

## The Ground State Fundamentals of *p*-Benzoquinone and *p*-Benzoquinone- $d_4$

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The solid state infrared and Raman spectra of *p*-benzoquinone and several isotopic derivatives are reported and compared with the results of previous solution and vapor phase studies and with the results of previously published normal coordinate analyses. The vibrational assignments are discussed in terms of the vibronic activity observed in the phosphorescence spectra of the individual isotopically related quinones in several host lattices at 2°K. The infrared and Raman inactive fundamentals of *p*-benzoquinone- $h_4$  obtained from vibronic analyses of the vapor phase resonance fluorescence are reported. The six Raman active lattice modes of *p*-benzoquinone- $h_4$  and  $-d_4$  are assigned with the aid of isotopic shifts and thermal-anisotropic-motion amplitudes from previously published X-ray diffraction data.

### INTRODUCTION

As part of a study of the low temperature electronic emission spectra of *p*-benzoquinone single and mixed crystals, a considerable amount of information has been obtained regarding the assignments of the ground state fundamentals of this molecule and those of several of its isotopically substituted derivatives. Unexpectedly large changes in the frequencies of several infrared active modes, observed as vibronic origins in the phosphorescence spectra, from the values reported for the solution and vapor phase infrared, have led us to reinvestigate the complete Raman and infrared spectra of single crystals of *p*-benzoquinone- $h_4$  and  $-d_4$ .

Stammreich and Forneris (1) obtained the first complete Raman spectrum of *p*-benzoquinone in 1952 and speculated on the assignment of some of the observed Raman shifts. Anno and Sado (2) recorded the infrared spectrum of quinone and, utilizing the Raman data of Stammreich and Forneris, published a complete vibrational assignment, drawing where necessary upon the results of calculations of the totally symmetric frequencies using force constants derived from those for benzene. A simple valence force field approximation was used in this calculation and the agreement between experimental and theoretical frequencies was poor. Davies and Pritchard (3) obtained the infrared spectra of quinone both in solution and in the vapor phase and, by using analogies to para-disubstituted benzenes, arrived at a complete assignment differing in several respects from that of Anno and Sado. Becker, Ziffer, and Charney (4) have studied, in detail, Fermi resonances in the carbonyl stretching region of the infrared spectrum of quinone and obtained the infrared spectra of several isotopically substituted quinones. A thorough reinvestigation of the Raman spectrum of quinone was undertaken by Stammreich and

Sans (5) in 1964, followed shortly by a complete normal coordinate analysis of quinone and its isotopic derivatives by Anno (6). The experimental and theoretical results for quinone and several of its isotopic derivatives have been correlated in a paper by Becker, Charney and Anno, setting forth complete vibrational assignments for quinone and six isotopic derivatives (7).

In summary, assignment of the molecular fundamentals of quinone has been accomplished by: (1) comparison of the observed vibrational frequencies with those of substituted benzenes; (2) analysis of the vapor phase infrared band contours and Raman band polarizations; (3) comparison with the theoretical frequencies from a complete normal coordinate calculation; and, (4) studies of the isotope shifts and application of the Teller-Redlich product rule to the final assignments. Using these methods, it has been possible to arrive at convincing assignments for many of the thirty fundamentals. However, for those fundamentals which are either Raman *and* infrared inactive, or too weak for contour or polarization analysis, agreement with the theoretical results is the only basis for assignment. Inevitably, with thirty fundamentals, there occur instances where the theoretical results alone cannot distinguish between alternative assignments.

Two of the thirty fundamentals of *p*-benzoquinone transform as the  $a_u$  representation of the  $D_{2h}$  molecular point group and are, accordingly, Raman and infrared inactive. The only experimental determination of these fundamentals is of an indirect type, from the analysis of the visible electronic absorption spectrum of vaporized quinone, in particular, that portion of the spectrum attributed to absorption from thermally populated ground state vibrational levels (8). The experimental frequencies of these fundamentals, therefore, depend entirely on the correct assignment of these features as 'hot bands.'

In the present paper, we have correlated the assignments obtained from analysis of the solid state low temperature phosphorescence spectra of *p*-benzoquinone- $h_4$ ,  $-d_4$ ,  $-d_4O_2^{18}$ , and the single crystal infrared and Raman spectra, with the results of previous analyses of the solution and vapor phase vibrational spectra. The increased resolution afforded by the use of low temperatures in obtaining the single crystal vibrational spectra, as well as limited band polarization information, when combined with the results of the analyses of the crystal phosphorescence spectra, yield unambiguous assignments of the Raman and infrared active fundamentals. In addition, the frequencies of the  $a_u$  fundamentals have been obtained from an analysis of the vapor phase fluorescence spectra of *p*-benzoquinone- $h_4$  and  $-d_4$ .

#### EXPERIMENTAL

Infrared spectra were obtained from crystalline samples prepared by melting the powdered material between polished flats of caesium iodide and allowing slow recrystallization. The samples were then examined between crossed sheets of polarizing material and uniformly oriented sections selected for study by masking. The sample was cooled by conduction to approximately 100°K in a liquid nitrogen dewar. Spectra were recorded on a Perkin-Elmer IR-12 recording spectrophotometer.

Raman spectra were recorded at 77°K on Jarrell-Ash and Spex laser Raman recording spectrophotometers using both single crystals of quinone grown from the melt in a vertical Bridgeman furnace and powdered samples contained in a narrow bore capillary tubes.

The techniques used to obtain the low temperature (2°K) single and mixed crystal phosphorescence spectra are described in Part II of this work.

