Electronic States of p-Benzoquinone. IV. Infrared Spectrum and Assignment of Vibrational Frequencies in the Ground Electronic State

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The infrared absorption band due to C=O stretching vibration of the *p*-benzoquinone molecule has been extensively studied by Josien, Fuson et al.¹⁾ together with those of other quinones. Rosenkrantz²⁾ measured the infrared spectrum of this substance in molten state in 12~2 μ region as one of the basic researches of the analyses of vitamine E and related compounds. Stammreich and Forneris³⁾ reported the Raman spectrum of *p*-benzoquinone. In spite of these spectroscopic works, however, the assignment of the fundamental frequencies to the modes of vibrations have not yet been reported.

In the present paper the infrared-spectral data of *p*-benzoquinone in carbon disulfide and carbon tetrachloride solutions in rock salt region will be presented and the vibrational analysis will be given utilizing the Raman data of Stammreich and Forneris³⁾ and the calculated values of the out-of-plane vibrational frequencies reported in a previous paper⁴⁾.

Experimental

The sample of *p*-benzoquinone was obtained from a commercial product recrystallizing it several times from ligroin. Solvents used were purified in the usual manner. The infrared spectrum was recorded with Perkin-Elmer model 21 spectrophotometer. The wavelength was calibrated by the spectrum of polystyrene. Wavelengths and relative intensities of observed absorption bands are given in Table I together with Rosenkrantz' data and interpretations discussed below.

Results and Discussion

Normal Coordinate Treatment of Totally Symmetrical Skeleton Vibrations.—In a later part of this series⁵⁾, in which the vibrational analysis of the electronic spectrum will be made, the calculation of the frequencies of the totally symmetrical skeleton vibrations in excited electronic state will be reported. The reason for restricting ourselves to totally symmetrical vibrations is that these are the only vibrations which form the vibrational structure of the electronic spectrum prominently. To compare with this later treatment, ground-state frequencies of the totally symmetrical skeleton vibrations were calculated as described in this subsection. This treatment is expected to help to some extent the vibrational assignment in the ground electronic state.

In this calculation the method proposed by the present authors⁶⁾ based on the simple valence force field approximation was used. The stretching force constants of the CC bonds were determined in the same way as in a previous article⁶⁾ from the bond order described in another paper⁴⁾ assuming the hybridization of carbon σ atomic orbital to be sp^2.

As for CO bond, the force constant was determined from the experimental value of CO distance (r_{CO}) 1.23Å⁷⁾ in the following manner since the order-length relation is less well established. In formaldehyde $r_{\mathrm{CO}}=1.21$Å⁸⁾ and it is determined that the CO stretching force constant (k_{CO}) is equal to 12.286×10^5 dyn./cm. from the CO stretching frequency of this molecule 1744 cm^{−1 9)} treating the CH_2 group in this

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1) M.-L. Josien, N. Fuson, J.-M. Lebas and T. M. Gregory, *J. Chem. Phys.*, **21**, 331 (1953); M.-L. Josien and N. Fuson, *Bull. soc. chim. France*, **19**, 389 (1952); *Compt. rend.*, **234**, 1680 (1952); **236**, 1879 (1953); *J. Am. Chem. Soc.*, **73**, 478 (1951); N. Fuson, M.-L. Josien and E. M. Shelton, ibid. **76**, 2526 (1954); M.-L. Josien and J. Deschamps, *J. chim. phys.*, **52**, 213 (1955); **53**, 885 (1956); *Compt. rend.*, **242**, 3067 (1956); A. Hadni, J. Deschamps and M.-L. Josien, ibid. **242**, 1014 (1956).

2) H. Rosenkrantz, *J. Biol. Chem.*, **173**, 439 (1948).

3) H. Stammreich and R. Forneris, *Z. Naturforsch.*, **7a**, 756 (1952).

4) Part III of this series. T. Anno and A. Sadô, This Bulletin, **31**, 728 (1958).

5) Unpublished.

6) T. Anno, A. Sadô and I. Matubara, ibid. **29**, 703 (1956).

7) S. M. Swingle, *J. Am. Chem. Soc.*, **76**, 1409 (1954).

8) R. B. Lawrence and M. W. P. Strandberg, *Phys. Revs.*, **83**, 363 (1951).

9) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand Co., Inc., New York (1945), p. 300.

