Assignments of the $n\pi^*$ Singlet States of p-Benzoquinone

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The vapor phase fluorescence spectra of p-benzoquinone-h_4 and d_4 are reported and discussed in relation to the assignment of the low lying singlet states. The low temperature, polarized single crystal electronic absorption spectra of p-benzoquinone and several of its isotopic derivatives are reported. From the isotope shifts and band polarizations of the various vibronic origins, a detailed vibronic analysis is offered of the electronic absorption spectrum of p-benzoquinone which indicates a near degeneracy of the ^1A_u and $^1B_{1g}$ electronic states.

INTRODUCTION

A large part of the experimental and theoretical interest in the spectrum of p-benzoquinone (PBQ) lies in the identification of the lowest lying $n\pi^*$ electronic excited states. Symmetry adapted linear combinations of the two carbonyl oxygen non-bonding orbitals give rise to delocalized moleculer orbitals, which are degenerate in zeroth order. To the extent that the energy splitting between these molecular orbitals is determined by the degree of through space orbital overlap, PBQ represents one of the simplest prototype models for the study of interactions which occur at long range between 'nonbonding' orbital sets. As such, it provides a model for the investigation of intermolecular interactions in molecular crystals and intramolecular interactions between chromophores in large molecules.

Recent theoretical results indicate that lone pairs may significantly interact with one another by indirect 'through-bond' mechanisms (*1, 2*) and some experimental support for this conclusion has been provided by the technique of photoelectron spectroscopy (*3, 4*). However, the extent of nonbonding orbital interaction implied by the splitting between electronic excited states involving these orbitals and a common π^* orbital is in some cases at variance with this interpretation (*5, 6*).

The electronic absorption spectrum of PBQ has been most thoroughly studied in the vapor phase. In the first such detailed investigation, Anno and Sado, compared the predictions of semiempirical molecular orbital calculations (*8, 9*) with their experimental results (*7*). Later work on the vapor high resolution (*10–12*) and magnetic rotation (*13*) spectra changed some of the earlier conclusions of Anno and Sado.

The early work by Sidman (*14, 15*), who obtained the polarized absorption spectrum of PBQ crystals at 20°K, provided the only experimental results with which to correlate the vapor phase spectra. Recently, additional low temperature crystal spectra of PBQ have been obtained by Trommsdorff (*6, 16*) and Kogayani (*17*). The efforts of the latter investigator have been largely confined to investigation of the longest wavelength crystal system observed in emission and will not be discussed in this paper.

The essential difficulty in the analysis of the spectrum of PQB arises from the zeroth order degeneracy of the two lowest $n\pi^*$ excited states which give rise to the long wavelength absorption systems. The two lowest singlet $n\pi^*$ transitions are forbidden by molecular symmetry and are, additionally, intrinsically weak due to the 'overlap forbiddenness' characteristic of $n\pi^*$ transitions in general. On the other hand, one of the corresponding $n\pi^*$ triplet states is unusually intense, due to large one-center spin-orbit coupling matrix elements on the carbonyl oxygens. Since all four transitions may gain electric dipole intensity by vibronic and/or spin-orbit coupling with the same dipole allowed singlet state, one is faced with the problem of disentangling four separate transitions whose electronic origins all lie within a 1500 cm^{-1} interval, and all of which may derive their radiative intensity from the same electronic state.

Since the polarization properties of the individual systems are essentially identical, analysis must proceed from a study of the vibrational species associated with each of the transitions. The lowest singlet $n\pi^*$ states are ^1A_u and $^1B_{1g}$ and these require b_{1g} and a_u vibrations, respectively, to vibronically couple them to a perturbing $^1B_{1u}$ state. The molecule is "deficient" in b_{1g} modes, possessing only one, a C–H bend and there are only two a_u modes which, unfortunately, are both Raman and infrared inactive.

EXPERIMENTAL

Most of the spectra were recorded in the first order on a Bausch and Lomb 1.5 meter grating spectrograph with a theoretical resolving power of 45,000. Crystal absorption spectra were obtained using a 10 micron slit width. Since the instrument was of only moderate speed, having an aperture of $f/20$ the vapor phase emission spectra required a 60 micron slit width in order to obtain reasonable exposure times of 1–4 hr. Spectra were recorded on Kodak Tri-X and Pan-X film, calibrated with the visible emission of an iron arc. A Glan–Taylor prism placed between the sample and the spectrograph slit and aligned with the crystal optic axes was used to obtain polarized absorption spectra. The cryostat was of the total immersion type, in which crystals were cooled to a temperature of 1.8°K, determined by the pressure above the liquid helium bath.

Optical density versus wavelength curves were obtained from a Joyce–Loebl microdensitometer. The major features of all spectra were measured on a traveling stage comparator, to an estimated accuracy of ±2 cm^{-1} for the emission spectra and ±1 cm^{-1} for the absorption spectra. Broad or weak features were interpolated directly from the microdensitometer traces to an estimated accuracy of ±4 cm^{-1}.

The PBQ used in this work was reagent grade, purified by either vacuum sublimation or extensive zone refining. Crystals with pronounced ($20\bar{1}$) cleavage were obtained during the purification process either as tablets elongated along the b axis from sublimation or as easily cleaved 1–2 cm long cylindrical sections from zone refining. The small samples of isotopically substituted quinones available (approx. 100 mg) were melted between fused silica plates with the result that the ($20\bar{1}$) face developed prominently (*15*).

TABLE I

SQUARED DIRECTION COSINES OF THE PBQ
MOLECULAR AXES X, Y AND Z WITH RESPECT
TO THE CRYSTALLOGRAPHIC AXES a', b, c
and p, THE DIRECTION PERPENDICULAR TO
b IN THE (20$\bar{1}$) PLANE

	a'	b	c	p[+]
Z	0.0973	0.6688	0.2338	0.3309
Y	0.1770	0.3295	0.4935	0.6681
X	0.7262	0.0002	0.2734	0.0024

Trotter (18) has reported a three-dimensional analysis of the crystal structure of PBQ taking into account the anisotropic thermal motions of the atoms in the structure refinement. The crystal structure of PBQ belongs to the space group C_{2h}^5 (P_{2_1}/a) and has two molecules per unit cell, both on sites C_i. The direction cosines of the three molecular symmetry axes with respect to the crystallographic axes are given in Table I. The molecular X axis is chosen normal to the molecular plane and Z along the carbonyl axis. All absorption spectra were taken with incident radiation normal to the (20$\bar{1}$) crystal face. The polarization directions corresponded to the b crystallographic axis and the axis normal to it in the (20$\bar{1}$) face.