### DISCUSSION

In the following, the molecular plane is regarded as the *YZ* plane, with the *Z* axis connecting the oxygen atoms. The thirty vibrational degrees of freedom are all related to nondegenerate symmetry species of the  $D_{2h}$  molecular point group. Fundamentals having symmetries  $a_g$ ,  $b_{3g}$ ,  $b_{1u}$ , and  $b_{2u}$  are related to vibrational motions in the plane of the molecule, and the  $a_u$ ,  $b_{3u}$ ,  $b_{1g}$ , and  $b_{2g}$  modes, to out-of-plane vibrations. The normal coordinates of these modes have been described in greater detail by Zimmermann (9) and by Garrigou-Lagrange, Lebas, and Josien (10).

The crystal structure of *p*-benzoquinone belongs to the space group  $C_{2h}^5$  ( $P_{2_1/a}$ ) and has two molecules per unit cell, both on sites  $C_i$  (11). The differences between the spectrum of quinone in the vapor phase and in the solid state arise from site group splitting ( $D_{2h} \rightarrow C_i$ ) and factor group splitting ( $C_i \rightarrow C_{2h}$ ) and combinations with lattice modes. The  $a_u$  fundamentals, infrared and Raman inactive in point group  $D_{2h}$ , are infrared active in the factor group  $C_{2h}$ .

The moments of inertia used in the calculation of the isotope product ratios are derived from the X-ray diffraction data using a C-H bond distance of 1.075 Å and are essentially identical to the values obtained when the vapor phase electron diffraction data (12, 16) are used.

The solid state low temperature infrared spectrum of quinone- $h_4$  obtained with incident radiation perpendicular to the (20 $\bar{1}$ ) crystal face is shown in Fig. 1. Due to the near coplanarity of the molecular and (20 $\bar{1}$ ) crystal planes,  $b_{3u}$  fundamentals appear with diminished intensity relative to the  $b_{1u}$  and  $b_{2u}$  fundamentals. The analysis of the solid state infrared spectrum of quinone- $h_4$  is given in Table I-h and that of quinone- $d_4$  in Table I-d.

The single crystal Raman spectrum of quinone- $h_4$  is shown in Fig. 2 and the analysis given in Table II-h). The analysis of the Raman spectrum of quinone- $d_4$  appears in Table II-d. In Table III the final assignments for the solid state fundamentals of *p*-benzoquinone- $h_4$  and - $d_4$  are collected and correlated with the assignments from previous

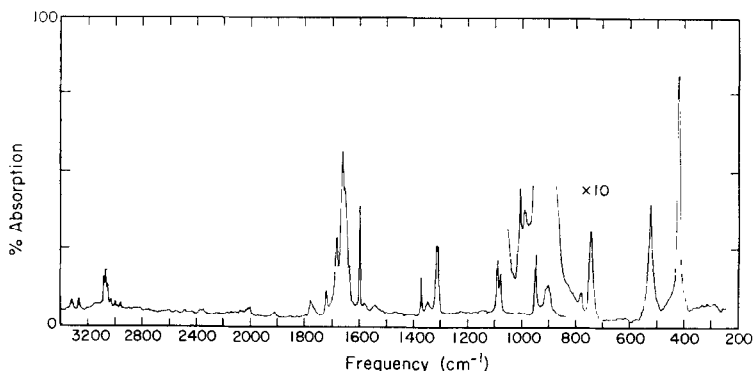


FIG. 1. Infrared spectrum of crystalline *p*-benzoquinone- $h_4$  at 77°K.

studies. With the exception of those fundamentals belonging to the irreducible representations  $b_{1u}$ , excellent agreement is obtained between the theoretical and experimental isotope product ratios shown in Table IV.

The six totally symmetric fundamentals of *p*-benzoquinone may be described approximately as: a C-H stretching vibration,  $\nu_1$ ; a C=O stretching vibration,  $\nu_2$ ; a C=C stretching vibration,  $\nu_3$ ; a C-H bending vibration,  $\nu_4$ ; a C-C stretching vibration,  $\nu_5$ ; and a ring bending vibration,  $\nu_6$ .

One of the most perplexing problems in the assignment of the vibrational modes of *p*-benzoquinone has been the identification of the carbonyl symmetric and antisymmetric stretching frequencies, and the C=C symmetric stretching frequency. The fundamentals  $\nu_2$  and  $\nu_3$  as noted above are related to the totally symmetric stretching modes of C=O and C=C, respectively, and are expected to couple strongly each involving coordinates of both motions. Evidently, from the NCA analysis (6), all three fundamentals are expected to lie in the frequency range 1640-1680  $\text{cm}^{-1}$  in the various isotopically substituted molecules of quinone. In addition to these fundamentals, several binary combinations are also found in this region, and the possibility of resonance interactions (4) further complicates assignment of the normal mode frequencies.

The assignments of  $\nu_2$ ,  $\nu_3$ , and  $\nu_{13}$  are obtained most conveniently from the analysis of low temperature phosphorescence spectra (14), in which the strong vibronic origins

