Optically Detected Magnetic Resonance of para-benzoquinone in its lowest nπ* triplet state

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Summary

The optically detected EPR data of para-benzoquinone (PBQ), with D_{2h} symmetry, in its lowest nπ* triplet state at 1.8 K showed the fine structure parameter D to be very sensitive to mild isotopic D- and ^{13}C-substitution, but insensitive to ^{17}O- or ^{18}O-substitutions. This shows that the b_{lu} vibronic coupling mode, which mixes the near degenerate nπ* triplet states is not the asymmetric carbonyl mode, but more likely one of the four other (mixed) b_{lu} vibronic modes.The optically detected ENDOR data of PBQ showed that these mild substitutions leaves the C_{2v} symmetry at the unsubstituted half of the molecule intact, which favours the dimer or Double Minimum potential (DMP) model of PBQ.

Hyperfine constants calculated by ab-initio are comparable with the experimental ENDOR hyperfine constants and showed the π*-unpaird electron to be spread over the molecule, while the unpaired n-electron is largely localized on the oxygen atoms.

The newly discoverd Cross REIaxation Double Resonance (CRENDOR) technique makes the inversion of an electronic into nuclear polarization possible, by a cross relaxation between a triplet and a doublet system. This electronic polarization enlarges the sensitivity of the optically detected nuclear transition. And this results in an improvement of the ENDOR data.

The low frequency EPR near the Level Anti Cross (LAC) signal exhibits a lineform which could be simulated by assuming a disorder of 0.9^0 in the tilt of the PBQ molecular planes.

The relatively strong dependence of the EPR and ENDOR spectra on mild isotopic substitutions favour the interpretation of the DMP of the lowest nπ* B_{1g} triplet state of PBQ, as guest in PBQ-d_4 at 1.8 K, as a vibronic strongly pertubated state.