DISCUSSION

Vapor Phase Spectrum

The essential discrepancy between the work of Hollas (10) and the earlier work of Anno and Sado (7), concerns the location of the electronic origin of the vapor phase $^1B_{1g} \leftarrow {}^1A_g$ system which is forbidden for electric dipole radiation in the vapor phase. The present observations and conclusions support the interpretation given by Hollas in which the (unobserved) electronic origin of the $^1B_{1g} \leftarrow {}^1A_g$ transition is located at 20031 cm^{-1} and vibronic intensity is induced principally by the activity of an a_u C–H bending mode (ν_{22}) observed at $0 + 944$ cm^{-1} in the excited state cold absorption and weakly at $0 - 969$ cm^{-1} in the 'hot' band absorption.

A prominent feature of the vapor phase spectrum is the presence of positively running sequences with a spacing of $+35$ cm^{-1}. Since these long series are observed even at room temperature, it is reasonable to postulate that the sequence forming vibration is ν_{26} (b_{3u}), the lowest frequency vibration of PBQ observed at 109 cm^{-1} in the infrared (19). If this interpretation is correct, the corresponding excited state frequency of this fundamental should be 144 cm^{-1}. In addition to its activity in sequence formation, b_{3u} fundamental ν_{26}, has the appropriate symmetry to make the $^1B_{1g} \rightarrow {}^1A_g$ transition vibronically allowed with a short axis electric dipole transition moment. The expected 26_0^1–26_1^0 band gap should then be 253 cm^{-1}. This gap is observed and the vibronic origins involving the a_u modes ν_{22} and ν_{23}, both in hot and cold absorption are determined from the position of the electronic origin deduced in this fashion.

The principle difficulty in the analysis lies in the fact that the major perturbing vibration ν_{22}, is both Raman and infrared inactive and no experimental verification of the ground state frequency is therefore available. The analysis of the vapor phase spectrum offered by Hollas thus relies on the correlation of the $+35$ cm^{-1} sequence interval with the less important ν_{26} vibronic origin.

When PBQ vapor is excited by a high voltage radio frequency discharge in the presence of flowing toluene vapor, the emission obtained is, in large part, a phosphorescence spectrum assigned correctly to the $^3A_u \rightarrow {}^1A_g$ transition (20). A small amount of fluorescence intensity, however, is present in addition to the phosphorescence. Although this data was available, in part, from the work of Jayswal and Singh (20) it was not recognized as vapor phase fluorescence but, rather, was analyzed as part of the vapor phase phosphorescence spectrum.

The prominent sequence interval observed in the vapor phase singlet absorption spectrum is $+35$ cm^{-1}, whereas the $^3A_u \leftrightarrow {}^1A_g$ absorption and emission spectrum exhibits a long series of positively running sequences with a separation of $+31$ cm^{-1}. The difference in this sequence interval is an important method of distinguishing bands associated with $^1B_{1g} \leftrightarrow {}^1A_g$ transition from those of the $^3A_u \leftrightarrow {}^1A_g$ transition and the bands in the fluorescence spectrum at about 4950 Å, 5010 Å, 5070 Å, and 5250 Å have been assigned using this criterion (see Fig. 1).

The fluorescence spectrum of both PBQ-h_4 and PBQ-d_4 together with the isotope shifts, confirm the vibronic assignments given in Table II. The features of the fluorescence spectrum correlate with the 'hot' band absorption analysis given by Hollas. The interval 20170–19920 cm^{-1} corresponds to the 26_0^1–26_1^0 band gap and the assignment of ν_{22}'' follows immediately. Only one other band is observed in the vapor phase fluorescence spectrum at 0–310 cm^{-1}. This band was assigned by Hollas as the remaining a_u funda-
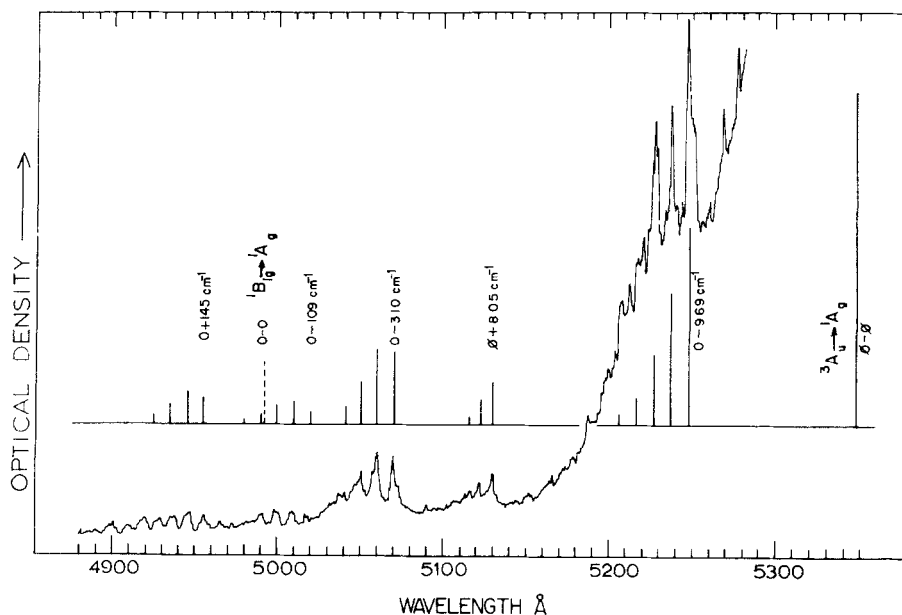

Fig. 1. The vapor phase fluorescence spectrum of p-benzoquinone-h_4.

