Resonance Raman detected triplet state magnetic resonance

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plus higher-order terms which become insignificant for large Z. Then, a comparison of Eqs. (9) and (11) shows that $D_1 V_{O,A} = D^2 E$ for large enough Z values, which is in agreement with the results presented by Teruya and Anno[2] and Castro et al.[8]

Similarly, the limiting values of $D_1 V_{ee}$ for the He and the B isoelectronic series given by Teruya and Anno[3] are in accordance with the published values for the perturbational coefficient e_1.[10,14]

The limiting behavior of V_{ee} and $V_{O,A}$ in the Hartree–Fock approximation is not a new result. In fact, Boyd[15] and Cohen[16] had previously called attention about the systematic behavior of certain Hartree–Fock expectation values, with special reference to $\langle r_1^{-1} \rangle$ and $\langle r_{12}^{-1} \rangle$. More recently, Bhattacharyya and Bhattacharyya[17] have discussed the limiting behavior of the ratio $\langle r_{12}^{-1} \rangle / \langle r_1^{-1} \rangle$ in the He sequence, and they found several interesting enough results.

In conclusion, we point out that the Z-perturbation theory is a valid alternative way to study the limiting behavior of $DV_{O,A}$ and DV_{ee} for a given isoelectronic series of atoms. Consequently, the explanation given in terms of the screening constants for the analysis of $DV_{O,A}$ and DV_{ee} is not unique, but just a possible manner

which is based upon the introduction on the concept of "effective nuclear charges"[6] when the nonnegligible V_{ee} energy is taken into account.[3]

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We have recorded the zero-field magnetic resonance transitions of the photoexcited triplet state of chlorophyll b (chl b) by monitoring the microwave induced changes of the resonance Raman spectral band intensities. This experiment offers an extension of optically detected magnetic resonance (ODMR) techniques whose applicability to investigations of the triplet states of organic molecules has been widely recognized.[1] Resonance Raman detected ODMR is expected to offer an advantage over the traditional phosphorescent and nonphosphorescent ODMR techniques in cases involving large, complex molecular systems, where the utilization of Raman scattering bands may provide high resolution, optical filtering capabilities superior to alternative methods detecting on broadband emissive or absorptive features.

In Fig. 1(a) we present the results of resonance Raman detected ODMR in which the intensity of the 1572 cm⁻¹ band of chl b was monitored. The spectra were obtained from a thin film of oleyl alcohol in which the chlorophyll had been dispersed to yield a mole fraction of ~ 10⁻³. Such a thin film was deposited on the basal plane of a

sample of freshly cleaved highly oriented pyrolytic graphite; the sample was mounted at the center of a slow-wave helix and cooled to 2 K. Optical excitation was achieved via the 200 mW output of an argon ion laser operating in the single line mode at 457.9 nm. A dry ice cooled photomultiplier tube interfaced to a SPEX 1403 double monochromator (slits set to a spectral bandpass of 5 cm⁻¹) provided the means of detection. Sweeping the microwave frequency region and accumulating the microwave-induced resonance Raman intensity changes then proceeded in the same manner as for methods described elsewhere regarding fluorescence detected magnetic resonance of the chlorophylls.[1]

The Raman detected ODMR spectrum in Fig. 1(a) may be compared with the spectrum of Fig. 1(b) recorded by means of fluorescence detection methods. Only the $|D| - |E|$ transition is shown. It is seen that the ODMR transition frequencies of the two spectra are somewhat shifted; the figures are similar, however, with respect to signal/noise ratio, band profile, and relative intensity. An obvious difference between the Raman detected and fluorescence detected ODMR lies in the
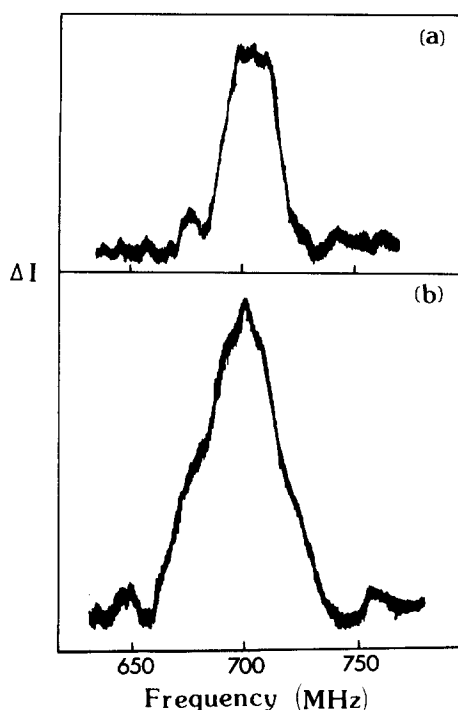
FIG. 1. Zero field ODMR spectra of the $|D| - |E|$ transition of chl b at 2 K: (a) detected on the resonance Raman band at 1572 cm^{-1}, (b) detected on the fluorescence band maximum at 648 nm.

observed bandwidth. That the former is approximately 15% narrower than the latter provides evidence for greater triplet site selectivity in the Raman detection experiment.

From the amount of signal averaging employed in these experiments, we estimate that the microwave-induced intensity change in the 1572 cm^{-1} Raman band is comparable to that observed in the steady state fluorescence. That is, microwave fields in resonance with the zero field triplet spin transitions of chl b produce a change of approximately 0.1% in the monitored transition intensities discussed here.

We note that a control-type experiment, in which the detection monochromator was set at 2500 cm^{-1}, was performed under conditions otherwise identical to those used in our resonance Raman ODMR scheme. While the intensity of background light emanating from the sample at this wavelength was found to be nearly equivalent to that found near 1572 cm^{-1}, no Raman bands were apparent in this region. Extensive averaging of the back-

ground radiation response to applied microwave fields revealed no ODMR patterns.

The mechanism of resonance Raman detected triplet state magnetic resonance is that common to all non-phosphorescence detected ODMR techniques.[1] With regard to the experiments described here, photons from the laser incident upon the chl b sample are subject to both absorption and scattering. Molecular pathways involved with the former event include intersystem crossing which leads to a significant, spin-polarized, steady state population of the triplet spin sublevels at low temperatures. As the microwave field is swept through a resonant frequency involving two spin sublevels, the steady state populations of all the dynamically coupled levels of the molecular system adjust. Since the absolute intensity of a given Raman scattering band is dependent upon the actual population of ground state molecules (among other factors), any adjustments in this population via microwave-driven triplet spin transitions will be manifest in changes of the band intensity. It is evident from our work that such Raman intensity fluctuations yield an ODMR effect similar to that obtained using other experimental methods.

It is anticipated that Raman detected magnetic resonance experiments will find their greatest utility for systems comprised of complex mixtures of chemical species where overlapping electronic spectral bands preclude clean assignment of the ODMR features to a particular system component. Foremost examples lie among the systems of photosynthetic interest; here a wide variety of chlorophyll–chlorophyll and/or chlorophyll-ligand species are often present in a single sample.[2] The greater optical resolution afforded in the light scattering/magnetic resonance techniques reported here facilitates the correlation of particular ODMR transitions with particular Raman bands. A fuller characterization of the system's components, not achievable by means of other triplet state detection methods, is then possible. Such utilization of resonance Raman detected ODMR is presently underway in this laboratory and is aimed toward evaluating complex chlorophyll-containing systems, both *in vitro* and *in vivo*.

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