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Density-functional calculations of field-dependent ionization potentials and excitation energies of aromatic molecules

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ABSTRACT

A recent method based on constrained density functional theory (CDFT) has been used to calculate the field-dependent ionization potential by determining the dissociation barrier for the interaction between a cation and an electron in an electric field. In the CDFT model, we rely on that the barrier is located somewhere outside the cation, which has limited the applicability for polyaromatic molecules where the barrier is located closer to the cation than for other molecules. Different density functionals, basis sets and choices of constraints in the CDFT calculations are tested for benzene as a case study. The field-dependent ionization potential calculated by constraining the charge with the B3LYP functional and the cc-pVDZ basis set shows a good agreement with our previous work and has a low computational cost for the larger aromatic molecules included here. In addition, field-dependent excitation energies are investigated using time-dependent DFT.

1. Introduction

In an electric field, the ionization potential (IP) of a molecule can be calculated from the dissociation barrier of the interaction between a molecular cation and an electron [1–4]. An electric field decreases the dissociation barrier required to ionize a molecule, and accelerates the charged particles. The field-dependent IP has been calculated in a numerical approach for the hydrogen molecule and the molecular hydrogen cation based on a classical theory for ionized atoms [5]. The critical fields for the ionization were obtained as a function of the distance between the nuclei of the molecule or the cation and the electron parallel to the external electric field.

Recently, a method has been developed to calculate the field-dependent IP, first based on the interaction between a point charge and a cation [1,2] and subsequently based on constrained density functional theory (CDFT) [3,4]. In the point-charge model, the electron is modeled as a point-charge [1,2] and the field-dependent IP is determined by finding the maximum of the energy barrier of the interaction between the point-charge and the molecular cation. In the CDFT method the electron is considered as a ghost atom (an atom without a nuclear charge, but with basis functions at the position of the atom) and the charge of the electron is constrained to -1 and/or the spin of the electron is constrained to a doublet state [3,4]. The CDFT method in general has provided insight in different chemical phenomena such as the prediction of transition state energies of chemical reactions or the lowest energy states of long-range charge-transfer systems [6–9]. A viable alternative approach that should be explored to calculate the field-dependent IP is via continuum wavefunction approaches developed for studying photoionization spectra [10–12].

It has been shown by DFT calculations that the decrease of the IP is proportional to the square root of the electric field [1], in agreement with the classical Poole–Frenkel effect describing the excitation of an electron to the conduction band at high electric fields [13]. The distance between the electron and the molecular cation at the energy barrier decreases as the electric field increases. In the CDFT method, we rely on that the electron orbital is sufficiently far away from the molecule so that we can control the position of the electron, i.e. the center of charge of the electron orbital is at the position of basis functions of the electron. At high electric fields and thereby at shorter distances between the electron and the cation, the CDFT method has a limitation since the orbital of the escaping electron becomes a linear combination of the basis functions of the electron with significant contributions from the basis functions of the cation. Consequently, the center-of-charge of the resulting orbital moves towards the molecule away from the position of the electron basis functions [3]. For molecules with diffuse π-systems such as polyaromatic molecules, the dissociation