TABLE II

VAPOR PHASE FLUORESCENCE SPECTRUM OF p-BENZOQUINONE

Wave Number			
Absorption*	Emission	Difference	Assignment
	20246	-215	26_2^3
	20211	-180	26_1^2
20174.3	20174	-143	26_0^1
(20030.9)		0	$0\text{-}0,\ {}^1B_{1g} - {}^1A_g$
	19995	36	26_3^2
	19958	73	26_2^1
19924.7	19918	113	26_1^0
	19792	239	26_5^2
	19754	277	26_4^1
19720.4	19718	313	26_3^0
	[19521]	[839]	$[5_0^1\ 26_1^1]$
[19491.6]	[19490]	[808]	$[5_0^1]$
	19240	791	$22_1^0\ 26_5^5$
	19202	829	$22_1^0\ 26_4^4$
	19186	845	
	19167	864	$22_1^0\ 26_3^3$
	19155	876	
	19132	899	$22_1^0\ 26_2^2$
	19095	936	$22_1^0\ 26_1^1$
19061.8	19059	972	22_1^0
	18982	1049	$22_1^0\ S_1^1$
[18682.1]	[18682]	[0]	$0\text{-}0,\ {}^3A_u - {}^1A_g$

* From Ref. (10). [ ] refers to bands based upon the triplet origin. S refers to the unknown vibration giving rise to the -78 cm^{-1} sequence.

mental ν_{23}'', corresponding to $0+398$ cm^{-1} in the excited state and, although this assignment is supported by an excellent agreement with the Teller–Redlich product rule, Hollas has pointed out that the supposed 23_0^1 band is considerably weaker than its counterpart 23_1^0 band. We note that the 0–310 cm^{-1} band in fluorescence is six times relatively more intense than the supposed corresponding band in absorption. Finally, there is evidence from the polarized single crystal absorption spectrum (vide infra), that this assignment is incorrect. Hollas has suggested that a reassignment of this band could involve the ^1A_u state but this is not supported by the present study (vide infra).

There appears to be no doubt, therefore, that the basic assignments made by Hollas are correct and that the transition is $^1B_{1g} \leftrightarrow {}^1A_g$ with the origin at 20031 cm^{-1}. This has also been checked in this study by a temperature dependent spectrophotometric study of PBQ-h_4 vapor in a 1 meter cell at temperatures from room temperature up to about 150°C in which all the sequence bands and progressions were clearly observed and agree completely with the analysis. Finally, the appearance of the 0–969 cm^{-1} band in fluorescence eliminates the possibility of the band at 20974 cm^{-1} being a separate electronic origin, rather than a vibronic origin based upon the electronic origin at 20031 cm^{-1}.
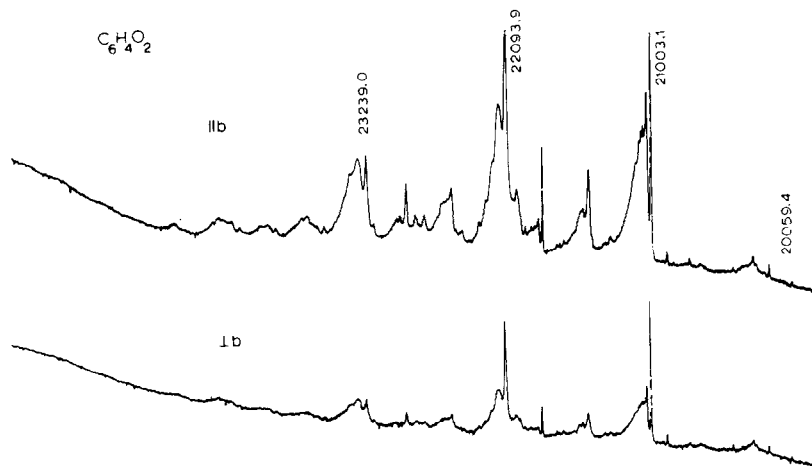
FIG. 2. The polarized absorption spectrum of p-benzoquinone-h_4 single crystal at 1.8°K.

CRYSTAL SPECTRA

The low temperature single crystal absorption of the 4500 Å system of PBQ-h_4, polarized parallel and perpendicular to the b crystallographic axis is shown in Fig. 2 and the analysis is given in Table III. The analysis of the corresponding PBQ-d_4 spectrum is given in Table IV. The crystal spectra of the -h_4 and -d_4 molecules polarized parallel to b are compared in Fig. 3. Polarized crystal spectra of PBQ-h_4O_2[18] and PBQ-d_4O[18] were also obtained in the 4500 Å region primarily to confirm the assignments of the carbonyl modes. The results of the vibronic analyses of these spectra are summarized in Table V.

The 4500 Å system is characterized by an intense vibronic origin preceded by a weak band system which has been expanded for greater detail in Fig. 4. In the weak onset region there are several bands with a polarization ratio $\|b/\perp b \cong 0.5$, corresponding to a short axis electric dipole transition moment, however, the vast majority of the bands recorded and all of the intense bands exhibit a polarization ratio $\|b/\perp b \approx 2$, corresponding to a long axis electric dipole transition moment. Spectra were reproducible and no dependence on the method of sample purification or preparation was ever noted.

Electronic Origins

Although both the $^1A_u \leftrightarrow {}^1A_g$ and $^1B_{1g} \leftrightarrow {}^1A_g$ transitions are electric dipole forbidden in the free molecule with full D_{2h} symmetry, the $^1B_{1g} \leftrightarrow {}^1A_g$ transition is magnetic dipole allowed with a long axis magnetic dipole transition moment. The $^1A_u \leftrightarrow {}^1A_g$ transition becomes allowed in the reduced site symmetry of the crystal lattice.