TABLE I

ABSORPTION BANDS OF *p*-BENZOQUINONE IN THE INFRARED REGION TOGETHER WITH INTERPRETATION (cm^{-1})

CS_2 solution	CCl_4 solution	Crystalline melt[a]	Interpretation
3322 mw[b]	3333 mw		$1667+1667=3334$ (B_{2u})
3268 mw	3279 mw		$3049+243=3292$ (B_{1u})
3049 w	3049 w	3058 s	$b_{2u}+b_{3u}$ fundamentals
2681 vw			
2577 vw			$876+1688=2564$ (B_{1u})
2445 vw			$1298+1149=2447$ (B_{2u})
1968 w	1976 w	2008 vw	
1869 w	1880 w	1908 vw	$1064+794=1858$ (B_{1u})
1764 m	1767 m	1761 vw	$99+1667=1766$ (B_{1u})
1715 ms	1721 ms		b_{2u} fundamental
1667 vs	1675 vs		$1064+610=1674$ (B_{2u})
1656 vs	1664 vs	1664 s	b_{2u} fundamental
	1597 ms	1595 s	$1064+540=1604$ (B_{2u})
1355 m	1357 m		b_{3u} fundamental
1323 m	1323 m	1337 s	$876+444=1320$ (B_{1u})
1297 vs	1300 vs	1302 vs	b_{2u} fundamental
1174 vw	1171 w		$730+444=1174$ (B_{2u})
1139 w	1139 w	1135 w	$370+770=1140$ (B_{3u})
1116 vw	1119 w		$876+243=1119$ (B_{2u})
1063 vs, b	1065 vs	1079 m	b_{3u} fundamental
983 mw		1001 w	$\begin{cases} 370+610=980 \ (B_{2u}) \\ 730+243=973 \ (B_{1u}) \end{cases}$
943 s	945 s	949 s	b_{3u} fundamental
876 vs	883 vs	909 m	b_{1u} fundamental
730 mw, b			b_{2u} fundamental

a) Estimated from absorption curve given in Ref. 2.

b) Abbreviations denoting relative intensities are as follows:
vs=very strong, s=strong, ms=medium strong, m=medium, mw=medium weak, w=weak, vw=very weak, b=broad.

molecule as a mass point. Since in Badger's relation[10]

$$r_{CO}=(C/k_{CO})^{1/3}+d_{CO},$$

C is considered to be a universal constant and $C^{1.3}=1.230$[6,10], d_{CO} can be determined from the r_{CO} and k_{CO} values for formaldehyde described above. Then it follows that $d_{CO}=0.677$ Å, which is in good agreement to the value given by Badger[10a]. From the d_{CO} value thus obtained and the experimental value of r_{CO} (1.23 Å) k_{CO} for *p*-benzoquinone is calculated to be 11.004×10^5 dyn./cm. As will be discussed later, it seems to be most appropriate to assign the Raman line reported as $444cm^{-1}$ to the ring-defomation vibration belonging to a_g. This frequency was used to evaluate the ring-deformation force constant. From these values of force constants the totally symmetrical vibrational frequencies shown in Table II are obtained.

TABLE II

CALCULATED FREQUENCIES OF TOTALLY SYMMETRICAL SKELETON VIBRATIONS OF *p*-BENZOQUINONE (cm^{-1})

(444)[a]
782
1596
1900

a) The value in parentheses is used to calculate the ring deformation force constant.

Assignment of Fundamental Frequencies.—In this subsection the assignment of the fundamental frequencies will be discussed using the Raman and infrared spectral data as well as the calculated values of frequencies. Group-theoretical considerations for the normal vibrations of *p*-benzoquinone were briefly given in a previous paper[4] and will not be repeated here. As to the planar vibrations the calculation of the frequencies is made only for the totally symmetrical skeleton vibrations, so the comparison with the

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[10] (a) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934).
(b) R. M. Badger, ibid., **3**, 710 (1935).