TABLE I-d: INFRARED ABSORPTION BANDS OF *p*-BENZOQUINONE- $\text{d}_4$

| Wave Number | Assignment                  | Relative Intensity |
|-------------|-----------------------------|--------------------|
| 410         | $\nu_{21}$ ( $b_{2u}$ )     | 60                 |
| 435         | $\nu_{25}$ ( $b_{3u}$ )     | 5                  |
| 674         | $\nu_{16}$ ( $b_{1u}$ )     | 5                  |
| 800         | $\nu_{24}$ ( $b_{2u}$ )     | 10                 |
| 805         | $\nu_{20}$ ( $b_{3u}$ )     | 35                 |
| 874         | $\nu_{15}$ ( $b_{1u}$ )     | 30                 |
| 1157        | 410 + 746 = 1156 $B_{2u}$   | 15                 |
| 1167        | $\nu_{14}$ ( $b_{1u}$ )     | 45                 |
| 1230        | 3x410 = 1230 $B_{2u}$       | 10                 |
| 1234        | 800 + 435 = 1235 $B_{1u}$   | 15                 |
| 1246        | 410 + 832 = 1242 $B_{2u}$   | 30                 |
| 1268        | $\nu_{19}$ ( $b_{2u}$ )     | 40                 |
| 1393        | 674 + 720 = 1393 $B_{3u}$   | 10                 |
| 1543        | 805 + 746 = 1551 $B_{2u}$   | 15                 |
| 1564        | $\nu_{18}$ ( $b_{2u}$ )     | 100                |
| 1597        | 674 + 927 = 1601 $B_{2u}$   | 15                 |
| 1616        | 874 + 746 = 1620 $B_{1u}$   | 40                 |
| 1628        | 905 + 832 = 1637 $B_{2u}$   | 40                 |
| 1655        | $\nu_{13}$ ( $b_{1u}$ )     | 100                |
| 1745        | 1167 + 582 = 1749 $B_{2u}$  | 5                  |
| 1848        | 1268 + 582 = 1850 $B_{1u}$  | 5                  |
| 1913        | 1167 + 746 = 1913 $B_{1u}$  | 7                  |
| 2012        | 1268 + 746 = 2014 $B_{2u}$  | 3                  |
| 2215        | 874 + 1337 = 2211 $B_{2u}$  | 3                  |
| 2278        | $\nu_{17}$ ( $b_{2u}$ )     | 15                 |
| 2300        | $\nu_{12}$ ( $b_{1u}$ )     | 50                 |
| 2505        | 1167 + 1337 = 2504 $B_{2u}$ | 5                  |
| 2820        | 1167 + 1643 = 2810 $B_{1u}$ | 2                  |
| 2902        | 1564 + 1337 = 2901 $B_{1u}$ | 4                  |
| 3280        | 1651 + 1643 = 3294 $B_{1u}$ | 30                 |

TABLE I-h: INFRARED ABSORPTION BANDS OF *p*-BENZOQUINONE-*h*<sub>4</sub>

| Wave Number | Assignment                     | Relative Intensity |
|-------------|--------------------------------|--------------------|
| 415         | $\nu_{21}$ ( $b_{2u}$ )        | 50                 |
| 524         | $\nu_{25}$ ( $b_{3u}$ )        | 20                 |
| 745         | $\nu_{16}$ ( $b_{1u}$ )        | 20                 |
| 903         | $\nu_{24}$ ( $b_{1u}$ )        | 35                 |
| 946         | $\nu_{15}$ ( $b_{1u}$ )        | 80                 |
| 1076        | $\nu_{20}$ ( $b_{2u}$ )        | 50                 |
| 1187        | $415 + 772 = 1187$ $B_{2u}$    | 10                 |
| 1248        | $3 \times 415 = 1245$ $B_{2u}$ | 10                 |
| 1312        | $\nu_{19}$ ( $b_{1u}$ )        | 70                 |
| 1345        | $903 + 443 = 1346$ $B_{1u}$    | 30                 |
| 1366        | $\nu_{14}$ ( $b_{1u}$ )        | 35                 |
| 1542        | $745 + 797 = 1542$ $B_{3u}$    | 10                 |
| 1570        | $415 + 1152 = 1567$ $B_{2u}$   | 10                 |
| 1595        | $\nu_{18}$ ( $b_{2u}$ )        | 60                 |
| 1655        | $\nu_2$ ( $a_g$ )              | 65                 |
| 1665        | $\nu_{13}$ ( $b_{1u}$ )        | 65                 |
| 1682        | $\nu_3$ ( $a_g$ )              | 60                 |
| 1718        | $946 + 772 = 1718$ $B_{1u}$    | 25                 |
| 1856        | $1076 + 772 = 1848$ $B_{2u}$   |                    |
| 1912        | $1312 + 600 = 1912$ $B_{2u}$   |                    |
| 1967        | $1366 + 600 = 1966$ $B_{2u}$   |                    |
| 1976        | $745 + 1235 = 1980$ $B_{2u}$   |                    |
| 2082        | $1312 + 772 = 2084$ $B_{1u}$   |                    |
| 2138        | $1366 + 772 = 2138$ $B_{1u}$   |                    |
| 2243        | $1076 + 1152 = 2228$ $B_{2u}$  |                    |
| 2342        | $946 + 1393 = 2339$ $B_{2u}$   |                    |
| 2745        | $1366 + 1393 = 2759$ $B_{2u}$  |                    |
| 2990        | $1595 + 1393 = 2988$ $B_{1u}$  |                    |
| 3030        | $1366 + 1665 = 3031$ $B_{1u}$  |                    |
| 3062        | $\nu_{17}$ ( $b_{2u}$ )        |                    |
| 3080        | $\nu_{12}$ ( $b_{1u}$ )        |                    |
| 3315        | $1665 + 1655 = 3320$ $B_{1u}$  |                    |

observed involve a single quantum of the antisymmetric carbonyl stretching vibration and strong progressions, built upon these vibronic origins, involve multiple quanta of the totally symmetric carbonyl stretching vibrations. This fortunate circumstance assists in identification of both the symmetric and antisymmetric carbonyl stretching modes. The totally symmetric C=C stretching mode, though observed, plays a less significant role in the emission spectra of quinone mixed crystals.