Two bands are observed in the onset region of singlet absorption in the crystal which have no apparent corresponding features in the vapor absorption spectrum. The first of these bands is the relatively sharp feature at approximately 20059 cm^{-1} [20081 cm^{-1}].[1] This band, previously assigned by Sidman to an excited state fundamental associated with the $^3A_u \leftarrow {}^1A_g$ transition has been shown not to split in a Zeeman field (22). Vibrational intervals based on this origin correspond closely to those observed by Hollas

1 Corresponding PBQ-d_4 frequencies are given in brackets.

TABLE III

THE 4500Å ABSORPTION SYSTEM OF CRYSTALLINE p-BENZOQUINONE-h_4 AT 2°K

WAVE NUMBER	DIFFERENCE	ASSIGNMENT	COMMENT
20057.8	0.0	0+0	$^1B_{1g} - {}^1A_g$
20061.0	3.2	∅+∅	$^1A_u - {}^1A_g$
20204.8	147.0	0+147	$b_{3u}(\nu_{26})$
20233.7	175.9	0+147+29	
20288.7	230.9		
20307.2	249.4		
20379.6	318.6	∅+319	$b_{2g}(\nu_{30})$
20411.4	350.4	∅+319+29	
20440.7	382.9	0+3X147	
20470.0	412.2	0+3X147+29	
20510.7	452.9	0+3X147+65	
20519.0	458.0	∅+458	$a_g(\nu_6)$
20663.5	605.7	0+147+458	
20734.5	676.7	0+677	$b_{3u}(\nu_{25})$
20763.8	706.0	0+677+29	
20791.8	734.0	0+677+2X29	
20816.0	758.0	0+677+3X29	
20844.9	783.9	∅+784	$b_{1g}(\nu_{27})$
20865.1	804.1	∅+804	$a_g(\nu_5)$
20868.7	807.7	∅+784+29	
20890.7	832.9	0+833	$b_{3u}(\nu_{24})$
20918.9	861.1	0+833+29	
20958.6	900.8	0+833+65	
20974.3	913.8	∅+2X458	
21003.1	945.3	0+945	$a_u(\nu_{22})$
21016.3	958.5	0+145+805	
21032.2	974.4	0+944+29	
21061.5	1003.7	0+944+2X29	
21074.8	1017.0	0+944+65	
21088.1	1030.3	0+944+3X29	
21101.5	1043.7	0+944+29+65	
21115.7	1062.9	0+944+4X29	
21296.8	1235.8	∅786+458	
21338.3	1280.5	0+831+458	
21458.9	1401.1	0+944+458	
21650.7	1589.7	∅+786+805	
21676.5	1615.5	∅+786+805+29	
21700.0	1642.2	0+831+805	
21808.5	1750.7	0+944+805	
21837.1	1778.7	0+944+805+29	
21865.8	1808.0	0+944+805+2X29	
21877.6	1819.8	0+944+805+65	
21894.5	1836.7	0+944+805+3X29	
21911.3	1853.5	0+944+2X455	
21939.2	1878.2	∅+786+1091	
21977.8	1920.0	0+831+1091	
22093.9	2036.1	0+944+1091	
22151.9	2094.1	0+944+1149	
22262.8	2205.0	0+944+805+458	
22614.0	2556.2	0+944+2X805	
22750.6	2692.8	0+944+2X805+29	
22897.8	2840.0	0+944+1091+805	
22957.1	2899.3	0+944+1149+805	
23172.4	3114.6	0+944+2X1091	
23239.0	3181.2	0+944+1091+1149	
23310.8	3253.0	0+944+2X1149	
24062.7	4004.9	0+944+1091+1149+805	
24404.5	4346.7	0+944+1091+2X1149	

in the vapor phase absorption spectrum associated with the $^1B_{1g} \leftarrow {}^1A_g$ electronic origin, suggesting its assignment as the $^1B_{1g} \leftarrow {}^1A_g$ electronic origin.

Under high resolution ($\sim$500,000) this feature is seen to be a doublet consisting of oppositely polarized bands, 20057.8 and 20061.0 cm^{-1} [20079.5 and 20082.4 cm^{-1}], recently assigned (6) as factor group components of the $^1B_{1g} \leftarrow {}^1A_g$ electronic origin (see Fig. 5). This assignment, however, presents two problems: first, the polarization data is not consistent with an assignment as Davydov components since both bands are present in the b-axis and ac-plane spectra and, second, no specific mechanism has been proposed for the appearance of the crystal forbidden electronic origin. It seems unlikely that crystal mechanical strain or included impurities leading to slight depolarization *and* loss of molecular inversion symmetry are responsible for both the anomalous intensity and polarization, since no sensitivity of the spectrum to either the degree of crystal purity or

TABLE IV

THE 4500Å ABSORPTION SYSTEM OF CRYSTALLINE p-BENZOQUINONE-d_4 AT 2°K

WAVE NUMBER	DIFFERENCE	ASSIGNMENT	COMMENT
20079.5	0.0	0+0	$^1B_{1g} - {}^1A_g$
20082.4	2.9	Ø+Ø	$^1A_u - {}^1A_g$
20225.0	145.5	0+146	$b_{3u}(\nu_{26})$
20254.4	174.9	0+146+29	
20304.3	226.3		
20320.3	240.8		
20389.4	307.0	Ø+307	$b_{2u}(\nu_{30})$
20422.6	343.1	0+3X146	
20449.5	370.0	0+3X146+29	
20486.9	407.4	0+3X146+2X29	
20541.0	458.6	Ø+458	$a_g(\nu_6)$
20667.2	584.8	0+585	$b_{3u}(\nu_{25})$
20689.5	607.1	Ø+607	$b_{1g}(\nu_{27})$
20717.4	635.0	Ø+606+29	
20802.3	722.8	0+723	$b_{3u}(\nu_{24})$
20839.3	759.8	0+760	$a_u(\nu_{22})$
20867.6	788.1	0+760+29	
20894.8	815.3	0+760+2X29	
20906.8	827.3	0+760+65	
20921.1	841.6	0+760+3X29	
20934.2	854.7	0+760+65+29	
20947.4	867.9	0+760+4X29	
21247.0	1167.5	0+723+458	
21297.4	1217.9	0+760+458	
21388.7	1299.2	0+146+1145	
21455.3	1372.9	Ø+607+788	
21582.7	1503.3	0+723+778	
21617.4	1537.9	0+760+788	
21645.0	1565.5	0+760+778+29	
21675.8	1596.3	0+760+778+2X29	
21774.8	1692.4	Ø+607+1091	
21815.4	1736.6	0+585+1145	
21919.5	1850.0	0+760+1091	
21952.3	1872.8	0+723+1145	
21994.3	1904.8	0+760+1145	
22389.8	2310.3	0+760+1091+458	
22395.6	2316.1	0+760+2X778	
22422.1	2342.6	0+760+2X778+29	
22457.9	2378.4	0+760+1145+458	
22772.7	2612.4	0+760+1091+778	
22837.7	2677.4	0+760+1145+778	
23058.8	2898.5	0+760+2X1091	
23097.4	2937.1	0+760+1145+1091	
23198.7	3038.4	0+760+2X1145	
24213.7	4053.4	0+760+2X1091+1145	

