands of quinones are very short (10—0.1 msec) in comparison with those of aromatic hydrocarbons,[10] though it is noticeable that the lifetime of the phosphorescence band of acenaphthenequinone is considerably longer than those of the others. The chlorine-atom substitution effect for the lifetime of the phosphorescence band of anthraquinone is very small in comparison with the case of aromatic hydrocarbons[10] (Table 2.)

2) As for solvent effect on the lifetime, in *o*-quinones (phenanthrenequinone and acenaphthenequinone) the lifetimes in alcohol are longer than those in MeCH and those in MeCH-toluene are between them, but with the *p*-quinones (anthraquinone and $\alpha$-naphthoquinone) those in MeCH and alcohol are nearly equal and smaller than that in MeCH-toluene. Those of benzophenone, benzil, and furil in MeCH and alcohol are nearly equal, and that of camphorquinone in MeCH is longer than that in alcohol (Table 2).

3) The shortest-wavelength peak of the phosphorescence band of *p*-benzoquinone in the gaseous state is at 535 m$\mu$.[3] On the other hand, those of $\alpha$-naphthoquinone and anthraquinone in MeCH are at 504 and 459 m$\mu$ respectively. In view of these facts, it is thought that the energy difference between the ground state and the lowest triplet

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[7] C. E. White, M. Ho and E. Q. Weimer, *Anal. Chem.*, **32**, 438 (1960).

[8] E. H. Gilmore, G. E. Gibson and D. S. McClure, *J. Chem. Phys.*, **20**, 829 (1952).

[9] T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **37**, 2413 (1962).

[10] D. S. McClure, *ibid.*, **17**, 905 (1949).

TABLE 1. PEAK WAVELENGTHS OF THE PHOSPHORESCENCE BANDS

| | MeCH | Alcohol | MeCH-tol. | EPA | Cryst. st. |
|---|---|---|---|---|---|
| Anthraquinone | **459**, 472, 475.5<br>486.5, **496**<br>504.5, 512, 527<br>**540**, 594 (m$\mu$) | **453.5**, 465<br>**489**, **532.5** | **455**, 468<br>**490.5**, 520.5<br>**533.5** | **457**, 469.5<br>**492.5**, 523.5<br>**535** | **510.5**, 524<br>**528.5**, 540.5<br>(572) |
| $\alpha$-Naphthoquinone | **504**, 515, 524.5<br>535, **550**, 562<br>575, 588, 605 | **498**, **540**<br>(593) | **496.5**, **540**<br>592 | | (557), **583**<br>(594) |
| Phenanthrenequinone | **586** | **558** | **575** | | |
| Acenaphthenequinone | **578** | **552** | **561.5** | | **599** |
| Benzophenone | **419.5**, **449.5**<br>**485**, 526 | **415**, **445**<br>**479**, 519 | | **416**, **445.5**<br>**479**, 518 | **434.5**, **468**<br>491.5, **504** |
| Benzil | **535**, (~590) | **526** | | | **527**, 574 |
| Furil | **525**, 576 | **524**, 572 | | | **578.5** |
| Camphorquinone | **557**, (~589) | **557.5**, (~587) | | | **579.5** |

TABLE 2. LIFE TIMES OF THE PHOSPHORESCENCE BANDS

| | MeCH | Alcohol | MeCH-tol. | EPA | Cryst. st. |
|---|---|---|---|---|---|
| Anthraquinone | 3.3 (msec) | 3.3 | 6.3 | 3.5 | 100 |
| $\alpha$-Naphthoquinone | 0.5 | 0.5 | 1.1 | | 13 |
| 2-Methyl-$\alpha$-naphthoquinone | | 1.7 | | | |
| Phenanthrenequinone | 4.5 | 9 | 7.5 | | |
| Acenaphthenequinone | 13 | 18 | 15 | | 4.3 |
| 1-Chloranthraquinone | 3.8 | | | | |
| 2-Chloranthraquinone | 3.2 | | | | |
| 2-Methylanthraquinone | 4.6 | | | | |
| Benzophenone | 5.2 | 5.5 | | 6.0 | 7.2 |
| Benzil | 5.1 | 5.6 | | | 4.1 |
| Furil | 4.6 | 5.6 | | | 5.9 |
| Camphorquinone | 2.5 | 1.6 | | | 1.0 |

state of *p*-quinones in the gaseous state is in the order of *p*-benzoquinone < $\alpha$-naphthoquinone < anthraquinone (Table 1).

