Electronic States of p-Benzoquinone. VIII. Vibrational Analysis of the Vapor Absorption Spectrum around 2900 Å

By Akira SADÔ

(Received July 26, 1961)

In Part VII⁽¹⁾ of series, the present author showed that the absorption spectrum around 2900 Å of the *p*-benzoquinone molecule due to the $^1B_{1g}\leftarrow{}^1A_g$ (π-π) transition. This transition is forbidden by molecular symmetry but allowed through vibronic interaction with the allowed $^1B_{2u}\leftarrow{}^1A_g$ transition. For this interaction, the perturbing vibration is almost b_{3u} C=O bending vibration only. Solvent effect study⁽²⁾ revealed that this absorption spectrum is due to a π-π ($^1B_{1g}\leftarrow{}^1A_g$) transition. In Parts I and II⁽³,⁴⁾, the author has calculated the energy levels of this molecule and shown that there are three transitions, ^1A_u, $^1B_{2g}$ and $^1B_{1g}\leftarrow{}^1A_g$, which are superposed in this region.

The vapor spectrum in this region has been studied by Light⁽⁵⁾ and by Seshan⁽⁶⁾. Light observed 21 bands. Seshan observed 32 bands between 3145∼2530 Å and represented them by the following formula:

$$\nu=31780+450n-230p \qquad (1)$$

where n and p are integers, n, running $0\sim17$, and $p=0$ or 1. However, nothing was mentioned in his paper as to the nature of the electronic transition concerned.

In order to clarify the nature of the absorption band of *p*-benzoquinone around 2900 Å, the vibrational analysis of vapor spectrum of this molecule has now been investigated.

Experimental

The sample of *p*-benzoquinone from hydroquinone was prepared in the same manner as in Part V⁽⁷⁾. The spectrum was taken on a "Fuji process" plate. The spectrograph used was a quartz spectrograph whose dispersion was 7 Å/mm. at 3000 Å. The absorption cell with quartz windows was 40 cm. long; to it a small side tube was attached. The sample was immediately placed in the side tube, and the absorption cell was evacuated, while its side arm was being cooled by using a freezing mixture of ice and sodium chloride to prevent the *p*-benzoquinone sample from sublimation, and sealed off. The temperature of the absorption cell was controlled between 40 and 120°C in a manner described elsewhere⁽⁸⁾.

Results

The absorption spectrum of *p*-benzoquinone in the region between 2580∼3290 Å appears at a lower temperature than that in the 4500 Å region. The microphotometer tracing curves of the spectrograms of this molecule is shown in Fig. 1, while Table I contains the measured frequencies and relative intensities of the main absorption bands, together with their interpretations. We have obtained about eightly bands. From a comparison of this table with Table I in Seshan's paper⁽⁶⁾, it can be seen that the present observation corresponds with region II of his work and that

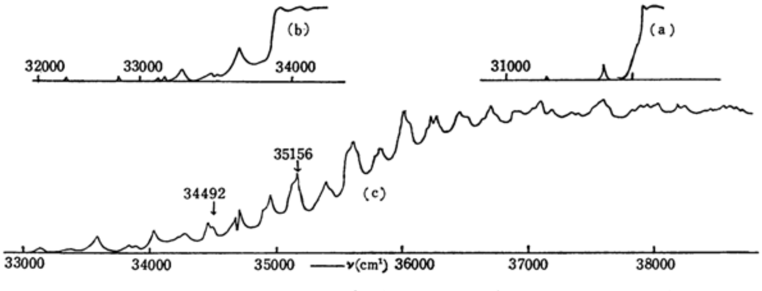

Fig. 1. Microphotometer tracing curves of the absorption spectrum of *p*-benzoquinone vapor; (a) 120°C, (b) 100°C, (c) 90°C.

---

1) A. Sadô, This Bulletin, **35**, 1514 (1962).

2) S. Nagakura and A. Kuboyama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **74**, 499 (1953); *J. Am. Chem. Soc.*, **76**, 1003 (1954).