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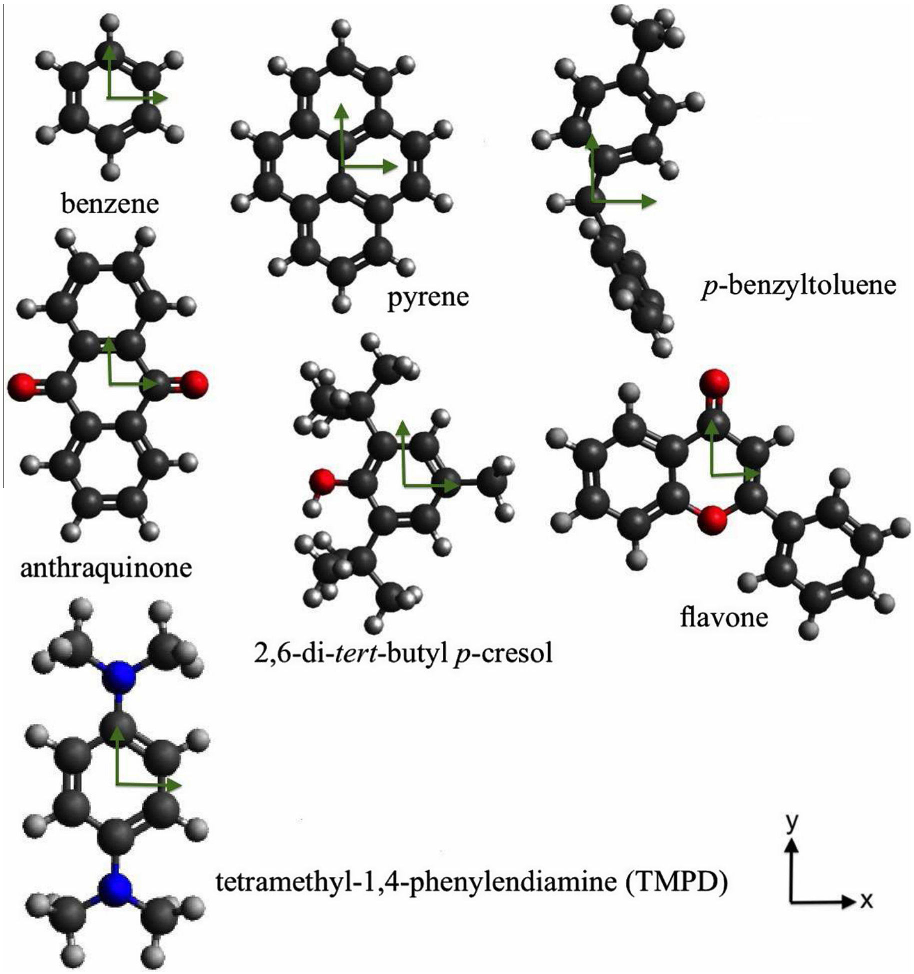

Fig. 1. The molecules included in this study with the coordinate system specified.

Table 1
IP (eV) in zero field.

Molecule	Vertical						Adiabatic	
	B3LYP		BNL		CAM-B3LYP		B3LYP	Exp.
	cc-pVDZ	cc-pVTZ	cc-pVDZ	cc-pVTZ	cc-pVDZ	cc-pVTZ	cc-pVDZ	
Benzene	9.54	9.63	10.47	10.57	10.20	10.27	9.53	9.24 [48]
Pyrene	7.09	7.16	7.03	7.14	7.20	7.28	7.00	7.42 [48]
Anthraquinone	9.00	9.30	8.98	9.16	9.43	9.55	8.90	9.30 [49]
p-Benzyltoluene	7.89	7.99	8.02	8.11	8.19	8.25	7.72	
2,6-Di-*tert*-butyl-*p*-cresol	7.42	7.51	7.18	7.31	7.51	7.59	7.20	
Flavone	8.40	8.19	8.09	8.28	8.32	8.44	8.27	
TMPD	6.30	6.20	5.87	6.03	6.23	6.35	5.97	6.25 [39]

barrier is located at shorter distances even at relatively low electric fields which has hampered studies of polyaromatic molecules in our previous work.

The field-dependent IP is an important parameter in ionization mechanisms in dielectric liquids at high electric fields, and recently, it has been used as a parameter in models describing streamer dynamics [14,15]. A streamer is a conductive plasma channel created in high-field regions of the dielectric liquid and propagates through the liquid and bridges the gap between two electrodes at a breakdown voltage [16,17]. Thus, the breakdown voltage is a measure of the dielectric strength of a liquid. It has been found that in dielectric liquids, polyaromatic additives with lower IPs than paraffinic and naphtenic molecules may increase the inception voltage of fast streamers with positive polarity [18]. It has been shown experimentally that a low-IP additive increases the streamer branching at relatively low voltages [18]. The branching becomes dense with increasing voltage leading to a lower electric field in front of the streamer. Thus, the speed of the streamer propagation decreases at a specific voltage [19].

In addition to the IP, excitation energies may influence the ionization processes [1,2]. The excitation energies has a relatively weak electric field dependence as compared to the IP [1,2,4]. In other words, the number of available excited states decreases with increasing electric field and at a specific field, different for different types of molecules, all the excited states of the molecule disappear [2]. For example, for alkanes this field is lower than for esters, diketones and azo dyes [2,4]. In an applied voltage, energy is continuously added to the liquid and the means of the liquid to release