4) In all cases except camphorquinone, the phosphorescence bands in MeCH are at longer wavelengths than those in other solvents, but this solvent shift of the phosphorescence bands in *o*-quinones is far greater than that in *p*-quinones (Figs. 1—8 and Table 1).

5) The phosphorescence bands of *p*-quinones show relatively sharp vibrational structures. The intervals of the main vibrational sequences in *p*-quinones, benzophenone, benzil, and furil are 1600—1700 cm$^{-1}$, but that of camphorquinone is *ca.* 980 cm$^{-1}$ (Figs. 1—8 and Table 1).

Of the facts mentioned above, (1) coincides with the characteristics of the carbonyl $\pi^* \rightarrow n$ phosphorescence band.[1,10-15] Furthermore, (3), (4), and the fact in (5) that the main vibrational sequences in *p*-quinones, benzophenone, benzil, and furil are those of the carbonyl C-O stretching vibration coincide with the characteristics of the $n \rightarrow \pi^*$ bands of these compounds.[13-17] In camphorquinone, the positions[18] of the $n \rightarrow \pi^*$ band in saturated hydrocarbons and in alcohol at room temperature are close to each other, as in the phosphorescence band. The vibrational sequence of the phosphorescence band of camphorquinone is thought to be approximately that of the stretching vibration of the bond between two

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[11] M. A. El-Sayed, *ibid.*, **41**, 2462 (1964).
[12] D. R. Kearns and W. A. Case, *J. Am. Chem. Soc.*, **88**, 5087 (1966).
[13] J. Sidman, *Chem. Revs.*, **58**, 689 (1958).
[14] S. K. Lower and M. A. El-sayed, *ibid.*, **66**, 199 (1966).
[15] F. Dörr, *Zeit. Elektrochem.*, **61**, 950 (1957); Y. Kanda, H. Kaseda and T. Matumura, *Spectrochim. Acta*, **20**, 1387 (1964); M. Akagi, Y. Amako and H. Azumi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 61 (1966).
[16] R. Shimada, *Spectrochim. Acta*, **17**, 14, 30 (1961).
[17] A. Kuboyama, This Bulletin, **33**, 1027 (1960); *ibid.*, **35**, 295 (1962); *Rep. Gov. Chem. Ind. Res. Inst., Tokyo*, **57**, 541 (1962); *ibid.*, **59**, 347 (1964).
[18] R. A. Ford and F. Parry, *Spectrochim. Acta*, **12**, 78 (1958); A. Kuboyama and S. Yabe, Preprints for the Symposium on Structural Chemistry (Osaka, 1966), p. 89.

adjacent carbonyl carbon atoms.[19,20] Therefore, the phosphorescence bands in a rigid solution may all safely be identified as $\pi^* \rightarrow n$ bands. Therefore, it may be concluded that the lowest triplet states of these quinones and $\alpha$-diketones in the rigid glass states are the $(n, \pi^*)$ state.

The differences between the energies of the phosphorescence bands of quinones in MeCH and those in MeCH-toluene are thought to be mainly due to the charge transfer interaction between quinones and toluene in MeCH-toluene.

