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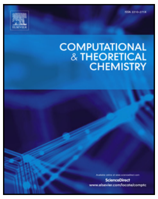

Electronic Stark effect for a single molecule: Theoretical UV response

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ABSTRACT

Theoretical analysis of optical absorption in the vacuum ultra-violet (VUV) region by single molecules placed in external electrostatic fields reveals characteristic absorption spectra completely at variance with their ‘zero-field’ counterparts consequent to appearance, disappearance, splitting, merging and shifts of absorption bands and extensive intensity redistributions. This ‘molecular electronic Stark effect’ can be tracked through electronic excitations involving frontier orbitals, energy-level splitting and shifts, molecular geometry changes and re-orientation, orbital mutation and migration. The UV spectra predicted herein should provide theoretical grounds for experimental endeavors on appraisal and characterization of the effect.

1. Introduction

Energy levels of a molecule can be altered by various external perturbations; most prevalent being the electric and magnetic fields. Electronic excitations in a molecule that primarily occur in the ultra-violet (UV) region undergo spectroscopic shifts, splitting and re-merging of salient absorption bands, intensity reorganization accompanied by molecular relaxation in an external electric field, leading to the molecular *electronic* Stark effect.

Applied electric field is crucial for experiments designed to manipulate a single atom or molecule particularly by scanning probes under atom-probe microscopy [1], field emission microscopy (FEM) and field ionization microscopy (FIM) [2], Atomic Force Microscopy (AFM) [3], and Scanning Tunneling Microscopy (STM) [4–19]. Among these, noticeable developments have led to determination of electronic and atomic structures, dynamics of a single molecule and its visualization and manipulation on an insulating surface under STM (lateral resolution of 1 Å and vertical resolution of 0.1 Å [11]), imparting remarkable ability for investigating detailed dynamics and allied aspects for single molecules [4–19]. Stuve [2] in his frontier article discussed the ionization of interfacial water and its electrochemical properties electric fields and furthermore he claimed STM being the promising tool for the high electric field research.

Rothfuss [20] investigated the behavior of water and methanol molecules adsorbed on a Pt emitter-tip in high fields (~ 1 V/Å) to explore the effects of temperature, field dependent dissociation and ion cluster emission. Bazalgette and others [21] used the ‘brute force’ technique (which essentially is the technique of rotation of molecular beams in an electric field [22]) to orient the beam of ICl molecules and after photo-dissociation, detected the iodine atoms recoiling near the electric field direction in the center-of-mass frame. The photo-dissociation of molecules in gaseous phase, at both infrared and ultraviolet wavelengths, has received considerable attention mainly because of its significance in atmospheric and interstellar chemistry [23,24]. Bachler and Gärtner [23], based on their theoretical analyses suggested an experimental setup for applying electric fields to imitate photochemical splitting of water molecule. Field evaporation is yet another technique which modifies the electronic properties of a given system, in which context Wang and others [25] within DFT mimicked evaporation of Polythiophene in electrostatic fields (higher than 1 V/Å), strong enough to close the HOMO-LUMO gap.

Glab and Hessler [26] reported an experimental study of the ionization and dissociation spectra of high-lying singlet *np* Rydberg levels of H_2 in an external electric field. They observed forced auto-ionization through the structured continuum of Stark states, electric-field-induced dissociation of Stark states, ionization behavior of molecular hydrogen near classical field-ionization energy, and a competition between the decay channels of ionization and dissociation. Bordas and Helm [27] analyzed both theoretically (using perturbation theory) as well as experimentally, the Stark spectra at low ($0–0.4 \times 10^{-8}$ V/Å) and high ($0–50 \times 10^{-8}$ V/Å) electric field strengths, of triatomic hydrogen for high Rydberg states $n = 30–125$, wherein they found a satisfactory agreement between the results from perturbation theory, the experimental spectra and field-induced pre-dissociation. More recently, Petrović and others [28] contrived an effective Hamiltonian to model the experimentally observed Stark effect in Rydberg states of highly polar

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CaF diatomic molecule with the calculations carried out in the energy region around n = 13, for the range of electric field strengths below the Inglis-Teller limit (whereby F, the field strength beyond which spectral lines cannot be resolved is proportional to $\sim 1/n^5$; about 4.6×10^{-5} V/Å for n = 13). Likewise, Stark effect for high-lying Rydberg states for N_2 [29], H_2 [30–34] molecules and hydrogen molecular ion [35,36] was extensively studied in early nineties.