the method of handling was observed. Accordingly, we currently favor an alternative interpretation, consistent with both the observed polarization and intensity data, in which the higher energy more intense component is assigned as the crystal allowed $^1A_u \leftarrow {}^1A_g$ electronic origin and the low energy component, as the long axis polarized magnetic dipole allowed origin of the $^1B_{1g} \leftarrow {}^1A_g$ transition. In the subsequent discussion of the vibronic structure, evidence is presented for the near degeneracy of the two electronic origins.

The second feature of the crystal spectrum with no evident vapor analog corresponds to a region of absorption centered about 20307 cm⁻¹ [20320 cm⁻¹] consisting of at least two broad overlapping bands. Originally assigned by Sidman (14) as complex lattice structure associated with the first vibronic origin, the most intense of the several overlapping bands at 20307 cm⁻¹ has recently been reassigned by Trommsdorff (6, 16) as the crystal allowed $^1A_u \leftarrow {}^1A_g$ electronic origin.

The conclusions reached by Trommsdorff regarding the nature and assignment of the singlet origins, based upon his experiments and the experimental results of other workers, may be summarized as follows.

I. Extrapolation of the $^1B_{1g}-{}^1A_u$ electronic origin splitting observed in a series of halogeno-substituted quinones, yields a rough estimate of 1000 cm⁻¹ for the splitting in
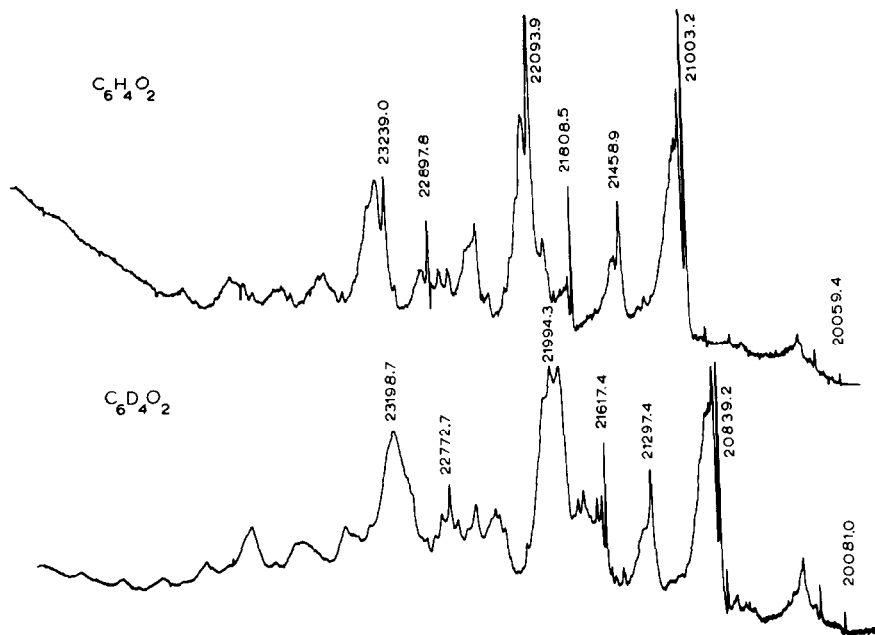
FIG. 3. Comparison of the b-axis polarized crystal absorption of p-benzoquinone-h_4 and $-d_4$.

PBQ. This is to be compared with 248 cm^{-1} required by that author's final assignment. Substitution of halogens for hydrogens has two effects. First, to lower the energy of the $\pi\pi^*$ transitions, the perturbation being roughly proportional to the number of halogen

<div align="center">TABLE V</div>

EXCITED STATE FUNDAMENTALS DERIVED FROM THE 4500 Å SYSTEMS

Type	$C_6H_4O_2$	$C_6D_4O_2$	$C_6H_4O_2^{18}$	$C_6D_4O_2^{18}$
$a_g(2)$	1149	1145	1126	1153
$a_g(3)$	1091	1091	1071	1067
$a_g(5)$	804	778	801	772
$a_g(6)$	458	459	443	446
$b_{1g}(27)$	784	607	786	610
$b_{1g}(30)$	319	307		
$a_u(22)$	945	760	945	758
$b_{3u}(24)$	833	723	830	721
$b_{3u}(25)$	677	585	---	---
$b_{3u}(26)$	147	146	143	140

substituents and, second, for the asymmetrically substituted quinones, to remove the Laporte restriction on the $^1B_{1g} \leftarrow {}^1A_g$ transition, thus enhancing the electric dipole intensity of this transition. The estimated splitting in PBQ is obtained by assuming equivalent crystal shifts of the individual electronic origins in the various neat lattices, a linear relationship between the number of halo-substituents and the splitting of the two electronic origins and, of course, correct identification of the respective origins in the various compounds studied.

II. The broad appearance of the feature assigned as the crystal allowed $^1A_u \leftarrow {}^1A_g$ electronic origin is said to be consistent with its assignment. There is extensive experimental evidence to indicate that excited states which are overlapped by lower lying excited states are broad in appearance. 'Interference' effects appear when the two overlapping excited states belong to different electronic configurations, and when the separation between the two 'interfering' states is on the order of 'normal' separations between excited states (23). When these conditions are fulfilled, discrete vibronic states of the higher lying excited state fall in a region of quasicontinuous absorption into high order harmonics and combinations of the lower lying state (large molecules).

