



Field-dependent molecular ionization and excitation energies: Implications for electrically insulating liquids

N. Davari, P.-O. Åstrand, M. Unge, L. E. Lundgaard, and D. Linhjell

Citation: *AIP Advances* **4**, 037117 (2014); doi: 10.1063/1.4869311

View online: <http://dx.doi.org/10.1063/1.4869311>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/adva/4/3?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

Excitation energies and ionization potentials at high electric fields for molecules relevant for electrically insulating liquids

J. Appl. Phys. **113**, 143707 (2013); 10.1063/1.4800118

Publisher's Note: "Field dependence on the molecular ionization potential and excitation energies compared to conductivity models for insulation materials at high electric fields" [*J. Appl. Phys.* 109, 073306 (2011)]

J. Appl. Phys. **109**, 129902 (2011); 10.1063/1.3592714

Field dependence on the molecular ionization potential and excitation energies compared to conductivity models for insulation materials at high electric fields

J. Appl. Phys. **109**, 073306 (2011); 10.1063/1.3562139

Observation of rotamers of m-aminobenzoic acid: Zero kinetic energy photoelectron and hole-burning resonantly enhanced multiphoton ionization spectroscopy

J. Chem. Phys. **121**, 8321 (2004); 10.1063/1.1802551

Effects of halogenation on the ionized and excited states of free-base and zinc porphyrins

J. Chem. Phys. **110**, 9135 (1999); 10.1063/1.478835

An advertisement for CISE (Computational Science and Engineering) featuring a bee on a yellow flower. The text 'Cross-pollinate.' is written in white on the left. On the right, there is a small image of a CISE journal cover with the title 'computing SCIENCE ENGINEERING' and 'NERSC' visible. To the right of the journal cover, the text reads: 'Submit your computational article to CISE.'

Field-dependent molecular ionization and excitation energies: Implications for electrically insulating liquids

N. Davari,¹ P.-O. Åstrand,^{1,a} M. Unge,² L. E. Lundgaard,³ and D. Linhjell³

¹Department of Chemistry, Norwegian University of Science and Technology (NTNU), NO 7491, Trondheim, Norway

²ABB Corporate Research, SE 72178 Västerås, Sweden

³Department of Electric Power Engineering, SINTEF Energy Research, NO 7491, Trondheim, Norway

(Received 6 January 2014; accepted 6 March 2014; published online 20 March 2014)

The molecular ionization potential has a relatively strong electric-field dependence as compared to the excitation energies which has implications for electrical insulation since the excited states work as an energy sink emitting light in the UV/VIS region. At some threshold field, all the excited states of the molecule have vanished and the molecule is a two-state system with the ground state and the ionized state, which has been hypothesized as a possible origin of different streamer propagation modes. Constrained density-functional theory is used to calculate the field-dependent ionization potential of different types of molecules relevant for electrically insulating liquids. The low singlet-singlet excitation energies of each molecule have also been calculated using time-dependent density functional theory. It is shown that low-energy singlet-singlet excitation of the type $n \rightarrow \pi^*$ (lone pair to unoccupied π^* orbital) has the ability to survive at higher fields. This type of excitation can for example be found in esters, diketones and many color dyes. For alkanes (as for example *n*-tridecane and cyclohexane) on the other hand, all the excited states, in particular the $\sigma \rightarrow \sigma^*$ excitations vanish in electric fields higher than 10 MV/cm. Further implications for the design of electrically insulating dielectric liquids based on the molecular ionization potential and excitation energies are discussed. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4869311>]

I. INTRODUCTION

The molecular ionization potential (IP) in high electric fields is an important parameter in pre-breakdown and breakdown phenomena in electrically insulating liquids.^{1,2} In addition to the applied electric field, a molecule is influenced by the electric moments of its neighboring molecules. Therefore, the local field at a liquid molecule becomes larger than the applied field that may result in a considerable effect on the ionization in models describing streamer dynamics.³⁻⁵ It has also been discussed that the molecular excitation energies may affect streamer propagation.^{1,2} It has been suggested that since the number of available excited states decrease with increasing electric field, it may be the molecular origin of different streamer modes.² For molecules with many low excitation energies, some excited states survive at higher fields as compared to molecules with only a few relatively high excitation energies. In an applied voltage, an insulating liquid may lose the continuously added energy by emitting heat or light. It may therefore be anticipated that additives with low excitation energies will improve the insulating properties of a liquid.² We may have excitations by electron impact or by photon absorption. If the excited states have long life-times compared to the frequency of either electron impact or photon absorption, a two-step ionization

