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The Ultraviolet Absorption Spectrum of Quinazoline Vapor Due to the n–π^* Transition

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The ultraviolet absorption spectrum of quinazoline vapor due to the n–π^* transition was photographed and analysed. The lowest n–π^* transition has its origin at 27581 cm^{-1}, and consists of two strong and prominent progressions, 515 and 784 cm^{-1}. The vibrational analysis of the strong bands is reported on.

The visible and ultraviolet absorption spectra of azanaphthalenes in solutions have been reported on by Hirt *et al.*,(1) Mason,(2,3) Favini *et al.*,(4) Müller and Dörr,(5) and Wait and Grogan.(6) In general, the weak bands at the longest wavelength in their spectral measurements have been assigned to the n–π^* transitions, on the basis of their blue shift in polar solvents, while the much stronger bands at the shorter wavelength have been assigned to the lowest π–π^* transitions, similar to the 3200 Å system of naphthalene.

The n–π^* and the lowest π–π^* absorption spectra of cinnoline(1,2-diazanaphthalene) vapor have been reported on by Wait and Grogan.(6) It has been found that the n–π^* transition of cinnoline has its origin at 22711 cm^{-1}, and that the vibronic structure of the n–π^* transition consists primarily of a strong prominent progression of 516.0 cm^{-1}, upon which singly-excited vibrations are superimposed, while the lowest π–π^* transition has its origin at 31542 cm^{-1}.

The n–π^* absorption spectrum of quinoxaline-(1,4-diazanaphthalene) vapor has been observed by Ito and Shiratsuchi(7) and by the present authors(8) independently. They all observed that the n–π^* absorption bands of quinoxaline consists of two band systems, one sharp and one broad band system. The broad bands have their origin at 26017 cm^{-1}, and the 525 cm^{-1} progression with the origin is very prominent. On the other hand, the sharp bands have strong false origins at 27496 and 27670 cm^{-1}, and also the 525 cm^{-1} progressions are very prominent.*[2]

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2) S. F. Mason, *Chem. Soc. (London), Spec. Publ.*, **3**, 139 (1955).

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4) G. Favini, S. Carro, V. Pierpaoli, S. Polezzo and M. Simonetta, *Nuovo Chimento*, **8**, 60 (1958).

5) R. W. Müller and F. Dörr, *Z. Elektrochem.*, **63**, 1150 (1959).

6) S. C. Wait, Jr., and F. M. Grogan, *J. Mol. Spectry.*, **24**, 383 (1967).

7) M. Ito and Y. Shiratsuchi, Private communcication.

8) Y. Hasegawa, Y. Amako and H. Azumi, The lecture at the 21st Annual Meeting of the Chemical Society of Japan, 1968.

*[2] Further work on quinoxaline is now in progress by Ito and Shiratsuchi and by the present authors.

The present authors have previously assigned the broad band system to the allowed n–π^* transition and the sharp band system to the "forbidden"[9,10] bands in the allowed n–π^* transition.

The electronic absorption spectra of the other azanaphthalenes in the vapor phase have never been reported on. The present investigation is concerned with the n–π^* absorption spectrum of quinazoline(1,3-diazanapthalene) vapor.

Experimental

The vapor spectrum of quinazoline was photographed with a Shimadzu Littrow quartz spectrograph with a dispersion of 8.9 Å/mm at 3700 Å, and with a Shimadzu GE-100 grating spectrograph (Ebert type) with a dispersion of 2.7 Å/mm in the third order. The bands were measured on microphotometer tracings of the plates. The wavelength calibration was made by an iron arc. The wavelengthes of the bands were converted into frequencies *in vacuo*. The frequencies are estimated to be accurate about $\pm 2\ \mathrm{cm}^{-1}$ for the strong bands, and to about $\pm 5\ \mathrm{cm}^{-1}$ for the weak and broad bands. The light source was a 500 W Xenon arc lamp. A Toshiba UV-D2 filter was used to eliminate all the radiation in the higher orders and lower orders. The absorption cell with quartz windows was helically wound with Nichrome wire over an asbestos sheet and covered with an asbestos sheet. The light-pass length of the absorption cell was 60 cm. The cell temperature could be regulated between room temperature and 250°C. The solution spectrum of quinazoline was obtained using a Cary automatic recording spectrometer, Model 14.

The quinazoline used in this study was prepared by following the method described by Riedel[11] and by Bogert and McColm[12]; it was recrystallized repeatedly, and finally sublimated before the experiment. The n-hexane was purified according to the procedure described by Morgan and Lowry.[13]

Results and Discussion

The ultraviolet absorption spectra of quinazoline have been reported on in solutions of heptane, ethanol, and an acidic solvent by Müller and Dörr,[5] and in a solution of cyclohexane by Mason.[3] The 3650 Å band system has been assigned to the n–π^* transition, and the 3100 Å band system, to the lowest π–π^* transition. The results of the present investigation in n-hexane are shown in Fig. 1, which corresponds well to that in heptane reported by Müller and Dörr.