3) T. Anno, I. Matubara and A. Sadô, This Bulletin, **30**, 168 (1957).

4) T. Anno, A, Sadô and I. Matubara, *J. Chem. Phys.*, **26**, 967 (1957).

5) L. Light, *Z. physik. Chem.*, **122**, 414 (1926).

6) P. K. Seshan, *Proc. Ind. Acad. Sci.*, **3A**, 172 (1936).

7) T. Anno and A. Sadô, *J. Chem. Phys.*, **32**, 1602 (1960).

8) T. Anno and I. Matubara, ibid., **23**, 796 (1955).

Table I. Absorption bands of *p*-benzoquinone vapor

Wave number cm^{-1}	Intensity[a)]	Assignment
		$t=120$°C
31 329	w	ν_{I}
778	m	$\nu_{\mathrm{I}}+450$
32 042	w	$0+\nu'-7\times444-45$
091	w	$0+\nu'-7\times444$
218	s	$\nu_{\mathrm{I}}+2\times450$
		$t=90$°C
32 218	w	$\nu_{\mathrm{I}}+2\times450$
676	w	$\nu_{\mathrm{I}}+3\times450$
937	vw	$0+\nu'-5\times444-45$
976	vw	$0+\nu'-5\times444$
33 128	m	$\nu_{\mathrm{I}}+4\times450$
367	w	$0+\nu'-4\times444-45$
414	w	$0+\nu'-4\times444$
587	s	$\nu_{\mathrm{I}}+5\times450$
804	w	$0+\nu'-3\times444-45$
833	w	$0+\nu'-3\times444$
34 032	s	$\nu_{\mathrm{I}}+6\times450$
		$t=60$°C
33 128	vw	$\nu_{\mathrm{I}}+4\times450$
587	vw	$\nu_{\mathrm{I}}+5\times450$
804	vw	$0+\nu'-3\times444-45$
833	vw	$0+\nu'-3\times444$
34 032	w	$\nu_{\mathrm{I}}+6\times450$
228	vw	$0+\nu'-2\times444-45$
272	vw	$0+\nu'-2\times444$
406	vw	
472	w	$0-\nu''-45$
492	w	$0-\nu''$
674	w	$0+\nu'-444-45$
712	w	$0+\nu'-444$
840	vw	
899	w	$0-\nu''+435-45$
939	m	$0-\nu''+435$
35 099	vw	
111	w	$0+\nu'-45$
156	m	$0+\nu'$
340	w	$0-\nu''+2\times435-45$
390	w	$0-\nu''+2\times435$
444	vw	
558	m	$0+\nu'+435-45$
591	m	$\begin{cases}0+\nu'+435\\0-\nu''+692+435-45\end{cases}$
630	m	$0-\nu''+692+435$
804	w	$0+\nu'+692-45$
35 841	w	$0+\nu'+692$
		$t=60$°C (Continued)
36 024	m	$\begin{cases}0+\nu'+2\times435\\0-\nu''+1560-45\end{cases}$
067	w	$0-\nu''+1560$
238	w	$0+\nu'+1560-444-45$
281	w	$\begin{cases}0+\nu'+1560-444\\0-\nu''+2\times692+435-45\end{cases}$
320	w	$0-\nu''+2\times692+435$
424	vw	
466	m	$0-\nu''+1560+435-45$
511	w	$0-\nu''+1560+435$
629	vw	
678	m	$0+\nu'+1560-45$
708	m	$\begin{cases}0+\nu'+1560\\0-\nu''+1560+692-45\end{cases}$
754	w	$0-\nu''+1560+692$
880	w	$0-\nu''+1560+2\times435-45$
910	vw	
922	w	$0-\nu''+1560+2\times435$
970	w	$0+\nu'+1125$
37 034	vw	
065	m	$0+\nu'+1560+435-45$
118	s	$0+\nu'+1560+435$
139	s	$0-\nu''+1560+692+435-45$
199	m	$0-\nu''+1560+692+435$
362	m	$0+\nu'+1560+692-45$
411	m	$0+\nu'+1560+692$
508	m	$0+\nu'+1560+2\times435-45$
550	s	$0+\nu'+1560+2\times435$
583	s	$0-\nu''+2\times1560-45$
632	m	$0-\nu''+2\times1560$
810	m	$0+\nu'+1560+692+435$
836	w	$0-\nu''+1560+2\times692+435-45$
891	w	$0-\nu''+1560+2\times692+435$
938	w	$0+\nu'+1560+3\times435-45$
38 026	m	$0+\nu'+1560+3\times435$
196	w	$0+\nu'+2\times1560-45$
244	w	$0+\nu'+2\times1560$
391	w	
441	vw	
469	vw	
562	vw	
613	w	$0+\nu'+2\times1560+435-45$
658	w	$0+\nu'+2\times1560+435$
717	w	$0-\nu''+2\times1560+692+435-45$
763	vw	$0-\nu''+2\times1560+692+435$