Neither of these conditions exist in PBQ where, for the proposed assignment of the electronic origins, overlap occurs in a region of extremely low vibronic state density, and both states are of the same orbital configuration. The situation in PBQ would at best correspond to line broadening in the resonance limit, in which event the zero order vibronic states are widely spaced and broadening occurs through coupling with the quasicontinuum of phonon states in the dense medium. We should then expect a corresponding broadening of the vibronic features associated with the $^1B_{1g} \leftarrow {}^1A_g$ transition in this region and this is not observed.

III. The assignment of a vibronic origin involving $\nu_{30}'' = 244$ cm^{-1} based upon the proposed $^1A_u \leftarrow {}^1A_g$ electronic origin. Hollas originally noted that the second most prominent vapor phase sequence interval ($+78$ cm^{-1}) is most probably associated with ν_{30}, the second lowest frequency mode of PBQ. If this is correct the excited state frequency of this fundamental should be 322 cm^{-1}. The assignment proposed by Trommsdorff would require an excited state frequency of 356 cm^{-1} (our measurements). Although the frequency of ν_{30}' may be somewhat different in the ^1A_u state than in the $^1B_{1g}$ state, the difference is unacceptably large considering that the frequency is identical, within experimental error, in the $^1B_{1g}$ and ^3A_u states. Moreover, the assignment is not in agreement with the observed isotope shifts recorded for the feature in question.

In an effort to further check the assignment of the 20307 cm^{-1} band, we have examined the absorption spectrum of PBQ in both p-dichlorobenzene and p-dibromobenzene host lattices. Although these spectra lack much of the detail obtained in spectra of the pure crystal, nevertheless, two important observations are possible: first, that the origin band remains with approximately the same intensity as in the pure crystal and second, that the broad feature at 20,307 cm^{-1} assigned as $^1A_u \leftarrow {}^1A_g$ by Trommsdorff, has completely vanished. Since it seems highly unlikely that the crystal shifts of the two configurationally related states should be so markedly different,[2] an alternative assignment should be sought for this feature.

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[2] This point of view is supported by the close agreement between the $^1B_{1g}-{}^3A_u$ energy separation as observed in mixed crystal (1190 ± 10 cm^{-1} in p-dichlorobenzene) and single crystal (1113 cm^{-1}) absorption.
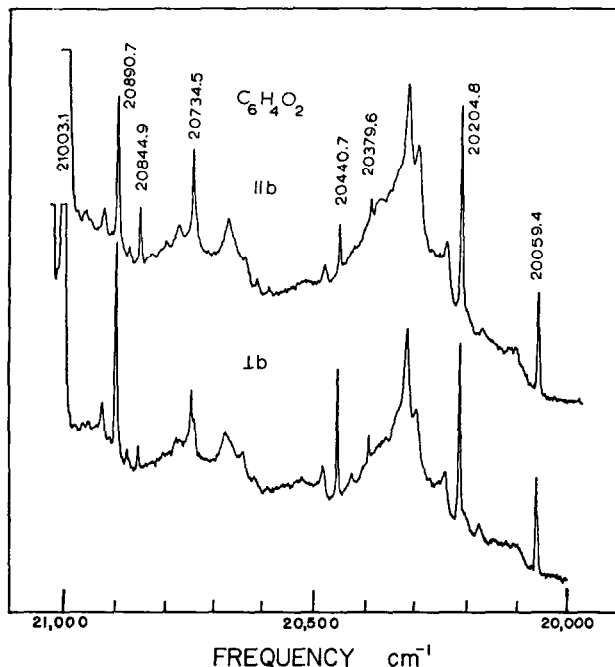
FIG. 4. Polarized absorption spectrum of p-benzoquinone-h_4 in the vibronic origin region at 1.8°K.

Vibronic Analysis

On the strength of the vapor phase absorption and emission analysis, we shall take as a starting point for the analysis of the crystal vibronic spectrum the following assignments:

(1)	21003 cm^{-1}	0 + 945 cm^{-1}	22_0^1	(a_u)
(2)	20204	0 + 147	26_0^1	(b_{3u}),
(3)	$\sim$20059	0–0	$^1B_{1g} \leftarrow {}^1A_g$.	

These assignments are supported by direct correlation with the corresponding vapor phase frequencies, vapor phase contour analysis, crystal band polarizations, and isotope shifts. It must be made clear that assignment (3) above refers to the inferred *frequency* of the electronic origin indicated and not to the assignment of the *band* which appears at this frequency. We shall confine our attention initially to the weak onset region of the absorption spectrum shown in Fig. 4 and assume that assignments may be made solely in terms of either electronic origins or vibronic origins involving out-of-plane vibrations. The latter assumption, which specifically excludes combination bands as vibronic origins,[3] is based upon the fact that Herzberg–Teller vibronic coupling between $\pi\pi^*$ and $n\pi^*$ states of a planar molecule requires the activity of an out-of-plane vibration. The 21 in-plane normal modes which transform as a_g (6), b_{3g} (5), b_{1u} (5), and b_{2u} (5) are

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[3] The only exception is the broad band at 20663.5 cm^{-1} [20689.5 cm^{-1}] which may be assigned to 0 + 147 + 458. The broad appearance of this band is characteristic of combinations involving the 458 cm^{-1} A_g (ν_6') mode. See, for example 0 + 945 + 458.
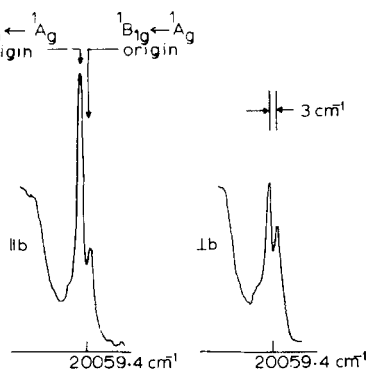
FIG. 5. Polarization and splitting of the crystal electronic origin at 1.8°K.

expected to be active as vibronic origins only to the extent that intensity is borrowed from allowed $n\pi^*$ or $\sigma\pi^*$ states.