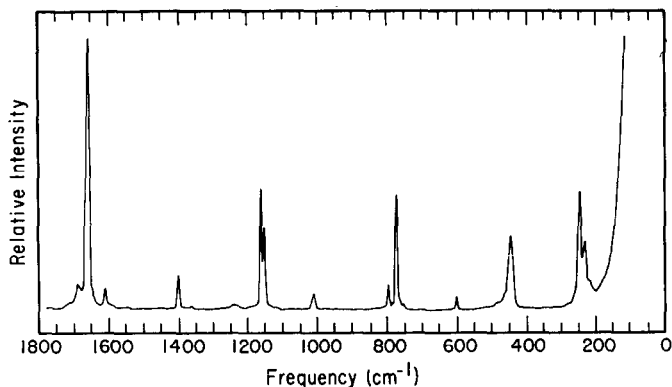
The assignments of  $\nu_2$  and  $\nu_3$  in *p*-benzoquinone-*d*<sub>4</sub> have been interchanged from those originally made by Charney *et al.*, primarily on the basis of the appearance of these two fundamentals in the emission spectra. Extensive Fermi resonance interaction in the carbonyl stretching region of the infrared spectrum *p*-benzoquinone-*h*<sub>4</sub> and -*d*<sub>4</sub> has been demonstrated previously (4). The phosphorescence spectra of pure quinone as well as mixed crystals of quinone in several dihalogenated benzenes yield slightly different frequencies for the normal modes  $\nu_{13}$ ,  $\nu_2$ , and  $\nu_3$ , suggesting a high degree of sensitivity to crystalline environment. Since Fermi resonance interactions depend critically on the anharmonic content of the modes involved, and since the anharmonicity of the vibrations will be influenced by the crystal field, such sensitivity is not wholly unexpected. Vibrational intervals of approximately  $1650\text{ cm}^{-1}$  and  $1645\text{ cm}^{-1}$  were observed in progressions of two or more members in the various emission spectra of quinone-*h*<sub>4</sub> and -*d*<sub>4</sub>,

TABLE II-d: RAMAN BANDS OF p-BENZOQUINONE-d<sub>4</sub> (77°K)

| Wave Number | Assignment                | Relative Intensity |
|-------------|---------------------------|--------------------|
| 63          | lattice                   |                    |
| 80          | lattice                   |                    |
| 105         | lattice                   |                    |
| 217         | $2 \times 105 = 210 A_g$  | 8                  |
| 235         | $\nu_{30} (b_{2g})$       | 16                 |
| 450         | $\nu_6 (a_g)$             | 45                 |
| 460         | $\nu_{11} (b_{2g})$       | 14                 |
| 575         | $\nu_{27} (b_{1g})$       | 5                  |
| 585         | $\nu_{10} (b_{3g})$       | 5                  |
| 700         | $\nu_{29} (b_{2g})$       |                    |
| 745         | $\nu_5 (a_g)$             | 35                 |
| 832         | $\nu_4 (a_g)$             | 45                 |
| 950         | $\nu_{28} (b_{2g})$       | 25                 |
| 985         | $\nu_9 (b_{3g})$          | 2                  |
| 1227        | $745 + 532 = 1377 B_{3g}$ | 10                 |
| 1337        | $\nu_8 (b_{3g})$          | 15                 |
| 1445        | $\nu_2 (a_g)$             | 100                |
| 1595        | $\nu_3 (a_g)$             | 60                 |
| 1711        | $\nu_7 (b_{3g})$          | 3                  |
| 2200        | $\nu_1 (a_g)$             | 10                 |

TABLE II-h: RAMAN BANDS OF p-BENZOQUINONE-h<sub>4</sub>

| Wave Number | Assignment                  | Relative Intensity |
|-------------|-----------------------------|--------------------|
| 20          | lattice                     |                    |
| 41          | lattice                     |                    |
| 65          | lattice                     |                    |
| 117         | lattice                     |                    |
| 237         | $2 \times 117 = 234$        | 25                 |
| 244         | $\nu_{30} (b_{2g})$         | 40                 |
| 445         | $\nu_6 (a_g)$               | 25                 |
| 476         | $\nu_{11} (b_{3g})$         | 3                  |
| 600         | $\nu_{10} (b_{3g})$         | 5                  |
| 753         | $\nu_{27} (b_{1g})$         | 3                  |
| 772         | $\nu_5 (a_g)$               | 45                 |
| 797         | $\nu_{29} (b_{2g})$         | 10                 |
| 1014        | $\nu_{28} (b_{2g})$         | 5                  |
| 1152        | $\nu_4 (a_g)$               | 30                 |
| 1164        | $745 + 417 = 1162 B_{3g}$   | 40                 |
| 1235        | $\nu_9 (b_{3g})$            | 1                  |
| 1363        | $772 + 600 = 1372 B_{3g}$   | 10                 |
| 1393        | $\nu_8 (b_{3g})$            | 15                 |
| 1543        | $2 \times 772 = 1544 A_g$   | 1                  |
| 1594        | $2 \times 797 = 1594 A_g$   | 1                  |
| 1614        | $600 + 1014 = 1614 B_{1g}$  | 1                  |
| 1660        | $\nu_2 (a_g)$               | 100                |
| 1687        | $\nu_3 (a_g)$               | 30                 |
| 1717        | $745 + 969 = 1714 B_{1g}$   | 1                  |
| 2948        | $1366 + 1595 = 2961 B_{3g}$ | 2                  |
| 3045        | $\nu_7 (b_{3g})$            | 1                  |
| 3060        | $\nu_1 (a_g)$               | 5                  |
| 3075        | $1684 + 1393 = 3077 B_{3g}$ | 2                  |
| 3183        | $2 \times 1595 = 3190 A_g$  |                    |
| 3347        | $1655 + 1684 = 3339 A_g$    |                    |
| 3360        | $2 \times 1665 = 3330 A_g$  | 1                  |

FIG. 2. Raman spectrum of crystalline *p*-benzoquinone-*h*<sub>4</sub> at 77°K.

respectively. In view of the fact that the electronic transition is localized largely on the carbonyl group, the most probable assignment of the totally symmetric progression interval is to the C=O totally symmetric stretching mode,  $\nu_2$ . The intense vibronic origins at approximately  $0-1660\text{ cm}^{-1}$  and  $0-1655\text{ cm}^{-1}$  for quinone-*h*<sub>4</sub> and -*d*<sub>4</sub>, respectively, must be assigned to the antisymmetric C=O stretching mode,  $\nu_{13}$ . The totally symmetric