a) v=very, w=weak, m=medium, s=strong

the main bands agree with those reported by him, although his one band is resolved into several components. Moreover, we can classify the bands into two groups by their characters. One of the two groups (group 1) consists of sharp and single bands and corresponds to Sidman's (d) band[9)] observed for a crystalline sample. The other band group (group 2)

[9)] J. W. Sidman, *J. Am. Chem. Soc.*, **78**, 2363 (1956); *J. Chem. Phys.*, **27**, 820 (1957).

consists of broad bands, each of which has two components, the frequency separation being 45 cm^{-1}

Analysis and Discussion

We have shown[3,4] that, if the *p*-benzoquinone molecule belongs to the V_h point group[10,11], three transitions (^1A_u, $^1B_{2g}$ and $^1B_{1g}\leftarrow{}^1A_g$) are superimposed in this region, and that these transitions are all forbidden by molecular symmetry but allowed through vibronic interaction with allowed $^1B_{2u}\leftarrow{}^1A_g$ transition[3,4]. If this assignment is correct, the spectrum should appear with the transition moment along the molecular axis (connecting two oxygen atoms). This is in agreement with the spectroscopic studies of crystalline *p*-benzoquinone by Fixl and Schauenstein[12], by Brand and Goodwin[13] and by Sidman[9]. The perturbing state and perturbing vibration in this case, are shown in Table II.

TABLE II. COMBINATIONS OF PERTURBED AND PERTURBING STATES OF *p*-BENZOQUINONE

Perturbing state	Perturbing vibration	Perturbed state
B_{2u}	b_{2g}	A_u
	a_u	B_{2g}
	b_{3u}	B_{1g}

In the first place, we will consider group 2. The band at 35156 cm^{-1} is taken as the origin of the analysis, which corresponds to the transition from the vibrationless ground state to the electronic excited state upon which a perturbing vibration is suberimposed by one quantum ($0+\nu''$). This band is the origin of two progressions: one has a frequency separation of 444 cm^{-1} for a long wavelength, and the other has a frequency separation of 435 cm^{-1} for a short wavelength. They may be totally symmetric vibration frequencies in the ground and excited electronic states, as will be discussed later. Similarly, the band at 34492 cm^{-1} is the transition from the ground state upon which a perturbing vibration is superimposed by one quantum to the vibrationless electronic excited state ($0-\nu'$). The difference between the two bands is 665 cm^{-1}, and the frequencies of the perturbing vibration may be 250~400 cm^{-1}. From Table IV in Part IV of this series[14] and Table II here, the C=O bending vibration belonging to the b_{3u} species whose frequency is 370 cm^{-1} may be considered to be the perturbing vibration. This result is consistent with the absorption intensity calculation[1]. Therefore, the absorption bands of group 2 can be assigned to the $^1B_{1g}\leftarrow{}^1A_g$ transition.

