VISTA Seminar

Seminar 13

9:30 – 11:00 am EST / 2:30 – 4:00 pm GMT / 3:30 pm – 5:00 pm Paris

TOC:

Development of a tool for the complete first-principles prediction of finite-temperature and generalized initial-state UV absorption spectra: Application to NO_2

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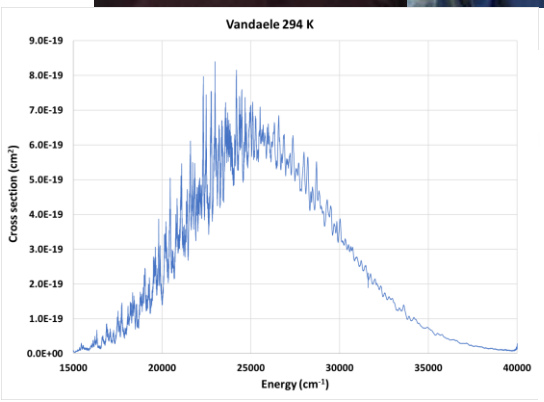

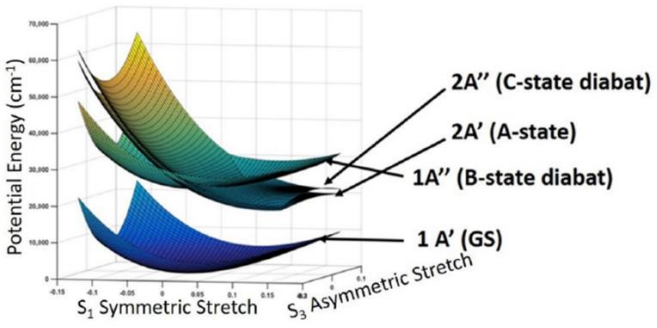

NO_2 has a rich complicated UV absorption spectrum, due in part to the intersection of two excited electronic states (B and C), directly in the Franck-Condon (FC) region. Indeed, the ground (X-state) and first excited state (A-state) intersect at smaller angles (just outside the FC region), while one component of each of the two coupled pairs of states (X/A and B/C) connect as a Renner-Teller pair at colinear geometries. This talk will describe an electronic structure protocol (MRCI-F12:GDW-CASSCF) that accurately and robustly describes the complete manifold of coupled states, their energies, and properties.

Neural-network fitting was used to represent analytically a total of 20 individual energy, property, and coupling surfaces. The MultiConfigurational Time-Dependent Hartree (MCTDH) quantum dynamics method was used first to compute the lowest 125 vibrational levels on the ground electronic state, and then to compute the complete set of UV absorption spectra from each of those 125 initial states. Each spectrum was computed including the coupled electronic states and full geometry-dependent dipole transition moment surfaces. The impact of rotation was tested with calculations up to J=20.

The data generated in this study was implemented into an interactive tool with several functions of analysis and plotting. The tool, which contains also some experimental datasets, allows spectral predictions and comparisons for a range of temperatures up to 2200 K. In addition to providing thermally weighted results (or scans), arbitrary initial states may be selected, including scans over various mode progressions. Some interesting spectral predictions will be shown, which can be interpreted in terms of the initial state probability densities combined with the topography of the coupled excited states.

Simulating Vibronic Spectra without Born-Oppenheimer Surfaces

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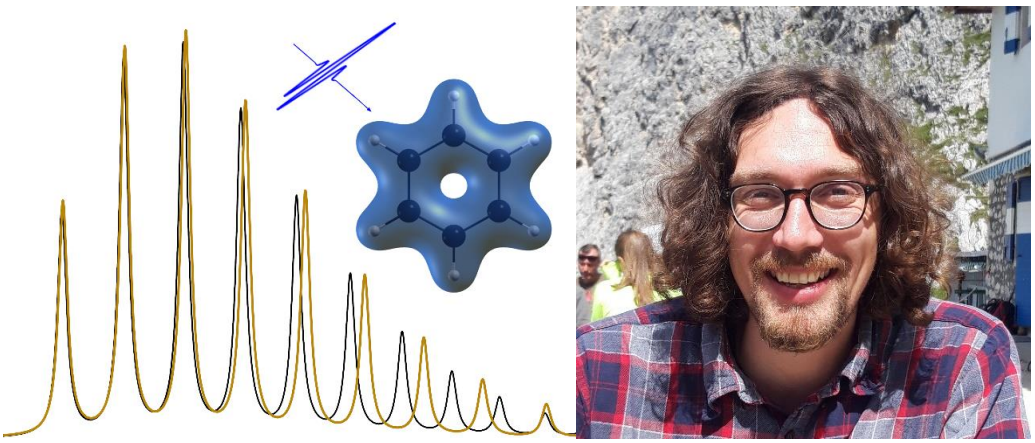

Being able to simulate coupled electron-nuclear processes for large molecular systems in a computationally tractable manner is a defining challenge of ab-initio condensed matter quantum dynamics. While the Born-Oppenheimer (BO) framework is a powerful framework, it's applicability is limited by the computational bottleneck of potential energy surface fitting and the calculation of non-adiabatic coupling terms. In this talk, we show how vibronic spectra in molecular systems can be simulated in an efficient and accurate way using first principles approaches without relying on the explicit use of multiple BO potential energy surfaces.

We demonstrate and analyze the performance of mean-field Multi Trajectory Ehrenfest (MTEF) and beyond mean-field Interacting Conditional Wavefunction (ICWF) dynamics techniques for the H_2 molecule in one dimension, in the both cases capturing the vibronic structure, including quantum Franck-Condon effects, with the ICWF results converging quite accurately to the exact results. In a practical application of this methodology we simulate the absorption spectrum of benzene in full dimensionality using Time-Dependent Density Functional Theory and MTEF, finding good qualitative agreement with experiment. These results show promise for future applications of this methodology in capturing phenomena associated with vibronic coupling in more complex molecular, and potentially condensed phase systems.

How to connect

Alexey Akimov is inviting you to a scheduled Zoom meeting.

Topic: VISTA, Seminar 13
Time: Mar 3, 2021 09:30 AM Eastern Time (US and Canada)

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