^aElectronic mail: per-olof.aastrand@ntnu.no



process may take place where the excited molecule can be ionized,^{1,2} meaning that the excited states of additives should have relatively short life times to improve the insulating properties of a liquid. The strong field-dependence of the molecular IP also implies that photoionization should be regarded as a local effect since high-energy photons generated in regions with a low field may give ionization in high-field regions of the insulating liquid.² The strong field-dependent IP therefore gives rise to multitude of possible processes on the molecular scale, where the importance of each process will depend on the chemical composition.

Experimental studies on the effect of additives on streamer behavior demonstrate that the chemical composition and electronic properties of the base liquids and additives are important in describing the changes of the streamer characteristics.⁶⁻¹² It has been demonstrated that additives with electron-scavenging capabilities increase the velocity of negative streamers, while additives with low IP speed up positive streamers.¹³ In a recent work, the effect of a low-IP additive (N,N-dimethylaniline) on white oil (Exxsol-D140 and Marcol-52) has been studied in a long point-to-plane gap.¹⁴ It was found that N,N-dimethylaniline increases the streamer branching and velocity at low voltages. The branching becomes widespread and dense with increasing the voltage and reduces the field in front of the streamer channels as a result of the shielding effect. Therefore, the streamer speed decreases at specific voltage. In another recent work, azobenzene and N,N-dimethylaniline were added to an ester liquid and it was shown that azobenzene with lower excitation energies than N,N-dimethylaniline causes a significant increase in the acceleration voltage.¹⁵

Quantum chemistry provides methods to calculate molecular parameters that are comparable with experiments in terms of accuracy. Among the different quantum-chemical methods, density-functional theory (DFT) calculations are accurate and computationally efficient based on the choice of exchange-correlation functionals.¹⁶ Methods for calculating the field-dependent IP has been developed recently.^{1,17} In the first studies, a point-charge model is used^{1,2} that is a quantum-classical method based on the electrostatic interactions between a negative point-charge and a cation to find the transition state for the dissociation of an electron in an electric field. A more recent method is based on constrained DFT (CDFT),¹⁷ which is a full quantum-chemical approach that includes both the electrostatic interactions and the exchange effects between the electron and the cation. In CDFT, a constraint is placed on the electron density by a potential that is optimized to minimize the total energy of the system.^{18,19} For example, in long-range charge-transfer systems, the charges on molecular fragments are constrained to +1 or -1^{20,21} and also the spin on molecular fragments can be constrained to a desired value.²² The CDFT method has been used successfully for numerous chemical phenomena.²³⁻²⁶ In our approach, the electron is represented with a ghost atom, i.e. basis functions are added to an expansion center without a nuclear charge, and the charge of this ghost atom is constrained to -1. If the total system is electrically neutral, we thus have a DFT model for the interaction between an electron and a cation.¹⁷

For the field-dependent IP, the CDFT method was applied on a few small molecules in a model study.¹⁷ In this work, the CDFT method is used for different types of molecules relevant for insulation in dielectric liquids. The type of insulating liquids used in high-voltage applications are mainly mineral oils composed of paraffinic, naphthenic and aromatic contributions.^{27,28} Ester liquids have recently become an alternative to mineral oil.²⁹ Different liquids have different dielectric performances because of different electrochemical properties of the molecules in the liquids. Here, the IP and excitation energies of different types of molecules in the electric field are studied and compared to each other, as well as with our previous work.^{1,2,17}

II. THEORY

The IP is here calculated from the dissociation energy barrier of the interaction between an electron and a molecular cation. In the point-charge model,^{1,2} the interaction between a negative point charge, as a model for the electron, and a molecular cation is calculated by varying the distance between the point charge and the molecular cation in the electric field. The IP is calculated as the difference between the energy of a neutral molecule and the dissociation energy barrier in the field.¹

In this work, the CDFT method is used in which the electron is considered as a ghost atom, i.e. an atom without a nuclear charge.¹⁷ The charge on the ghost atom is constrained to -1 as a model

