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Theoretical Study on Vibronic Spectra of a Boron Fused Double Helicene

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ABSTRACT

We present the theoretical study of the Vibrationally Resolved Absorption (ABS), Electronic Circular Dichroism (ECD), Emission and Circularly Polarized Luminescence (CPL) spectra of a boron-fused double helicene with a detailed and complete discussion of the alternative possible approximate methods. Our results show that both Adiabatic Hessian (AH) and Vertical Hessian (VH) models have well reproduced the experimental vibronic structures and VH model shows a better performance in the simulation of spectral line-shapes. They also show that HT effect dominates the shapes of EMI and CPL, tuning the relative heights of the different vibronic peaks. Improving the agreement with the experiment for EMI. Moreover, Herzberg-Teller (HT) effect is the main reason for the mirror-symmetry breaking between ECD and CPL spectra.

Keywords: Vibrationally resolved spectra, Adiabatic hessian model, Electronic circular dichroism, Circularly polarized luminescence.

ABOUT THE STUDY

Recently, Katayama, et al. have synthesized two double helicenes possessing two boronate substructures at the ring junction with deep blue fluorescence and CPL activity [1,2]. However the theoretical studies conducted failed to capture the rich patterns of the peaks observed in the experiment, are not able to interpret the fine structures observed in the experimental spectra. This is not surprising since vibronic couplings play an important role in helicenes derivatives in such transition and our previous study on hexahelicenes [3, 4].

Directly motivated by those work, herein, we aimed to undertake a detailed study of the vibrationally resolved ABS, ECD, EMI and CPL spectra of the boron-fused double helicene (Figure 1). In the contribution, we will focus on reproducing the experimental spectral line shapes, identifying the fine structures, and assigning the main vibronic contributions, applying both Time-Independent (TI) and Time-Dependent (TD) approaches. Both Franck-Condon (FC) and HT effects are considered [5-9]. To make sure the reliability of the HT linear approximation, we compared the results of HT_i and HT_f. To be specific, HT_i model expands the transition dipoles around the geometry of the initial state while HT_f model calls for the geometry of the final state. If HT_i and HT_f predict with similar results, the linear approximation implicit in HT is an adequate treatment.

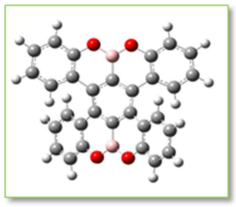

Figure 1: Molecular geometries for the compound.

The computed the vibronic ABS and ECD, EMI and CPL spectra are shown in Figure 2. We can see that all theoretical spectra at both AH and VH models are in nice agreement with the experimental ones. Thermal effect reduces the resolution and increases the width of the vibronic spectra affecting the performance of simulations.

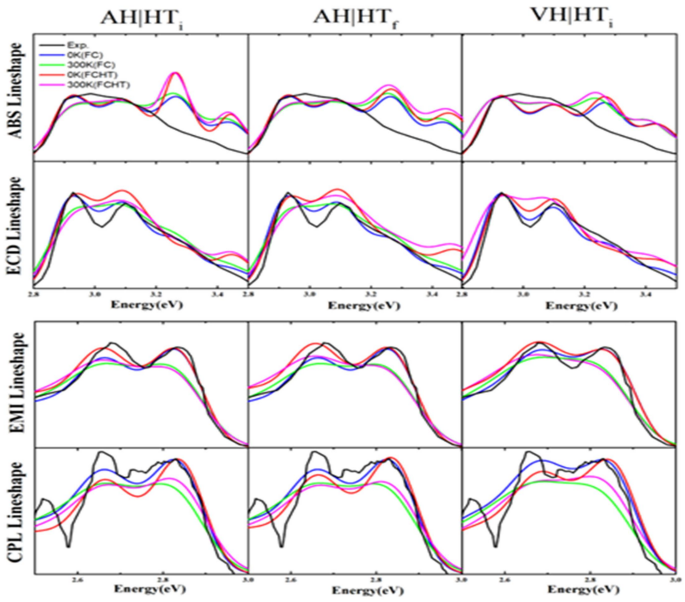

Figure 2: Vibronic normalized ABS, ECD, EMI, and CPL in CH_2C_{l2}, convoluted with a Gaussian with HWHM of 0.06 eV, AH spectra have been blue-shifted by 0.21 eV, VH spectra of ABS and ECD have been blue-shifted by 0.22 eV, EMI and CPL has been blue-shifted by 0.20 eV.

ABS spectra

HT effect is extremely small, leading to the FC and FCHT (FC+HT) spectra indistinguishable at both AH and VH models. Moreover, the thermal effect further improves the performance on the line shapes with a reduced resolution at 300 K, especially at VH model. With respect to VH, AH slightly underestimate the 0-0 band at 300 K, which can attribute to a slight overestimate of the displacements between S_0 and S_1.

ECD spectra

Both AH and VH have nicely simulated the experimental ECD spectrum. Comparison of FC and FCHT spectra shows that FC contribution plays a dominant role in ECD. In contrast, HT effect has slightly overestimated the height of the second band, which can be due to the bias made on the high frequencies.

EMI spectra

Both AH and VH have nicely reproduced the fine structures in the experiment. Noteworthy that VH outperforms AH in describing the spectral shape by slightly enhancing the height of the first band. Moreover, VH is red-shifted by 0.01 eV with respect to AH spectra, which may because of the different displacements computed with the two models, and (or) the differences between frequencies of S_0 and S_1.

The HT effect is more significant in EMI than ABS, which promotes the mirror symmetry breaking down between ABS and EMI. Moreover, the highlighted effect of HT is that it tunes the relative height of the two bands and improves the agreement with experiment for EMI.

CPL spectra

Even though the experience of CPL calculation is very limited [10-12], we have already successfully investigated the CPL spectra of four different small helicenes [4] and pointed out the important effect of HT contribution in correcting the signs of chiral spectroscopies and tuning the relative intensities of different vibronic bands. The theoretical spectra are in good agreement with the experiment. Moreover, both AH and VH predict with similar CPL spectra and the results of $FCHT_i$ AH and $FCHT_f$ AH also resembles with each other, which further supports the reliability of our methods. With respect to AH, the VH spectra are little red-shifted which is in consistent to the behavior of EMI.

CONCLUSION

Our results show that HT effect behaves different for the four different spectra. The result of ABS spectrum is barely influenced by HT effect or the choice of the HT models. However, HT effect is significant and remarkable in EMI spectrum, improving the performance by tuning the relative height of the vibronic bands. Moreover, HT effect modifies the spectral shapes of ECD and CPL by overestimating the height of the band on high frequencies. Vibronic analysis shows that HT effect is responsible for the mirror-symmetry breaking between ECD and CPL spectra.

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