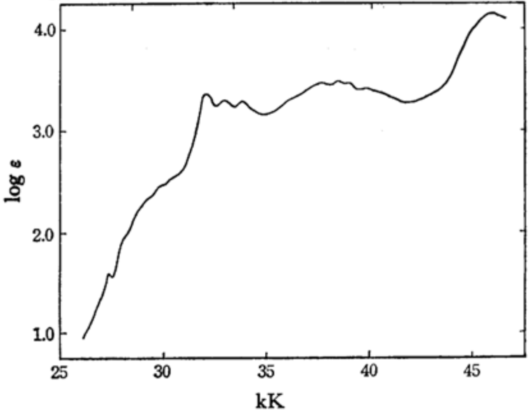

Fig. 1. The ultraviolet absorption spectrum of quinazoline in n-hexane.

The n–π^* absorption spectrum of quinazoline vapor under a low dispersion consists of a number of band groups. Each of the strong band groups under a moderate dispersion consists of a principal band and of associated $15\ \mathrm{cm}^{-1}$ sequence bands, which appear with up to two or three members.

The n–π^* absorption spectrum of quinoxaline vapor has been observed by Ito and Shiratsuchi and by the present authors, as has been stated above. The spectrum consists of two systems, one sharp and one broad, as is shown in the Plate. The n–π^* absorption spectrum of quinazoline vapor, however, does not show such two band systems.

The vibronic structure shown in Fig. 2 consists of three progressions with their origins[*3] at 27581 cm^{-1}; the members are separated by 515, 784, and 879 cm^{-1} respectively. On their progressions are superimposed a number of singly-, doubly- or triply-excited vibrations. The band at 27581 cm^{-1}, which is the first member of their progressions, was assigned to the 0–0 band. The frequecies and assignments of the principal bands are shown in Table 1. No bands could be observed below 27494 cm^{-1}, and so the frequencies corresponding to the ground state vibrations could not be obtained.

The quinazoline molecule has two nitrogen atoms in the "meta" position of the naphthalene-like ring, and belongs to the C_s point group in the ground state. Because of the interaction between the respective nonbonding orbitals of these nitrogen atoms,[14-16] two allowed n–π^* transitions of the $^1A' \rightarrow {}^1A''$ type may be expected to appear. However, no suggestion with respect to the "n–π^*

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[9] A. C. Albrecht, *J. Chem. Phys.*, **33**, 156 (1960).
[10] A. C. Albrecht, *ibid.*, **33**, 169 (1960).
[11] J. D. Riedel, *Chem. Zentr.*, **1906** II, 1372.
[12] M. T. Bogert and E. M. McColm, *J. Am. Chem. Soc.*, **49**, 2650 (1927).
[13] S. O. Morgan and H. H. Lowry, *J. Phys. Chem.*, **34**, 2385 (1930).

[*3] With moderate dispersion the origin shows several broad structures, probably due to its sequence bands. Unfortunately, under the conditions used, they do not have intensities sufficient for definite assignments to be made. Therefore, the apparenly strongest peak on the microphotometer tracing was taken as the 0–0 band, which might be one of the sequences of the true origin.

[14] S. F. Mason, *J. Chem. Soc.* (*London*), **1959**, 1240.
[15] L. Goodman, *J. Mol. Spectry.*, **6**, 109 (1961).
[16] K. K. Innes, J. P. Byrne and I. G. Ross, *ibid.*, **22**, 125 (1967).

TABLE. 1. FREQUENCIES AND ASSIGNMENTS OF PRINCIPAL BANDS

Wave numbers (cm^{-1})	Intensities	Differences (from 0-0)	Assignments (cm^{-1})	Differences (from cald. value)
27494	w	−87	0−87	0
27581	s	0	origin	0
27632*	vw	51	(0+51)	0
27834	vw	253		
27883*	vw	302		
27941*	vw	360	(0+360)	0
27976	w	395	(0+395)	0
28007	w	426	0+515−87	−2
28096	s	515	0+515	0
28147	w	566	(0+51+515)	0
28213	w	632	0+632	0
28365	vs	784	0+784	0
28460	s	879	0+879	0
28501*	vw	920	(0+395+515)	+10
28522*	vw	941	0+2×515−87	−2
28613	s	1032	0+2×515	+2
28668*	vw	1087	(0+51+2×515)	+6
28727	vw	1146	(0+632+515)	−1
			or (0+360+784)	+2
28753	vw	1172	(0+395+784)	−7
28787*	vw	1206	(0+784+515−87)	−6
28869	vs	1288	0+784+515	−11
28933	w	1352	(0+51+515+784)	+2
28974	s	1393	0+879+515	−1
29025	w	1444	(0+1444)	0
29153	s	1572	0+2×784	+4
29242	vs	1661	0+879+784	−2
29346*	m	1765	0+2×879	+7
29382*	s	1801	0+784+2×515	−13
29446	vw	1865	(0+51+2×515+784)	0
29493	m	1912	0+879+2×515	+3
29649	vs	2068	0+2×784+515	−15
29751	vs	2170	0+879+784+515	−8
29804*	vw	2223	(0+1444+784)	−5
29860*	w	2279	0+2×879+515	+6
29897*	w	2316	0+784+3×515	−13
30028	s	2447	0+879+2×784	0
30154*	s	2573	0+2×784+2×515	−25
30267	s	2686	0+879+784+2×515	−7
30529	s	2948	0+879+2×784+515	−14