TABLE III: Summary of *p*-Benzoquinone Fundamental Assignments

|          |    | $C_6H_4O$ |      |      |      |       | $C_6D_4O$ |       |
|----------|----|-----------|------|------|------|-------|-----------|-------|
|          |    | I         | II   | III  | IV   | V     | IV        | V     |
| $A_g$    | 1  | 3058      | 3058 | 3058 | 3062 | 3060  | 2290      | 2286  |
|          | 2  | 1688      | 1688 | 1688 | 1667 | 1660  | 1668      | 1643  |
|          | 3  | 1667      | 1667 | 1667 | 1606 | 1607  | 1657      | 1650  |
|          | 4  | 1149      | 1149 | 1149 | 1147 | 1152  | 828       | 832   |
|          | 5  | 770       | 770  |      | 770  | 772   | 746       | 746   |
|          | 6  | 444       | 444  |      | 443  | 445   | 433       | 435   |
| $B_{2g}$ | 7  | 3058      | 3058 |      | 3044 | 3045  | 2277      | 2271  |
|          | 8  | 1360      | 1360 |      | 1374 | 1384* | 1318*     | 1306* |
|          | 9  | 1149      | 610  | 1360 | 1235 | 1235  | 919       | 928   |
|          | 10 | 610       |      | 610  | 600  | 600   | 582       | 582   |
|          | 11 | 540       |      |      | 476  | 476   | 464       | 460   |
| $B_{1u}$ | 12 | 3012      | 3049 | 3061 | 3062 | 3062  | 2277      | 2300  |
|          | 13 | 1660      | 1667 | 1669 | 1666 | 1665  | 1660*     | 1659  |
|          | 14 | 1357      | 1715 | 1353 | 1354 | 1366  | 1160      | 1167  |
|          | 15 | 944       | 1297 | 1063 | 944  | 946   | 873       | 874   |
|          | 16 | 743       | 730  |      | 728  | 743   | 635       | 674   |
| $B_{2u}$ | 17 | 3058      | 3049 | 3061 | 3062 | 3080  | 2277      | 2278  |
|          | 18 | 1592      | 943  | 1296 | 1592 | 1595  | 1560      | 1564  |
|          | 19 | 1302      | 1063 | 1592 | 1239 | 1312  | 1248*     | 1268  |
|          | 20 | 1066      | 1355 | 1063 | 1066 | 1076  | 793       | 805   |
|          | 21 | 409       | 370  |      | 409  | 415   | 402       | 410   |
| $A_u$    | 22 |           |      |      |      | (969) | (766)     |       |
|          | 23 |           | 553  |      |      | (310) | (272)     |       |
| $B_{1u}$ | 24 | 884       | 876  | 879  | 882  | 903   | 793       | 800   |
|          | 25 | 508       | 99   |      | 505  | 524   | 418       | 435   |
|          | 26 | 108       | 533  |      | 109  | 109   | 104       | (104) |
| $B_{2g}$ | 27 | 794       | 794  |      | 745  | 753   | 574       | 573   |
|          | 28 | 932       |      |      | 998  | 1014  | 843       | 890   |
| $B_{2u}$ | 29 | 610       | 790  |      | 794  | 797   | 711       | 720   |
|          | 30 | 243       | 243  |      | 241  | 244   | 228       | 236   |

I Prichard and Davies

II Anno and Sado

III Claverie

IV Charney et al.

V This study

\* Fermi Resonance

( ) Vapor Phase Values

TABLE IV : Theoretical and Experimental Product Ratios

| Type     | Calculated Value | Experimental Value |       |
|----------|------------------|--------------------|-------|
|          |                  | Solid              | Vapor |
| $a_g$    | 1.99             | 2.00               | 2.00  |
| $b_{1g}$ | 1.29             | 1.29               | 1.30  |
| $b_{2g}$ | 1.39             | 1.39               | 1.40  |
| $b_{2g}$ | 1.93             | 1.99               | 1.98  |
| $a_u$    | 1.41             |                    | 1.43  |
| $b_{3u}$ | 1.96             | 1.86               | 1.95  |
| $b_{4u}$ | 1.96             | 1.93               | 1.95  |
| $b_{3u}$ | 1.39             | 1.39               | 1.37  |

C=C stretching mode,  $\nu_3$ , was observed in the phosphorescence spectra of quinone- $h_4$  only. From the analysis of the phosphorescence spectrum of quinone- $d_4O_2^{18}$ , the corresponding fundamental frequencies are:  $\nu_2$  (1628  $\text{cm}^{-1}$ ),  $\nu_3$  (1600  $\text{cm}^{-1}$ ),  $\nu_{13}$  (1633  $\text{cm}^{-1}$ ).

The above assignments are consistent with the expectation that, in the uncoupled motions, the influence of deuteration manifests itself predominantly in the skeletal vibration, while the effect of  $O^{18}$  substitution is distributed between the carbonyl and skeletal motions. These assignments are essentially those originally proposed by Stammreich and Sans, (5) but later revised by Charney, Becker, and Anno (7) who interchanged the assignments of  $\nu_2$  and  $\nu_3$ . It is somewhat surprising to find the frequency of the C=C stretching vibration to be higher than that of the carbonyl group. Evidently, the effect of the carbonyl is to concentrate charge in the ring, thereby increasing the C=C bond order. This interpretation is supported by the X-ray diffraction data from which a C=C bond length of 1.32 Å slightly shorter than the corresponding bond length in ethylene, was deduced.

Of the remaining totally symmetric fundamentals,  $\nu_5$   $\nu_6$  appear in numerous combinations and progressions in the crystal emission spectra, thus supporting the assignments by Charney, Becker and Anno. The frequencies of  $\nu_5$  and  $\nu_6$  in the solid state Raman spectrum are essentially the same as those reported by previous investigators for the solution and vapor phase spectra. The totally symmetric C-H bending vibration  $\nu_4$ , however, was found to increase 10  $\text{cm}^{-1}$  in the solid.