TABLE III

COMPARISON OF FUNDAMENTAL FREQUENCIES OF IN-PLANE MODES OF VIBRATION IN MOLECULES OF TYPE  $^{a)}$

(Frequencies are given in the unit of cm^{-1})

Modes	Species a_g			Species b_{1g}			Species b_{2u}			Species b_{3u}		
	X=D$^{b)}$	F$^{c)}$	O	D$^{b)}$	F$^{c)}$	O	D$^{b)}$	F$^{c)}$	O	D$^{b)}$	F$^{c)}$	O
CH stretching	3050 (ν_{7a})	3048	3058	3042 (ν_{7b})	3080	3058	3060 (ν_{13})	3028	3049	3079 (ν_{20b})	3088	3049
CX stretching	2280 (ν_2)	1245	1667				2275 (ν_{20a})	1183	1667			
CC stretching	1587 (ν_{8a})	1617	1688	1569 (ν_{8b})	1285	610	1469 (ν_{19a})	1511	1715	1603 (ν_3)	1437	943
CC breathing	978 (ν_1)	859	770				992 (ν_{12})	737	730	1413 (ν_4)	1212	1063
CX bending				909 (ν_{9b})	635	[~400]				814 (ν_{18b})	350	370
CH bending	1173 (ν_{9a})	840	1149	1309 (ν_3)	1142	1360	1033 (ν_{18a})	1012	1297	1106 (ν_{15})	1085	1355
ring bending	597 (ν_{6a})	451	444	601 (ν_{6b})	507	540						

a) X=D, F and O for *p*-dideuterobenzene, *p*-difluorobenzene and *p*-benzoquinone, respectively.
b) Frequencies taken from Garforth, Ingold and Poole (*J. Chem. Soc.* **1948**, 406) are followed by Wilson's numbering scheme (*Phys. Revs.*, **45**, 706 (1934)).
c) E. E. Ferguson, R. L. Hudson, J. R. Nielsen and D. C. Smith, *J. Chem. Phys.*, **21**, 1457 (1953).

spectral data of similar molecules may be helpful. The data used for comparison are those of *p*-dideuterobenzene[11] and *p*-difluorobenzene[12]. These are listed in Table III together with the assignment to the mode of vibrations.

Raman-active Frequencies.—*Species* a_g. —Although of the Raman-active frequencies those belonging to species a_g give polarized Raman lines, the depolarization factors of the Raman lines of *p*-benzoquinone have not been studied yet. However, it is known that the totally symmetrical vibrations produce, in general, stronger Raman lines in comparison with the other types of vibrations. It will be natural to assign the Raman lines at 3058 cm^{-1} and 1667 cm^{-1} to CH and CO stretching vibrations belonging to a_g, respectively, from the intensities and the magnitudes of so-called group frequencies[13]. The ring bending vibration belonging to a_g in this molecule corresponds to 606 cm^{-1} benzene value. As can be seen in Table III the corresponding frequency in *p*-benzoquinone should be sought around 450 cm^{-1}. It is reporteted that the Raman line at 444 cm^{-1} is a relatively stronger one in its neighborhood[3]. Moreover, in the normal-coordinate treatment of totally symmetrical skeleton vibrational frequencies described above a fairly large change of the ring deformation force constant results, if we change the value of the frequency to be inserted for the determination of this constant a little in the neighborhood of 444 cm^{-1}. These facts suggest that 444 cm^{-1} may be assigned to the a_g ring-bending vibration. As described previously if the ring-bending force constant is determined from this frequency, the calculated values of totally symmetrical skeleton vibrational frequencies shown in Table II are obtained. Of these values the calculated value of 1900 cm^{-1} which may correspond to the experimental value of 1667 cm^{-1} agree with the experiment only poorly. This may be due either to the experimental error of CO bond length or to the fact that the bond length-force constant relation has not been established well. Moreover, from the calculation of **L**-matrix elements[14] it can be shown that this frequency is fairly sensitive to the interaction constants, so use of valence-force field approximation may not be adequate for the calculation of this frequency. On the other hand, since the order-length and the length-force constant relations are established fairly well for CC bonds, it is expected that the agreement between the calculated values and the experimental ones is fairly good for CC breathing and stretching vibrations. Therefore, 770 and 1688 cm^{-1} Raman lines may be assigned to CC breathing and stretching vibrations belonging to a_g from comparison with the calculated values. The remaining vibration belonging to this species is an in-plane bending vibration of the hydrogen atom and is expected to

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[11] F. M. Garforth, C. K. Ingold and H. G. Poole, *J. Chem. Soc.*, **1948**, 406.

[12] E. E. Ferguson, R. L. Hudson, J. R. Nielsen and D. C. Smith, *J. Chem. Phys.*, **21**, 1457 (1953).

[13] L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen and Co., Ltd., London (1954).

[14] E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941). See also the last section of Ref. 6.

