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On the Interpretation of the Factor Group Splitting in Naphthalene Crystal

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In a recent note Sarti-Fantoni¹ has discussed the effect of deuteration on the factor group splitting in the lowest excited singlet state of crystalline naphthalene. There are two tentative explanations for the origin of this splitting, one favoring² higher transition multipole moment couplings, the other suggesting the interaction of nearby charge transfer states with the lowest excited singlet.³ Good agreement is obtained with experiment in both cases. In the first case, both octupole moment parameters are used to fit the spectrum, while in the second case, the position of the first charge transfer state relative to the excited singlet state is used to fit the spectrum. Because in perdeuteronaphthalene the difference in the excitation energy from the ground state to the first excited state (α band) is 118 cm^{-1} larger than the corresponding transition in the perhydro compound,⁴ and since the explanation of the splitting invoking charge transfer states requires close proximity of the charge transfer state to the α -band, Sarti-Fantoni has suggested that there should be a detectable change in the splitting on deuteration due to the quoted change in zero-point energy. In particular, he states that a 15 cm^{-1} shift in the difference (δ) between the

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charge transfer state and the α band can produce a measurable change in splitting.

We find that when the calculation is performed³ using vibronic states in the weak coupling model,^{3, 5} a 20 cm^{-1} change in δ gives rise to a $\sim 2\%$ change in the splitting of the 0-0 band and a $\sim 8\%$ change in the splitting of the 0-1 band (this calculation was performed with the 0-0 transition of the charge transfer state 300 cm^{-1} above the 0-0 transition of the α band⁵). Since the experimental splitting of the 0-0 transition in both compounds¹ is $151 \pm 4\text{ cm}^{-1}$ and that of the 0-1 transition is $28 \pm 4\text{ cm}^{-1}$ in perhydronaphthalene and $26 \pm 6\text{ cm}^{-1}$ in the perdeutero compound, we find that these changes are within experimental error. With a 30 cm^{-1} change in δ , we find the changes in the splittings are $\sim 3\%$ in the 0-0 transition and 20% in the 0-1 transition, again just within experimental error.

Sarti-Fantoni¹ has also mentioned that in the calculation of the band structure using octupole moments, the lowest state in the band (E versus k) is the ac polarized $k=0$ state. We find the same state is lowest in the charge transfer calculation, and that the band is flat (to within $\sim 0.5\text{ cm}^{-1}$) along the direction $k||c^{-1}$. There is indirect experimental evidence for the $k=0$ state of the ac branch being the lowest state in the band.⁶

We are *not* suggesting that the charge transfer state mechanism is correct or to be favored, only that the evidence is still not conclusive one way or the other. The calculation of the charge transfer state interaction is crude, and can only be considered to be an estimate of the effect. However, we believe that this explanation cannot be ruled out without the performance of further experiments.

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4. One must keep in mind that this number is extremely small when compared to the total zero-point energy (which is of the order of $2,5000\text{ cm}^{-1}$) and that this number is the change upon deuteration of the difference in zero point energy of the excited state and the ground state. It therefore represents a delicate balance between many effects, since almost every

vibration is changed in frequency. It is impossible at present to estimate the change in zero point energy of the charge transfer state upon deuteration.

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