With the advent of LASER technology, Lemeshko and others [37], presented a compendium on modern developments for understanding the role of molecule-field interactions in high-frequency laser fields. Meanwhile, Filsinger [38] accomplished control and manipulation of large neutral molecules in gas phase using strong *laboratory* electric fields ($\sim 10^{-3}$ V/Å). Bækhøj and Madsen [39] carried out attosecond transient-absorption (ATA) spectroscopy of aligned molecules showing dependence of spectra on the angle between the molecular alignment axis and the polarization of the pump and probe fields and discussed the underlying dipole couplings and manipulation of spectra exploiting the sensitivity of the transition dipoles on the relative orientation. Employing ATA measurement, Warrick and others [40] investigated nuclear and electronic dynamics in a wavepacket comprising bound Rydberg and valence electronic states of molecular nitrogen from 12 to 15 eV, where, the near-infra-red (NIR) pulse modified the structure of the wave packet by coupling to neighboring states. They proposed the observation of quantum beats in individual vibrational levels of $b'\ {}^1\sum_u^+$ valence state. Abu-samha and Madsen [41] presented a theory in agreement with the experiments to study the ionization of aligned CO_2 in strong-laser field ($\sim 10^{13}$–10^{14} W/cm^2), explaining breakdown of semi-analytical theories, where the excited electronic structure was ignored. They found that the excited electronic structure was vital in strong-field ionization of CO_2, and the measured ionization yields did not follow the electron density of the initial state. Further they extended [42] the strong-field ionization of molecules with large permanent dipole moments and polarizabilities, to include the linear and quadratic static Stark shifts of the ionizing molecular orbital; the method capable of capturing the essential physics underlying the process.

Judson and Rabitz [43] simulated a method to monitor a laser pulse sequence to excite specific molecular states. For manipulation of ultrafast processes in atoms, molecules, and solids, Bustard et al. [44] proposed a non-resonant dynamic Stark effect (NRDSE), which essentially yields the quasi-static shift in energy levels due to the application of optical fields [45]. Manipulative experiments such as state-selective dissociation of single molecules [8] and Rydberg-Stark deceleration of atoms and molecules [46,47] as well as field induced molecular rotation should prove particularly useful in molecular reaction dynamics [48], deflectometry and interferometry [49].

These works and techniques offer possibilities to modify the surfaces right at the atomic scale and bolster further work on molecular manipulation under an applied electric field. Here we will primarily be dealing with one of such aspects- field induced alterations in *electronic excitation spectra*. To theoretically probe this *electronic Stark effect* of a single molecule, we consider the static field strengths of the order of ~1 V/Å about which only a tenuous volume of information is available in the literature on the *electronic* excitation spectra of molecules subjected to an external electric field. Characterizing the Stark effect right at the molecular orbital level requires appraising its UV absorption spectrum at various applied field intensities, thence unraveling its finer nuances attributed to splitting and merging of absorption bands. This endeavor theoretically tracks down cogent electronic transitions, surrounding frontier orbitals of a molecule subjected to an applied, tunable, static electric field. Energetically close transitions that merge together, forming absorption bands in the Vacuum Ultra-Violet (VUV) region are simulated for some prototypical polar molecules H_2O, CH_3OH, H_2O_2 as well as for the non-polar CO_2 molecule subjected to a uniform electrostatic field. One atomic unit (a.u.) of electric field corresponds to $|e|/(4\pi \epsilon_0\, a_B^2) = 51.42$ V/Å with a_B = hydrogenic Bohr radius, and has the value 5.142×10^{11} V/m ≡ 51.42 V/Å.