The five  $b_{3g}$  fundamentals may be described approximately as: a C-H bending vibration,  $\nu_7$ ; a C-C stretching vibration,  $\nu_8$ ; a C-H bending vibration,  $\nu_9$ ; a ring bending vibration,  $\nu_{10}$ ; and a C=O bending vibration,  $\nu_{11}$ . The frequencies of the fundamentals observed in the solid state Raman spectrum agree well with those reported for the solution Raman spectrum by Stammreich and Sans. Only  $\nu_8$  requires special comment. Two bands of moderate intensity at 1392/1356  $\text{cm}^{-1}$  in the solution spectrum of quinone- $h_4$  and 1337/1299  $\text{cm}^{-1}$  in quinone- $d_4$ , provide possible assignments for  $\nu_8$ . Only one fundamental is expected in this region and the appearance of a second band of moderate intensity has been explained by a resonance splitting arising from the interaction of the fundamental  $\nu_8$  with the combination band  $\nu_5 + \nu_{10}$ , which belongs to the symmetry class  $b_{3g}$ . This argument leads to the assignment of a frequency of 1374  $\text{cm}^{-1}$  and 1318  $\text{cm}^{-1}$  for  $\nu_8$  in the  $-h_4$  and  $-d_4$  compounds, respectively. Similar diads were observed in the solid state Raman spectrum at 1393/1363  $\text{cm}^{-1}$  ( $-h_4$ ) and 1337/1297  $\text{cm}^{-1}$  ( $-d_4$ ). The corresponding combinations of  $\nu_5 + \nu_{10}$  are 1372  $\text{cm}^{-1}$  and 1328  $\text{cm}^{-1}$  leading to assign-



TABLE I: Lattice frequencies of crystalline *p*-benzoquinone

| p-Benzoquinone- <i>h</i> : |             |              | p-benzoquinone- <i>d</i> : |            |
|----------------------------|-------------|--------------|----------------------------|------------|
| 298°K(calc.)               | 298°K(obs.) | 77°K(obs.)   | 77°K(calc.)                | 77°K(obs.) |
| 48 · 4 ( $\nu_x$ )         | 40 · 4      | { 49<br>57   | 48                         | 48         |
| 64 · 7 ( $\nu_y$ )         | 66 · 4      | { 75<br>82   | 76                         | 76         |
| 68 · 16 ( $\nu_z$ )        | 117 · 10    | { 107<br>135 | 101                        | 94         |
|                            |             |              | 128                        | 122        |

ments of  $\nu_8$  of  $1384 \text{ cm}^{-1}$  ( $-h_4$ ) and  $1306 \text{ cm}^{-1}$  ( $-d_4$ ). It has been noted (5) that the resonance interaction suggested above is completely analogous to the well-known case of Fermi resonance observed in the spectrum of benzene. A combination frequency arising from a planar ring distortion mode ( $e_{2g}$ ,  $606 \text{ cm}^{-1}$ ) and a ring breathing mode ( $a_{1g}$ ,  $992 \text{ cm}^{-1}$ ) interacts with the C-C stretching fundamental ( $e_{2g}$ ) and leads to the band splitting  $1585/1606 \text{ cm}^{-1}$ . The  $e_{2g}$  modes under point group  $D_{6h}$  are directly correlated with the  $b_{3g}$  modes in  $D_{2h}$  and correspond to similar vibrational motions.

The five  $b_{1u}$  fundamentals may be approximately described as: a C-H stretching vibration,  $\nu_{12}$ ; a C=C stretching vibration,  $\nu_{13}$ ; a C-H bending vibration,  $\nu_{14}$ ; a C-C stretching vibration,  $\nu_{15}$ ; and a ring bending vibration,  $\nu_{16}$ .

The assignments of the  $b_{1u}$  fundamentals reported by Charney, Becker and Anno have been completely confirmed by polarization effects in the solid state infrared spectrum and by correlation with the fundamentals observed in the crystal emission spectrum. The ring bending mode,  $\nu_{16}$ , is expected, from the normal coordinate analysis, to lie in the region  $760\text{--}700 \text{ cm}^{-1}$ . The only bands observed in the solution infrared spectrum in this range are the very weak ones at  $728 \text{ cm}^{-1}$  and  $635 \text{ cm}^{-1}$  in quinone- $h_4$  and  $-d_4$ , respectively, hence, these bands have been assigned to  $\nu_{16}$ . Since no vapor phase band contours were observed for  $\nu_{16}$  the assignment of this fundamental was regarded as one of the weakest points in the vibrational analysis. In the infrared spectrum of the crystalline materials,  $\nu_{16}$  is observed at  $745 \text{ cm}^{-1}$  and  $674 \text{ cm}^{-1}$  in the  $-h_4$  and  $-d_4$  compounds, respectively, and its in-plane polarization established by its intensity relative to the  $b_{3u}$  mode  $\nu_{24}$ . The assignment of this fundamental is confirmed by its activity in the crystal emission spectra (14). Finally, the C-H bending mode,  $\nu_{14}$ , increases by  $12 \text{ cm}^{-1}$  from the free molecule to the crystal lattice.

The poorer product rule agreement obtained for the  $b_{1u}$  fundamentals in the solid state is primarily a consequence of the change in the frequency of  $\nu_{16}$  upon crystallization. Since the ratios are in the form ( $-h_4/-d_4$ ), anharmonic effects tend to make the observed ratio less than the calculated ratio and the deviation from theoretical may involve a marked increase in the anharmonicity of  $\nu_{16}$  in the solid state.