The observed frequencies forming the main progressions are shown in Table III and are compared with the data of the Raman spectrum and the data from the 4500 Å region absorption. The obtained frequencies, 444 in the ground state and 435, 692 and 1560 cm^{-1} in the excited state, are assigned to the a_g vibration. The 435, 692 and 1560 cm^{-1} frequencies in the excited state may correspond to the ground state frequencies of 444, 770 and 1667 cm^{-1}.

We have not been able to observe that band corresponding to the transition from the ground state in which both the perturbing vibration and the (totally symmetric) 444 cm^{-1} vibration are excited by one quantum each to the vibrationless excited state ($0-\nu''-444$), probably because this band is hidden by a band of group 1 ($\nu_I+6\times450$). The band at 36970 cm^{-1} is assigned to $0+\nu'+1125+692$, but other bands can be assigned using $1560(=1125+435$ cm^{-1}). The frequency of 1125 cm^{-1} is uncertain.

Group 1 has seven components at equal intervals of about 450 cm^{-1} between 31336 cm^{-1}

TABLE III. FUNDAMENTAL FREQUENCIES OF TOTALLY SYMMETRIC VIBRATION OF *p*-BENZOQUINONE

Raman effect[a]	3500 Å region[b]		Present work		
	Ground state	Excited state	Ground state	Excited state	
444	440	436	444	435	Ring bending
770	770	796		692	C–C breathing
1149	1144	1109			C–H bending
1667	1667	1220		1560	C=O stretching
1688					C–C stretching
3058					C–H stretching

a) H. Stammreich and R. Formeris, *Z. Naturforsch.*, **7a**, 756 (1952).
b) T. Anno and A. Sadô, *J. Chem. Phys.*, **32**, 1602 (1960).

---

[10] J. M. Robertson, *Proc. Roy. Soc.*, **A150**, 106 (1935).

[11] S. M. Swingle, *J. Am. Chem. Soc.*, **76**, 1409 (1954).

[12] J. O. Fixl and E. Schauenstein, *Monatsh.*, **81**, 598 (1950); *Chem. Abstr.*, **45**, 4136f (1951).

[13] J. C. D. Brand and T. H. Goodwin, *Trans. Faraday Soc.*, **53**, 295 (1957).

[14] T. Anno and A. Sadô, This Bulletin, **31**, 734 (1958).

(ν_I) and 34032 cm^{-1} ($\nu_I + 6 \times 450$). The shapes of these bands are sharp and they are distinguished from the shape of the bands in group 2. It is probable, though not certain, these absorption bands are due to the n-π (^1A_u or $^1B_{2g} \leftarrow {}^1A_g$) transition. The bands belonging to group 1 are shown by the form $\nu_I + n \times 450$ in Table I.

Summary

The absorption spectrum of *p*-benzoquinone vapor was observed at 2900 Å region and the vibrational analysis was carried out. Two absorption groups were found. The bands in group 1 are sharp and single, but the nature of the transition is uncertain. Group 2 is composed of a doublet whose frequency separation is 45 cm^{-1}. It corresponds to the $^1B_{1g} \leftarrow {}^1A_g$ transition and is allowed by vibronic interaction with the allowed $^1B_{2u} \leftarrow {}^1A_g$ transition. The perturbing vibration is a C=O bending vibration belonging to the b_{3u} species whose frequency is 370 cm^{-1} in the ground state. The vibration frequencies of the main progression are 444 cm^{-1} and 435, 692 and 1560 cm^{-1} in the ground and excited electronic states respectively.

The author wishes to express his sincere thanks to Professor Sunao Imanishi and Dr. Yoshiya Kanda of Kyushu University for their encouragement throughout this research, and to Dr. Tosinobu Anno for his helpful guidance and discussions. Thanks are also due to Dr. Ryoichi Shimada and Dr. Ikuo Matubara for guidance and assistance in the experiments.

Department of Chemistry
Faculty of Science
Kanazawa University
Kanazawa