2. Computational method

We simulate theoretically, the electron absorption spectra in the VUV region within the Time-Dependent Density Functional Theory (TD-DFT) [50,51], employing the versatile Minnesota M06-2X [52,53] dispersion corrected functional in conjunction with Dunning's aug-cc-pvtz basis set [54] well suited for TD-DFT calculations and required for the diffuse nature of Rydberg states [55] involving particular transitions. This basis set being 'correlation consistent', also been benchmarked for the calculations of molecular dipole moments and polarizabilities [56,57]. All calculations have been performed with the GAUSSIAN-09 [58] suite of program. Each of the molecules was initially optimized without any external perturbation; geometries thereafter subjected to an external electric field initially applied along the direction opposite to the net electric dipole moment (the direction of dipole moment vector is per the "physicist's convention" i.e. from negative to the positive end) with gradual increase in the field strength allowing the molecule to completely relax for each subsequent field value. The range of applied electric field strengths is *less* than the maximally sustainable threshold value beyond which the fragmentation or, "breakdown", designating breaking of the (covalent) bond of a molecule takes place and the SCF algorithm fails. The vibrational frequencies of the molecules were all found to be real ascertaining their local minimal-energy configuration. TDDFT [50,51] was then introduced, at the same level of theory and basis set, to estimate excited singlet-state energies. All the allowed transitions and corresponding wavelengths (λ_{max}) and oscillator

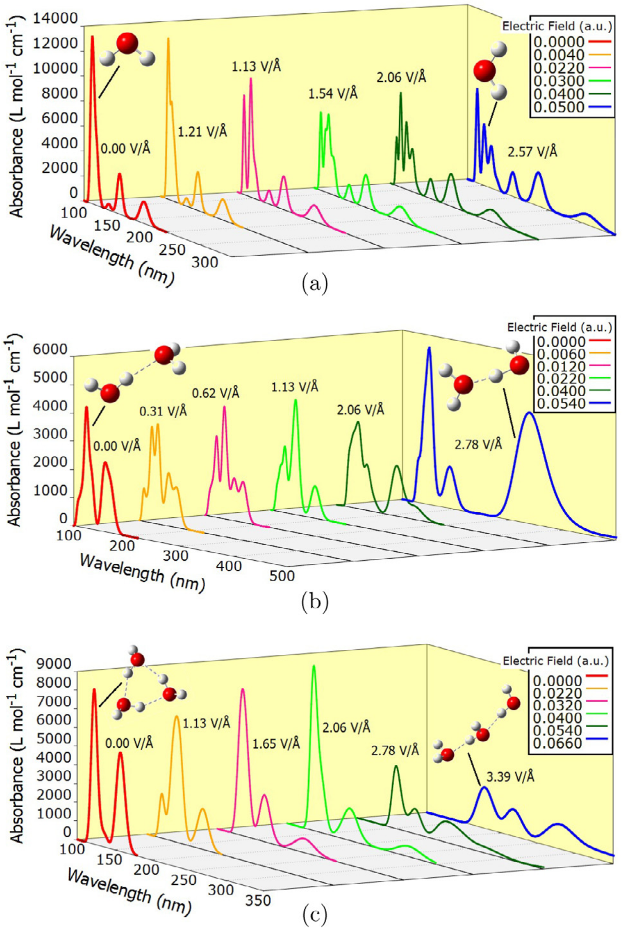

Fig. 1. UV absorption spectra of (a) isolated H_2O molecule, (b) water-dimer (c) water-trimer in electric field with strengths in the inset: zero- (red), interim-fields (various colors), and large (blue). [1 atomic unit (a.u.) of electric field = 51.42 V/Å.] (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)