a) Symbol * denotes that the corresponding frequencies are accurate to about 5 cm^{-1}.
b) Usual abbreviation for intensities is taken as; v=very, w=weak, m=moderate and s=strong.
c) The assignments shown by parenthesis are less certain.

splitting" could be obtained under the experimental conditions used; further studies under better conditions will be necessary.

The totally symmetric vibrational intervals, 515 and 784 cm^{-1}, are very prominent. Superimposed on 0–0, 0+879 cm^{-1} and other bands, the 515 and 784 cm^{-1} progressions appear with up to two or three members. According to Wait and Grogan,[6] the interval, 516.0 cm^{-1}, in the n-π^* transition of cinnoline is very prominent. The interval, 525cm^{-1}, in the n-π^* transition of quinoxaline is also very prominent, as has been mentioned above. This normal mode of quinazoline with the 515 cm^{-1} frequency probably corresponds to the same type of mode of cinnoline and quinoxaline with frequencies of 516.0 and 525 cm^{-1} respectively.

In the case of azines,[15,16] the ring breathing vibrations of ~900 cm^{-1} dominate the progressions

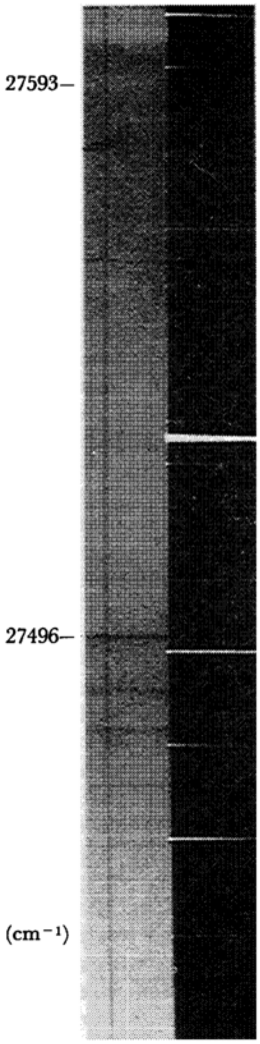

Plate. The two different band systems in the n-π^* absorption spectrum of quinoxaline vapor.
(a) the ▲ broad band at 27593 cm^{-1}
(b) the ▼▲ sharp band at 27496 cm^{-1}

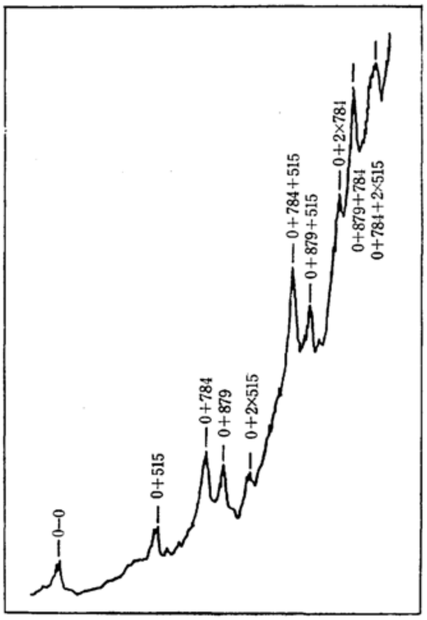

Fig. 2. The microphotometer tracing of the n-π^* absorption spectrum of quinazoline vapor (cm^{-1}).

in the π-π^* transitions, while the ring angle bending modes, notably the ν_{6a} of ~600 cm^{-1}, are prominent in the n-π^* transitions. These normal modes of the n-π^* states of these three diazanaphthalenes with ~520 cm^{-1} are probably ring angle bending modes, or ring deformation modes. The other prominent frequency, 784 cm^{-1}, will be a skeletal stretching mode.

At the present time no further detailed attempts to assign these and other frequencies have been carried out for lack of experimental data.

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