# EPR and optical studies of the lowest nπ* triplet state of p-benzoquinone in an isotopic mixed crystal

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# EPR and optical studies of the lowest $n\pi^*$ triplet state of p-benzoquinone in an isotopic mixed crystal

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In this Communication we wish to report our preliminary results of magnetic resonance and phosphorescence studies of p-benzoquinone-$h_4$ (PBQ-$h_4$) as a trap in PBQ-$d_4$. Previous Stark effect studies[1,2] on pure PBQ-$h_4$ crystals gave strong support for the assignment of the lowest triplet state in the pure crystal as the $B_{1g}n\pi^*$ triplet state with the unobserved origin in the pure crystal at 18 602.8 cm$^{-1}$. It was further suggested that this lowest state was so severely distorted that for certain $b_{1u}$ type nuclear motions the molecule had acquired a double minimum potential well along these nuclear motions, with the unobserved origin being the g-inversion level of this well. It thus seems very important to further establish the nature of the lowest excited state in PBQ since this molecule seems very suitable for a detailed study of the subtle effects that may occur in a molecule where the electronic and nuclear motions cannot be considered independent. In such a molecule small nuclear perturbations (as isotopic substitution) may drastically disturb the spin density distribution and possibly spin–orbit coupling selectivity. We now wish to present some preliminary results of our experiments on the p-benzoquinone isotopic mixed crystal system that focus on these suggestions.

Single crystals of PBQ-$d_4$ doped with 1 mol% PBQ-$h_4$ were grown from a Bridgeman oven and oriented conoscopically. A selection of the phosphorescence bands observed (all polarized along the long molecular axis) in a 1% mixed crystal at 1.8 °K is given in Table I.

Crucial to the analysis of this spectrum is the fact that the origin (g-inversion level) of the PBQ-$h_4$ trap was placed at 18 613.0±1 cm$^{-1}$. This position was deduced from our Stark[2] and mixed crystal absorption studies.[3]

With phase sensitive detection of the phosphorescence at different chopping frequencies it was possible to separate $b_{1u}$, $b_{2u}$, and $b_{3u}$ modes in the emission arising from independently decaying $T_z$, $T_y$, and $T_x$ spin substates, respectively. This is as expected for emission from a $^3B_{1g}n\pi^*$ state that is spin–vibronic coupled to a strongly allowed $^1B_{1u}(\pi\pi^*)$ state. At 4.2 °K emission exclusively from the $T_z$ spin substate is observed and all bands of assigned $b_{2u}$ and $b_{3u}$ symmetry are completely absent. The same situation can be created at 1.8 °K when a magnetic field is applied.

Further conformation of the analysis presented came from ODMR experiments. Zero field transitions at

TABLE I. Microwave effect on and assignment of selected phosphorescence bands of p-benzoquinone-$h_4$ (1 mol%) in p-benzoquinone-$d_4$ at 1.8 °K [$L = z$ ($B_{1u}$), $M = y(B_{2u}$)].

| Position (VAC cm$^{-1}$) | Assignment[a] | Microwave effect (% ± 2%) 1927 MHz | 2165 MHz |
|---|---|---|---|
| 18 613 | Origin; not observed | | |
| 18 195 | 418 ($\nu_{21}, b_{2u}$) | −18 | None |
| 18 082 | 531 ($\nu_{25}, b_{3u}$) | None | −4 |
| 17 863 | 750 ($\nu_{16}, b_{1u}$) | +41 | +15 |
| 17 832 | 781 ($\nu_{25}, b_{3u}$) + ($\nu_{30}, b_{2g}$) | +41 | +15 |
| 17 747 | 866 ($\nu_{21}, b_{2u}$)+ ($\nu_6, a_g$) | −2 | None |
| 17 705 | 908 ($\nu_{24}, b_{3u}$) | None | −9 |
| 17 666 | 947 ($\nu_{15}, b_{1u}$) | +26 | +12 |
| 17 422 | 1191 ($\nu_{21}, b_{2u}$) + ($\nu_5, a_g$) | −7 | None |
| 17 294 | 1319 ($\nu_{19}, b_{2u}$) | −7 | None |
| 17 242 | 1371 ($\nu_{14}, b_{1u}$) | +25 | +12 |
| 16 953 | 1660 ($\nu_{13}, b_{1u}$) | +41 | +12 |

[a]Ground state fundamentals have been taken from A. H. Francis, Ph.D. thesis, University of Michigan, Ann Arbor, MI, 1969.