The five  $b_{2u}$  modes may be described approximately as: a C-H stretching vibration,  $\nu_{17}$ ; a C=C stretching vibration  $\nu_{18}$ ; a C-C stretching vibration  $\nu_{19}$ ; a C-H bending vibration,  $\nu_{20}$ ; and a C=O bending vibration  $\nu_{21}$ . In the vapor phase and solution infrared spectra only one band is observed in the C-H stretching region. Accordingly, in previous vibrational analyses, both  $\nu_{12}$  and  $\nu_{17}$  have been assigned to the moderately intense band observed at  $3062 \text{ cm}^{-1}$  and  $2277 \text{ cm}^{-1}$  in the vapor phase infrared spectrum

of the ( $-h_4$ ) and ( $-d_4$ ) compounds respectively. Two bands were observed in the infrared spectrum of the crystalline compounds in the C-H (C-D) stretching region. There seems to be no compelling reason to favor one assignment of the two bands observed to the two infrared active C-H (C-D) stretching modes over another, other than the relative ordering suggested by the normal coordinate analysis which places the  $\nu_{17}$  slightly lower in frequency for both the C-H and C-D stretches.

The band observed at  $1066\text{ cm}^{-1}$  in the solution infrared spectrum of *p*-benzoquinone- $h_4$  was assigned to  $\nu_{20}$  by Becker, Charney, and Anno (7) from considerations of benzene derivatives and the results of the normal coordinate analysis (6). No band of appropriate contour in a suitable spectral region was observed for ( $-d_4$ ) in the vapor phase. The normal coordinate analysis and a calculation of the approximate value of the fundamental needed to satisfy the product rule suggested that the missing ( $-d_4$ ) fundamental is quite probably hidden under the very intense  $b_{1u}$  fundamental,  $\nu_{25}$ , at  $793\text{ cm}^{-1}$ . Two bands were observed at  $800\text{ cm}^{-1}$  and  $812\text{ cm}^{-1}$  in the solid state infrared. The lower frequency band is satisfactorily assigned to the  $b_{3u}$  C-H out-of-plane stretch  $\nu_{24}$ . The remaining band cannot be assigned to a combination band and is therefore assigned as  $\nu_{20}$ .

The ( $-d_4$ ) value previously reported for  $\nu_{19}$  is that for the unperturbed fundamental estimated from the Fermi diad observed at  $1226/1258\text{ cm}^{-1}$  in solution (7). The low frequency component was assigned as  $\nu_4 + \nu_{21}$  which has the unperturbed value  $1230\text{ cm}^{-1}$  and is of symmetry type  $b_{2u}$ . A similar diad is observed in the infrared spectrum of the crystalline material at  $1234/1268\text{ cm}^{-1}$ . The combination band  $\nu_4 + \nu_{21}$  in the solid state spectrum should have the unperturbed value  $1242\text{ cm}^{-1}$ . However, a moderately intense band observed at  $1246\text{ cm}^{-1}$  can be assigned to this combination. The band observed at  $1234\text{ cm}^{-1}$  may be satisfactorily assigned to the combination  $\nu_6 + \nu_{24}$  which has the value  $1235\text{ cm}^{-1}$  and belongs to the symmetry class  $b_{3u}$ . This combination has the value  $1226\text{ cm}^{-1}$  in the infrared solution spectrum of *p*-benzoquinone ( $-d_4$ ) which is in agreement with the experimental data. The analysis of this data suggests assignment of the  $1234\text{ cm}^{-1}$  band to the combination  $\nu_6 + \nu_{24}$  and the band at  $1268\text{ cm}^{-1}$  as the  $b_{2u}$  fundamental,  $\nu_{19}$ .

The two  $a_u$  fundamentals may be described approximately as: an out-of-plane C-H bending vibration,  $\nu_{22}$ ; and a ring distortion vibration,  $\nu_{23}$ . Neither of these fundamentals is active in the infrared spectrum of the free molecule. Although the  $a_u$  fundamentals are formally active in the  $C_{2h}$  factor group, crystal interactions are apparently too weak to induce appreciable intensity and no bands of appropriate frequency were observed which could be assigned to these fundamentals in the crystal.

Experimental values of the  $a_u$  fundamentals have been obtained previously from analysis of the vapor phase electronic absorption spectrum (8), in which the  $a_u$  fundamentals are active. The absolute value of the ground state  $a_u$  frequencies, however, depends on the frequency of the electronic origin which is not observed in the vapor phase. In the present study the electronic origin was observed in the absorption spectra of single and mixed crystals of *p*-benzoquinone (15), unambiguously determining the excited state values of the  $a_u$  fundamentals. When this information is combined with the resonance fluorescence analysis, the absolute values of the  $a_u$  fundamentals in the ground state for quinone- $h_4$  and  $-d_4$  are obtained. These values are in agreement with those reported by Hollas (8) from his analysis of the vapor phase electronic absorption spectrum.

The three  $b_{3u}$  fundamentals may be approximately described as: a C-H out-of-plane bending vibration,  $\nu_{24}$ ; a C=O bending vibration,  $\nu_{25}$ ; and a ring distortion vibration,  $\nu_{26}$ . In the solution infrared spectrum of *p*-benzoquinone ( $-d_4$ ),  $\nu_{25}$  was observed as a shoulder so that the frequency of  $418\text{ cm}^{-1}$  reported by Charney *et al.*, is somewhat uncertain. This fundamental was observed at  $435\text{ cm}^{-1}$  in both the low temperature solid infrared spectrum and in the emission spectra of ( $-d_4$ ) in mixed crystal lattices. The corresponding fundamental in ( $-h_4$ ) increases from  $595\text{ cm}^{-1}$  in solution to  $524\text{ cm}^{-1}$  in the solid state, indicating the approximate frequency reported for  $\nu_{25}$  in solution by Charney, Becker and Anno is close to the correct value for the solution spectrum.  $\nu_{26}$  was observed in both the vapor phase fluorescence spectrum (15) and in the solid state at room temperature where it is blended with the  $117\text{ cm}^{-1}$  phonon. The frequency obtained agrees well with that reported by Charney and its activity in the electronic emission spectrum is consistent with this assignment.