TABLE IV

FUNDAMENTAL FREQUENCIES OF *p*-BENZOQUINONE (GROUND ELECTRONIC STATE) (cm^{-1})[a, b]

	a_g	b_{1g}	b_{2g}	b_{3g}	a_u	b_{1u}	b_{2u}	b_{3u}
C—H stretching	3058	3058					3049	3049
C=O stretching	1667						1667	
C—C stretching	1688	610					1715	944
C—C breathing	770						730	1064
C=O bending		[~400][c]		243 (—)		—(533)		370
C—H bending	1149	1360	794(839)	932(959)	—(962)	876(871)	1298	1356
ring bending	444	540		—(790)	533(403)	99 (98)		

a) Calculated values of non-planar vibrational frequencies are closed in parentheses.

b) Experimental values with underlining are obtained from combination bands or electronic spectral data (see text).

c) Estimated.

appear in the region of 1100~1300 cm^{-1}. From its intensity the Raman line at 1149 cm^{-1} may be assigned to a_g. Therefore it is natural to assign this frequency to the CH in-plane bending vibration belonging to a_g.

Species b_{2g} and b_{3g}.—Before discussing the Raman-active in-plane mode other than those belonging to species a_g the Raman-active out-of-plane species b_{2g} and b_{3g} will be discussed.

Of the C=O out-of-plane bending vibrations the one which is symmetric with respect to inversion belongs to b_{3g}. Although the out-of-plane deviations of the oxygen atom from the molecular plane decreases the overlap of the σ AO of the oxygen atom with the σ AO of the carbon atom to which the oxygen atom in question is attached, the increase of the potential energy thus results will be partially compensated by the increase in the overlap of π AO of the oxygen atom with σ AO of the carbon atom. Compensation of such a kind in the potential energy is not expected in the case of C=O in-plane bending mode. Therefore it is expected that C=O out-of-plane bending frequency is rather low and lower than that of C=O in-plane bending. The Raman line reported at 243 cm^{-1} may represent this vibration. This is the Raman line of lowest frequency reported by Stammreich and Forneris[3)] and the Raman line of lowest frequency is assigned to species b_{3g} (in our notation) also in the case of *p*-difluorobenzene[12)].

As described in a previous paper[4)] if 243 cm^{-1} is used as the b_{3g} C=O out-of-plane bending vibrational frequency in order to determine the force constant of C=O out-of-plane bending motion, the other nonplanar vibrational frequencies of *p*-benzoquinone shown in parentheses in Table IV are obtained. From the comparison with these calculated values Raman lines at 794 and 932 cm^{-1} are assigned to b_{2g} and b_{3g} fundamentals, respectively. The remaining calculated frequency belonging to species b_{3g} is 790 cm^{-1} and has no corresponding Raman line.

Species b_{1g}.—One of the five b_{1g} fundamentals is a hydrogen stretching mode which is assumed to overlap the Raman line at 3058 cm^{-1} assigned to a_g. Raman lines at 540, 610 and 1360 cm^{-1} which have been left unassigned may all be assigned to the b_{1g} fundamentals. The last frequency may be assigned to an in-plane hydrogen bending vibration with considerable certainty, while the other two may be caused by carbon vibrations. It is true that one of the C=O in-plane bending modes is contained in this species and 540 or 610 cm^{-1} Raman line might be assigned to this vibration. However, the C=O in-plane bending frequency belonging to species b_{1g} is expected to lie around 400 cm^{-1} from comparison with the data of *p*-difluorobenzene (see Table III) and with the frequency of another C=O in-plane bending vibration belonging to species b_{3u} of *p*-benzoquinone. Therefore we believe that none of the three Raman frequencies mentioned above correspond to this vibration and there fails the Raman line corresponding to this vibration. We assign 540 cm^{-1} to ring bending mode and 610 cm^{-1} to C—C (single bond) stretching mode. This assignment for 540 cm^{-1} is also consistent with the fact, which may be seen in Table III, that b_{1g} component of 606 cm^{-1} e_g^+ benzene vibration diminishes in frequency only slightly although the a_g component is lowered considerably.