Intensity borrowing from $n\pi^*$ states is not expected to be important, since there are no electric dipole allowed $n\pi^*$ eigenstates of PBQ, and the high energy of the $\sigma\pi^*$ states should make them relatively less important as sources of vibronically induced electric dipole intensity.

The nine out-of-plane normal modes of PBQ belong to the irreducible representations a_u (2), b_{3u} (3), b_{1g} (1), and b_{2g} (3). These may be subclassified as, principally, ring distortion modes, a_u (ν_{23}), b_{3u} (ν_{25}), and b_{2g} (ν_{29}) or substituent (C–H), (C=O) bending modes, a_u (ν_{22}), b_{3u} (ν_{26}, ν_{24}), b_{1g} (ν_{27}) ,and b_{2g} (ν_{28}, ν_{30}).

Assignments (1) and (2) above involve modes of the latter variety, both vibrations being derived from the same e_{2u} (C–H) bending mode of benzene (see Fig. 6). Since ν_{28}' (b_{2g}) is expected to be higher in frequency than ν_{22}' (a_u) and thus fall in a region of diffuse lattice absorption associated with this intense vibronic origin, there remain only six out-of-plane modes which may be assigned to the six remaining sharp vibronic bands of the onset region.

Because the assignment of ν_{22}' and ν_{26}' based upon the $^1B_{1g} \leftarrow {}^1A_g$ origin suggests a greater vibronic activity of the substituent bending modes relative to the ring distortion modes, we shall first consider the corresponding gerade modes, $\nu_{27}'(b_{1g})$ and $\nu_{30}'(b_{2g})$ derived from the single e_{1g} (C–H) bending mode of benzene as the most likely to induce vibronic intensity in the $^1A_u \leftarrow {}^1A_g$ transition. Noting that ν_{30} is simply the phase variant of ν_{26}, and using the vapor phase frequencies of ν_{26}' and ν_{26}'', we may estimate the frequency of ν_{30}' as $(\nu_{26}'/\nu_{26}'')\,\nu_{30}'' = 324$ cm^{-1} [305 cm^{-1}]. These frequencies may be compared with those inferred from analysis of the vapor phase sequence structure. The second most intense sequence in the vapor phase is expected to be associated with $\nu_{30}'' = 244$ cm^{-1} [228 cm^{-1}]. The observed sequence interval is $+78$ cm^{-1} [$+77$ cm^{-1}] and the corresponding excited state frequency should then be 322 cm^{-1} [305 cm^{-1}], in good agreement with the above estimate. Although the sequence interval is prominent in the vapor phase spectrum, the fundamental is not observed. In the crystal spectrum, however, bands are observed based upon the 20061.0 cm^{-1} [20082.4 cm^{-1}] electronic origin at $0+319$ cm^{-1} [$0+307$ cm^{-1}]. The short axis polarization of this band is
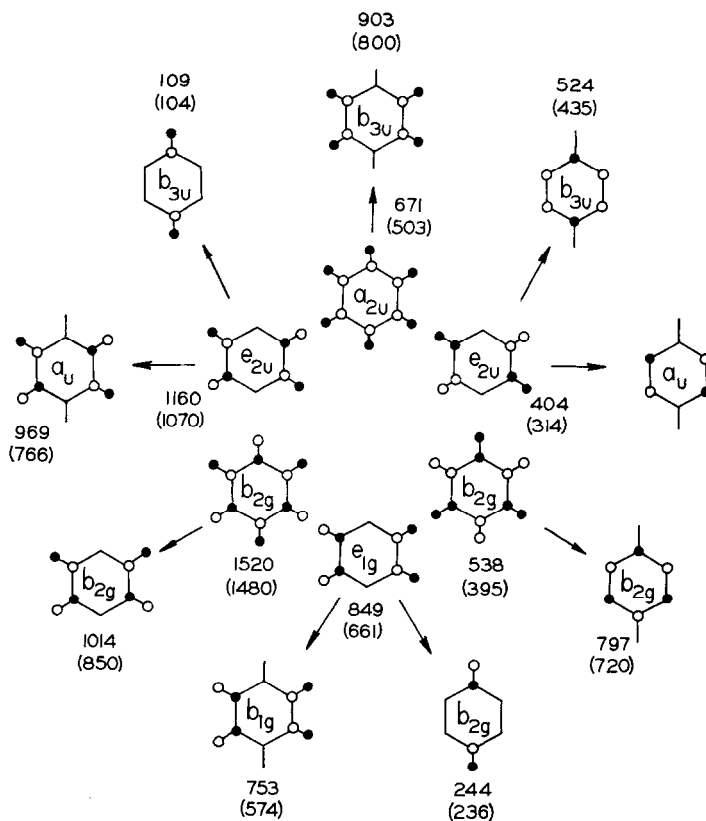
FIG. 6. Normal coordinates of vibronically active fundamentals of *p*-benzoquinone showing their benzene parentage.

consistent with its assignment as ν_{30}'. This assignment would, of course, imply that the two electronic origins are very nearly degenerate.

For the assignment of $\nu_{27}'(b_{1g})$ we used the Teller–Redlich product rule and the fact that this vibration is the only member of its class. Assuming that the dimensional changes in the excited state are such that the I_z inertial moment is essentially unchanged from its ground state value,[4] we have that:[5]

$$\nu_{27}'(h_4)/\nu_{27}'(d_4) = 1.29$$

Assignment of the long axis polarized band $0+784$ cm^{-1} $[0+607$ cm$^{-1}]$ as ν_{27}' based upon $^1A_u \leftarrow {}^1A_g$ at 20061.0 cm^{-1} gives both polarization and *precise* Product Rule agreement.

The only substituent bending mode yet unassigned is $\nu_{24}'(b_{3u})$ which has a frequency of 903 cm^{-1} $[800$ cm$^{-1}]$ in the ground state. Since the frequency of this mode is not ex-

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[4] This is consistent with the excited state model proposed by Hollas, in which the major dimensional changes occur along Z and with the appearance of a long progression in both the C = C and C = O stretching modes.