The single  $b_{1g}$  vibration,  $\nu_{27}$ , involves an out-of-plane C-H bending motion. Observed  $745\text{ cm}^{-1}$  in the solution infrared spectrum of ( $-h_4$ ), the frequency increases to  $753\text{ cm}^{-1}$  in the solid state spectrum. In the ( $-d_4$ ) solution infrared spectrum  $\nu_{27}$  is observed at  $573\text{ cm}^{-1}$  and is virtually unchanged in the solid state spectrum.

The three  $b_{2g}$  fundamentals may be approximately described as a C-H bending vibration,  $\nu_{28}$ ; an out-of-plane ring distortion,  $\nu_{29}$ ; and a C=O bending vibration,  $\nu_{30}$ . In general, both the ( $-h_4$ ) and ( $-d_4$ )  $b_{2g}$  fundamentals increase by about 1% in the solid state.

#### PHONON STRUCTURE AND EXCITON INTERACTIONS

The normal lattice modes involve two types of motion which may be approximately described as rotation about the principal molecular momental axes and translations of the molecular center of mass. If there is more than one molecule per unit cell, phase relationships between similar motions must also be considered. Cruickshank (13) has extended the simple Debye-Waller theory for the vibrations of a monatomic lattice to include the rotational vibrations present in the lattices of molecular crystals. For rotational oscillations of amplitude  $\phi_i$ , the following relation was derived for a molecular crystal with two molecules per unit cell:

$$\phi_i^2 = \frac{h}{8\pi^2 I_i} \left[ \frac{1}{2\nu_1} \coth \frac{h\nu_1}{2kT} + \frac{1}{2\nu_2} \coth \frac{h\nu_2}{2kT} \right]$$

where  $I_i$  is the amount of inertia about axis  $i = x, y, z$  and  $\nu_1, \nu_2$  are the in-phase and out-of-phase frequencies of oscillation about axis  $i$ , at temperature  $T$ . Frequently  $\nu_1 \sim \nu_2$  and the above relation may be used to calculate a mean frequency of oscillation  $\bar{\nu}_1$  about axis  $i$  at temperature  $T$ , given  $\phi_i$  from x-ray diffraction investigations of the thermal molecular anisotropic motion. So that,

$$\phi_i^2 = 5.483 \times 10^4 / I_i (1/\nu_i) \coth 0.719 (\bar{\nu}_i/T)$$

for  $\phi_i$  in degrees,  $I_i$  in atomic units and  $\bar{\nu}_i$  in  $\text{cm}^{-1}$ . For *p*-benzoquinone, with two molecules per unit cell, there are 12 lattice modes, of which three correspond to in-phase translations of the molecular centers-of-mass rotational modes (optical phonon modes).

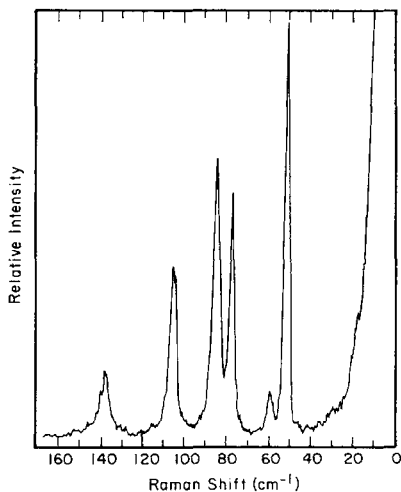


FIG. 3. Raman spectrum of crystalline *p*-benzoquinone-*h*<sub>4</sub> in the lattice frequency region at 77°K.

The lattice modes may be classified in the  $C_{2h}$  factor group as follows:

$$\begin{aligned} &3 \text{ acoustic: } 1a_u + 2b_u; \\ &9 \text{ optical: } 3 \text{ translational; } 2a_u + b_u, \\ &\quad \quad \quad 6 \text{ rotational; } 3a_g + 3b_g. \end{aligned}$$

Since the molecular inversion center is preserved in the crystal, the optical rotational lattice vibrations are Raman active, but infrared inactive. The converse is true for the optical translational lattice vibrations.

The Raman spectrum of crystalline *p*-benzoquinone in the lattice frequency region at 77°K is shown in Fig. 3. Unlike the molecular fundamentals, the band widths and frequencies of the lattice modes show a dramatic temperature dependence, narrowing considerably and shifting to higher frequency with decreasing temperature between 298°K and 77°K. Below 77°K little change in either band width or frequency is observed. The mean frequencies of the rotational vibrations about the three-principal molecular momental axes were calculated from the x-ray diffraction determination of the thermal anisotropic motion tensors ( $II$ ) of *p*-benzoquinone at 298°K, and are given, together with the experimental frequencies at 298°K and 77°K in Table V. The in-phase and out-of-phase components of each libration are clearly resolved at 77°K, and six bands are observed grouped in pairs corresponding to rotational oscillations about the three molecular momental axes. The six lattice frequencies of *p*-benzoquinone-*d*<sub>4</sub> were calculated from the experimental *p*-benzoquinone-*h*<sub>4</sub> lattice frequencies using the relation:

$$\bar{\nu}_i(-h_4)/\bar{\nu}_i(-d_4) = [I_i(-d_4)/I_i(-h_4)]^{\frac{1}{2}}$$

with  $[I(d_4)/I(h_4)]^{\frac{1}{2}} = 1.011 (R_x), 1.031 (R_y), 1.058 (R_z)$  and the results compared with the experimental frequencies in Table 5. Finally, we note that the splitting between the  $R_x$  and  $R_y$  band pairs is small (ca. 7  $\text{cm}^{-1}$ ), indicating relatively little coupling between the in-phase and out-of phase oscillations about these axes. The splitting of the high fre-

quency band pair, however, is quite large (ca.  $28\text{ cm}^{-1}$ ) and is taken to indicate significant coupling between the in-phase and out-of-phase oscillations about the  $z$  axis.

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