$1927 \pm 5$ MHz and $2164 \pm 5$ MHz were detected with this technique and the percentages change in phosphorescence observed at these frequencies for the individual bands are also given in Table I. It must be concluded that $T_z$ is the most radiative ($\tau_z = 100$ $\mu$sec) and underpopulated level at 1.8 °K. The third zero field transition could not be detected with this method but was inferred to arise at $237 \pm 10$ MHz from ODMR experiments in a magnetic field. These measurements also gave the relative signs of $D$ and $E$ and the $g$-tensor principal values:

$$\left| (D+E)/_h \right| = 1927 \pm 5 \text{ MHz} \quad g_{xx} = 2.0043 \pm 0.0010$$

$$\left| (D-E)/_h \right| = 2164 \pm 5 \text{ MHz} \quad g_{yy} = 2.0010 \pm 0.0006$$

$$\left| 2E/_h \right| = 237 \pm 10 \text{ MHz} \qquad g_{zz} = 2.0080 \pm 0.0006$$

The large deviation of $g_{zz}$ from the free electron value shows the expected effect of direct spin–orbit coupling of the $T_z$ spin sublevel with the ground state. Quite surprising is also the fact that our measured ZFS parameters of PBQ-$h_4$ in PBQ-$d_4$ are completely different from those measured by Attia *et al.*[4] in a $p$-dibromobenzene host crystal:

$$\left| (D+E)/h \right| = 5224 \text{ MHz}; \quad \left| (D-E)/h \right| = 5379 \text{ MHz} ,$$

and

$$\left| 2E/h \right| = 155 \text{ MHz} .$$

This fact already indicates that the $p$-benzoquinone $B_{1g}$ state is extremely sensitive to perturbations. This is also evident from the drastic change that occurs when the ZFS parameters of PBQ-$dh_3$ in the same host crystal (PBQ-$d_4$) are measured. We report the following numbers: $\left| (D+E)/_h \right| = 2316 \pm 5$ MHz, $g_{xx} = 2.0040 \pm 0.0010$; $\left| (D-E)/_h \right| = 2526 \pm 5$ MHz, $g_{yy} = 2.0012 \pm 0.0006$; $\left| (2E)/_h \right| = 210 \pm 10$ MHz, $g_{zz} = 2.0080 \pm 0.0006$. Such an enormous change in $D$ can only be accounted for on the basis of an electronic state that is extremely sensitive to the exact form of the vibrational force field. In the case of a dou-ble minimum potential well, asymmetric ring substitution favors one of the distorted configurations that may result in a drastic change in the spin density distribution. We therefore take the observed hypersensitivity of the ZFS parameters of PBQ to asymmetric deuteration as a strong argument in favor of the proposed[2] double minimum well of the $^3B_{1g} n\pi^*$ state. Further EPR, ENDOR, and Stark-experiments on PBQ and its deutero isotopes are now underway and will be reported in a future paper.

Finally we would like to report observation of strong level anticrossing and cross relaxation effects in the phosphorescence of PBQ at 1.8 °K completely similar to the effects observed by Veeman and van der Waals[5] on the lowest $n\pi^*$ triplet state of benzophenone.

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# Theoretical calculations of the second virial coefficient of water

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In the process of investigating the water pair potential we have calculated the second virial coefficient for a number of potentials which have in common a Lennard-Jones spherically symmetric part and various representations of the water molecule electrostatic charge interaction. The numerical calculation yields results with a precision of 1%, which is better than the experimental measurements. The results of these calculations also allow us to estimate the second virial coefficient for the Hartree–Fock potential surface calculated by Del Bene and Pople.[1]

The electrostatic-type potentials, $U_{M1} = U_{LJ} + U_{\mu\mu}$ (Stockmayer[2]), $U_{M2} = U_{LJ} + U_{\mu\mu} + U_{\mu Q}$, $U_{M3} = U_{LJ} + U_{\mu\mu} + U_{\mu Q} + U_{QQ} + U_{\mu \Omega}$, and $U_{BNS} = U_{LJ} + U_{point\ charge}$ (Ben-Naim and Stillinger[3]), form a sequence with increasingly more complete descriptions of the electrostatic interactions. The multipole moments used for $M1$, $M2$, and $M3$ (calculated relative to the center of mass of $H_2^{16}O$) are $\mu_z = 1.85 \times 10^{-18}$ esu·cm, $Q_{zz} = -.13 \times 10^{-26}$ esu·cm$^2$, $Q_{xx}$