Infrared-active Frequencies.—*Species b_{2u}*.—Infrared bands at 3049 cm^{-1} and 1667 cm^{-1}

may be assigned to two of the five b_{2u} fundamental vibrations, namely the hydrogen and oxygen stretching vibrations, with considerable certainty by comparison with the values of the corresponding symmetric (a_g) vibration. We note here that the double maximum of the latter band (1667 and 1656 cm^{-1} in carbon disulfide) is interpreted to be caused by Fermi resonance between the b_{2u} fundamental and 1064(b_{3u})+610(b_{1g})=1674(B_{2u})cm^{-1} combination as shown in Table I. A medium strong band at 1715 cm^{-1}, which can not be explained as a combination, may represent CC stretching vibration. This assignment is consistent with the corresponding values of the frequencies in *p*-dideuterobenzene and *p*-difluorobenzene as shown in Table III. A medium weak and broad band at 730 cm^{-1} may be assigned to the ring-breathing vibration from comparison with the corresponding vibrations in other molecules (see Table III). The remaining vibration of this species is the hydrogen bending vibration. It must be searched for in the region between 1100 and 1400 cm^{-1} from the values of the corresponding Raman-active mode. They must be selected among medium to very strong bands observed at 1355, 1323 and 1297 cm^{-1}, of which the middle one can also be explained as a combination band as shown in Table I. We assign the remaining bands to hydrogen bending vibration, 1355 cm^{-1} and 1297 cm^{-1} being taken as b_{3u} and b_{2u} fundamentals, respectively. It is to be noted that the following sequence results for frequency values of hydrogen bending vibration from this assignment together with the assignment of the Raman-active fundamentals described previously: $b_{1g} > b_{3u} > b_{2u} > a_g$. This sequence also exists in the case of *p*-difluorobenzene[12].

Species b_{3u}.—One of the five b_{3u} fundamental vibrations is the hydrogen stretching mode which is assumed to overlap the band at 3049 cm^{-1} assigned to a b_{2u} fundamental. Mention was made of another fundamental, i. e., the hydrogen bending vibration, which was taken to be 1355 cm^{-1}. Strong or very strong bands at 943 and 1063 cm^{-1} may also be taken as b_{3u} fundamentals. The remaining fundamental vibration is an oxygen in-plane bending mode and this is expected to have a frequency of 400 cm^{-1} from the comparison with the corresponding vibrational frequency of *p*-difluorobenzene. Although this region is outside our measurements, we tentatively assign the value of 370 cm^{-1} to this vibration because this assumption favors the explanation of some of the absorption bands as combinations.

Species b_{1u}.—Calculated values of three non-planar frequencies belonging to this species are 98, 533 and 871 cm^{-1}. The highest frequency is realized in the spectrum by the band at 876 cm^{-1}. Although we could not obtain the experimental value of frequency corresponding to the calculated value of 533 cm^{-1} even from the combination bands, we infer the experimental value of the lowest b_{1u} fundamental to be 99 cm^{-1} from the combination band (see Table I).

Inactive Frequencies.—*Species* a_u.—The two vibrations in species a_u are neither active in the Raman nor in the infrared spectra. Calculated values of these vibrational frequencies are 403 and 962 cm^{-1}. Although we infer the "experimental" value corresponding to the former frequency to be 533 cm^{-1} from the vibrational analysis of the electronic spectrum, this value should be considered to be tentative for reasons described briefly in a previous paper[4].

TABLE V

INTERPRETATION OF RAMAN SPECTRUM OF *p*-BENZOQUINONE

$\Delta\nu$ (cm^{-1})[3]	Interpretation
243 (3)	b_{3g} fundamental
444 (4)	a_g fundamental
540 (2)	b_{1g} fundamental
610 (3)	b_{1g} fundamental
770 (2)	a_g fundamental
794 (1)	b_{2g} fundamental
932 (2)	b_{3g} fundamental
1149 (7)	a_g fundamental
1360 (3)	b_{1g} fundamental
1667 (10)	a_g fundamental
1688 (5?)	a_g fundamental
3058 (4)	a_g+b_{1g} fundamentals

Interpretation of Spectra. — Fundamental frequencies assigned are summarized in Table IV. The interpretations of the Raman and infrared spectra are included in Tables V and I, respectively. In interpreting the bands as combinations only the possibilities of binary combinations were considered. In Table IV, underlined values were obtained from the combination bands (lower a_u fundamental was obtained from the electronic spectral data — see above) and the calculated values of non-planar frequencies are given in parentheses. The value of frequency of C=O bending vibration belonging to species b_{1g} is only an estimated value and is included in brackets.

Summary

The infrared absorption spectra of *p*-benzoquinone in carbon disulfide and carbon tetrachloride solutions in rock salt region are measured and interpreted together with the Raman data reported by Stammreich and Forneris[3]. A complete, although more or less tentative, assignment of the fundamental frequencies to modes of vibrations is proposed.

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