Challenges for the *ab initio* simulation of the spectra of large molecules: Absorption and fluorescence spectra of poly(p-phenylenevinylene) oligomers

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INTRODUCTION

Poly(p-phenylenevinylene) (PPV) oligomers (Figure 1) are widely studied as model systems for electroluminescent and photovoltaic material design. Most *ab initio* studies have focused on the smaller PPV oligomers, due to the rapidly increasing computational cost along the oligomer series.

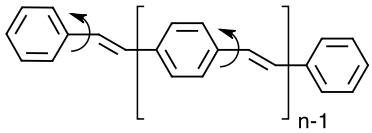

Figure 1. Structure of $(PV)_nP$ oligomers

In this work, we tackle the problem of simulating spectra for these large molecules with *ab initio* methods. We show that obtaining a qualitatively correct description of the spectra of these species becomes feasible with a judicious selection of model, basis set and approximations.

METHODS

Ground state calculations were done at the RI-MP2 level, and excited state calculations with the RI-ADC(2 level, with both SV and SV(P) basis set. The spectra were simulated with the nuclear ensemble method. Electronic structure calculations were done with the TURBOMOLE 6.5 program and the spectra simulations were carried out with the NEWTON-X program.

RESULTS AND DISCUSSION

The simulated spectra show a trend of decreasing photon energy along the series. The shapes of the spectra are quite close to available experimental data[1], but the predicted photon energies are considerably higher. This difference can be attributed to a number of effects which can be independently estimated.

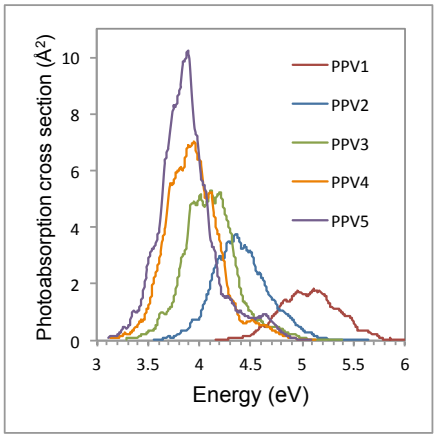

Figure 2. Absorption of $(PV)_nP$ oligomers

CONCLUSIONS

The simulated spectra are shown to reproduce some important features and trends of the experimental spectra. The differences in the photon energy can be independently estimated.

ACKNOWLEDGMENTS

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[1] Rauscher, U.; Bassler, H.; Bradley, D. D. C.; Hennecke, M. Phys Rev B, 42, 9830, (1990)