[5] This value was obtained using the inertial moments given in Ref. (*10*).

pected to change appreciably in the excited state, the $0+833$ cm^{-1} [723 cm^{-1}] vibronic origin offers the only possible assignment. This band was originally reported by Sidman to be long axis polarized, which is inconsistent with its assignment as an excited state b_{3u} fundamental based upon $^1B_{1g} \leftarrow {}^1A_g$. In the present examination of the crystal spectrum this band was found to be short axis polarized as required by the above assignment and in agreement with the direction of the transition moment predicted from the vapor phase band contour analysis.

The short axis polarized band $0+677$ cm^{-1} [$0+585$ cm^{-1}] is assigned to the remaining b_{3u} fundamental, ν_{25}'. This is in agreement with the vapor phase assignment by Hollas based upon the observed perpendicular contour. The calculated product ratio of excited state fundamentals belonging to the b_{3u} irreducible representation is independent of the excited state inertial moments and the Teller–Redlich theorem may be applied quantitatively to further check the assignments of ν_{24}', ν_{25}', ν_{26}'. The calculated and observed values of the product ratio for the excited b_{3u} fundamentals in the crystal are 1.39 and 1.34, respectively.

Unfortunately, with the available experimental data, no completely satisfactory assignment is possible for the remaining sharp vibronic feature at $0+383$ cm^{-1} [$0+343$ cm^{-1}] corresponding, apparently, to the band at $0+398$ cm^{-1} [$0+357$ cm^{-1}] in the spectrum of the vapor. The assignment of this feature as ν_{23}' (a_u) is in substantial agreement with the observed isotope shift and does not require an excessively large change in frequency upon electronic excitation. Furthermore the assignment is in reasonable agreement with the ground state frequency of 310 cm^{-1} [275 cm^{-1}] inferred from the vapor phase hot band absorption and the vapor fluorescence spectrum.

Although, as is consistent with its assignment, the vapor phase band was reported initially by Hollas as a parallel type (10), a later reinvestigation of the spectrum by the same author concluded that this feature of the spectrum is not intense enough for detailed contour analysis (11). This difficulty is not encountered in the analysis of the crystal spectra, where the band is quite clearly *short* axis polarized, *inconsistent* with the above assignment. Additionally, Hollas has pointed out that the above assignment would require the (1–0) band in ν_{23} to be considerably weaker than the corresponding (0–1) band. In the corresponding fluorescence spectrum the (0–1) feature should be relatively six times more intense than the (1–0) band of the absorption spectrum.

In view of these difficulties we have assigned this band as $0+26_3^0$, with the corresponding fluorescence band similarly attributed to $0+26_3^0$. This assignment is in agreement with the observed polarization, but requires a fair anharmonicity in ν_{26}. Considering the nature of the vibration, however, the anharmonicity required does not seem disproportionate, although it must be somewhat larger than originally assumed in the calculations of Hollas, Innes, and Ross (12). No other assignment is as satisfactory as this and it certainly seems obligatory that 26_0^3 and 26_3^0 be strong features of the electronic spectrum.

CONCLUSION

On the basis of 'through space' interaction solely, the electronic origins of the two transitions are expected to be very nearly degenerate, reflecting the slight spatial overlap between the oxygen nonbonding orbitals. Consideration of 'through bond' interactions in PBQ, however, predicts a splitting of several thousand wavenumbers between the

electronic origins. The energy difference between the nonbonding orbitals of PBQ has been calculated recently by numerous investigators and a considerable range of prediction of both the splitting and ordering of the nonbonding orbitals has been reported. Some of the more recent results are summarized in the following table.

Method	Splitting[6]	Ref.
CNDO	$+15,500$ cm^{-1}	(1)
EHT	$+ 3,790$	(1)
CNDO	$+ 2,180$	(6)
CNDO	$- 5,560$	(24)
CNDO	$- 5,970$	(25)
EHT	$- 6,210$	(3)

[6] Positive value indicates antisymmetric combination is higher in energy than the symmetric combination.

The available experimental work with which to compare these results consists largely of several assignments of the photoelectron spectrum of PBQ. In this connection we note that the assignments of the nonbonding orbital ionization energies is evidently not at this time unambiguous. Experimental splittings of $-11, 210$ cm^{-1} (26), $-7,259$ cm^{-1} (3), and $\pm2,400$ cm^{-1} (4) have been reported in the literature.

Several values of the splitting between the $n\pi^*$ states have also been calculated theoretically using the CNDO/CI approach, but these values, predictably, vary as much as the theoretical splitting of the ground state orbitals. The sole experimental determination of the splitting between the excited states has been reported by Trommsdorff. While we feel that this assignment is probably incorrect based on the arguments presented above, we nevertheless must agree that any splitting of greater than 2000 cm^{-1} is simply incompatible with the available experimental data. The Hollas analysis of the vapor phase absorption spectrum has established the origin of the ^3A_u–^1A_g absorption at 18947 cm^{-1}. Since we would not expect the singlet–triplet splitting of an $n\pi^*$ state to exceed 3000 cm^{-1}, in any event, the ^1A_u–^1A_g electronic origin must lie well below approximately 22,000 cm^{-1}.

It is clear that there are too many vibronic origins between the band at approximately 20059 cm^{-1} and the very strong origin at 21003 cm^{-1} to be accounted for solely in terms of ungerade fundamentals based upon the $^1B_{1g}$–^1A_g electronic origin. The vibronic analysis suggests, both from the Product Rule and polarization, that several of the vibronic origins involve gerade fundamentals also based upon the origin at about 20059 cm^{-1}, suggesting the presence of the ^1A_u–^1A_g origin at an almost coincident frequency to that of the $^1B_{1g}$–^1A_g. On the basis of the analysis presented above it would appear that both EHT and CNDO considerably overestimate the magnitude of the nonbonding orbital interaction in PBQ.

The proper assignment of several prominent features in the absorption spectrum of PBQ remain in question. The most important of these is the broad compound region of absorption centered about 20307 cm^{-1}. The absence of this feature in the mixed crystal absorption spectra, suggests that the band in question may belong to either a triplet or singlet $\pi\pi^*$ state, either of which could lie in this spectral region. Such an assignment

would be consistent with the markedly different crystal shifts leading to the disappearance of the band in p-dichloro and p-dibromobenzene hosts.

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