As for the phosphorescence bands in the crystalline state, those of anthraquinone and $\alpha$-naphthoquinone are at far longer wavelengths than those in MeCH and have no distinct progression corresponding to the carbonyl C-O stretching vibration, as Figs. 1 and 2 show. The lifetimes of these bands are far longer than those in rigid solutions. These $p$-quinones are classified as group I for convenience. On the other hand, in all other compounds except for benzophenone and furil the positions, shapes, and lifetimes of the phosphorescence bands in the crystalline state are rather similar to those in a rigid solution, though it is noticeable that in acenaphthenequinone the lifetime in the crystalline state is considerably shorter than those in a rigid solution. These compounds are classified as group II for convenience. The above classification seems to be analogous to that of fluorescence bands in crystalline aromatic hydrocarbons reported by Stevens.[21] Groups I and II correspond to types B and A respectively in Stevens' paper,[21] although the parallel, sandwich-like pairs of molecules he observed in the crystals of type B are not observed in the case of group I.[21,22] The electronic transitions in the phosphorescence bands of group II in the crystalline state are thought to be similar to those in rigid solutions. The possibility that the phosphorescence bands of group I in the crystalline are due to impurities is thought to be obviated by the fact that the phosphorescence band of anthraquinone in the crystalline state is identical in both the sample purified by recrystallization and that purified by zone refining. At this stage it is uncertain whether the phosphorescence bands of group I in the crystalline state are essentially of the $\pi^* \rightarrow n$ type or of the $\pi^* \rightarrow \pi$ type. Further studies of these phosphorescence bands by the authors are now in progress.

As for the phosphorescence band of benzophenone in the crystalline state, as is shown in Fig. 5, the phosphorescence band has sharp peaks similar to that in a rigid solution, and a broad peak seems to overlap those sharp peaks in the long-wavelength region. This is consistent with the findings about the decay curves described above. Therefore, the lifetime of the sharp phosphorescence band is nearly equal to those in rigid solutions and that of the broad phosphorescence band is far longer than that of the sharp phosphorescence band. The peak which is denoted with an arrow in Fig. 5 is thoght to be that of this broad phosphorescence band. These sharp and broad phosphorescence bands are thought to be essentially identical with the so-called blue and green emission bands[14,23] respectively. Benzophenone is classified into group II in regard to the sharp phosphorescence band. As for the broad phosphorescence band, it remains unexplained whether or not it is due to some impurity. In furil, the phosphorescence band in the crystalline state is at far longer wavelengths than those in rigid solutions,[24] but its lifetime in the crystalline state is nearly equal to those in rigid solutions. Therefore, it seems difficult to apply the above classification to furil.

In the excitation spectra of the phosphorescence bands of anthraquinone and benzophenone in the crystalline state, as Fig. 9 shows, sharp peaks are observed on the longest-wavelength sides (at 445 m$\mu$ in anthraquinone and 412 m$\mu$ in benzophenone). The gaps between the above excitation peaks and the shortest-wavelength peaks of the phosphorescence bands in the crystalline state are 2100 cm$^{-1}$ in anthraquinone and 1280 cm$^{-1}$ in benzophenone. These peaks are thought to correspond to the $n \rightarrow \pi^*$ singlet-triplet absorption peaks.[12,25]

From the results obtained concerning the dichroism of the excitation spectrum of the phosphorescence band of anthraquinone, it is determined that the phosphorescence band is polarized perpendicularly to the 320 m$\mu$ band and parallel to the 270 m$\mu$ band.

The authors wish to thank Mr. H. Tomita of this Institute for offering anthraquinone purified by zone refining.

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[19] C. L. Carpenter, Jr., and L. S. Forster, *J. Phys. Chem.*, **62**, 874 (1958).

[20] T. Miyazawa, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **75**, 86 (1954); A. Kuboyama, Preprints for Symposium on Structural Chemistry (Nagoya, 1965), p. 1.

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[22] B. V. R. Murty, *Zeit. Krist.*, **113**, 445 (1960); J. Gaultier and C. Hauw, *Acta Cryst.*, **18**, 179 (1965).

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[24] The positions of the $n \rightarrow \pi^*$ bands of furil and anthraquinone in crystalline state are near those in solution at room temperature respectively.

[25] W. Rothman, A. Case and D. R. Kearns, *J. Chem. Phys.*, **43**, 1067 (1965); N. Hirota, *J. Chem. Phys.*, **43**, 2199 (1965).