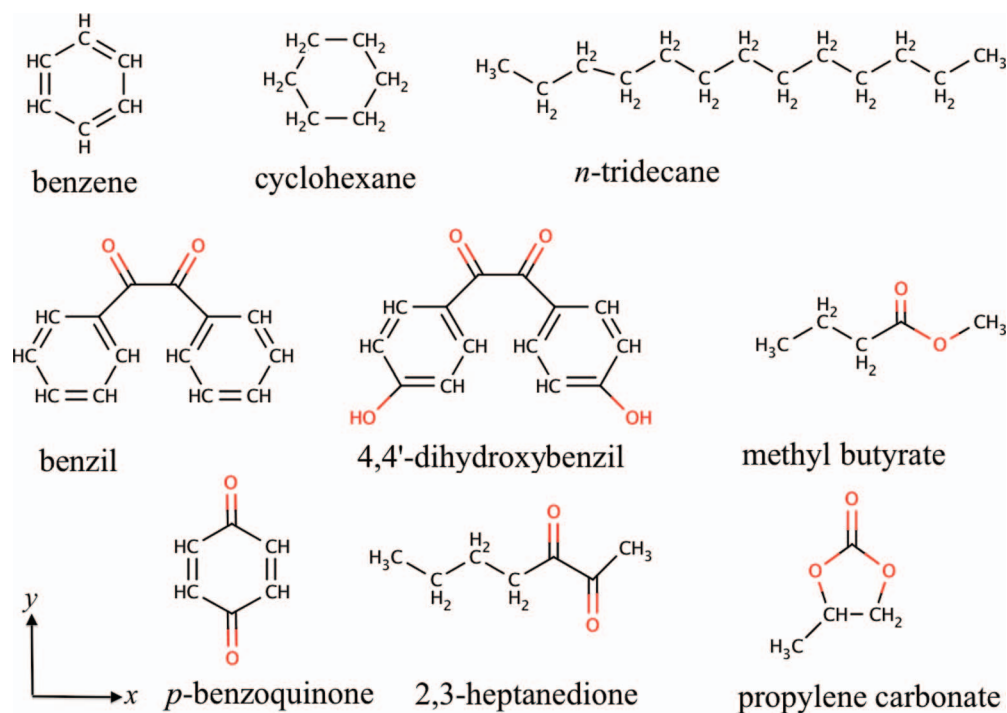


FIG. 1. The molecules included in this study with the coordinate system specified.

for the electron, and the spin of the electron is constrained to a doublet state while the entire system is kept electrically neutral with a singlet spin state. The distance between the ghost atom and the molecular cation is changed to obtain the dissociation barrier in an electric field.

The basis set on the ghost atom, i.e. the electron, is a linear combination of 6 primitive Gaussian *s*-functions with the exponents 0.5, 0.1, 0.02, 0.004, 0.008 and 0.00016. The number of basis functions is obtained to converge the IP to the order of 0.01 eV.¹⁷ Spherically symmetric *s*-functions are used so that the centre-of-charge of the electron remains at the expansion point of the basis functions, leading to that the position of the electron can be defined. There are some limitations in the calculation of the dissociation barrier since the dissociation barrier becomes closer to the molecule at higher fields.¹⁷ In these cases, the orbital of the electron becomes a linear combination of the basis functions of the electron and the basis functions of the cation and it therefore becomes difficult to control the position of the electron.

The geometry optimizations of all the molecules in zero field are done using the B3LYP functional^{30,31} with the cc-pVTZ basis set.³² This molecular geometry is used in subsequent calculations on the molecule and the cation at all electric fields. The Löwdin population scheme³³ is applied in the CDFT calculations for partitioning the electron distribution. The unrestricted open-shell DFT method is used for the cation calculations. More details about the approach is found in Ref. 17. The time-dependent DFT (TDDFT)³⁴ method is used to calculate the 20 lowest singlet-singlet excitation energies. For the excitation energies the aug-cc-pVTZ basis set³⁵ is applied since the excited states become more diffuse in the electric field. All the DFT calculations are performed using the NWChem software.³⁶ The electric field in NWChem is simulated by point charges that in this work are located at 50 and -50 Å whereas the molecule is located at the origin. The electric field is in the range 0 to 30 MV/cm.

III. RESULTS AND DISCUSSION

Figure 1 shows the structure of the included molecules, and in this figure also the coordinate system is defined. Different types of molecules are investigated related to electrically insulating

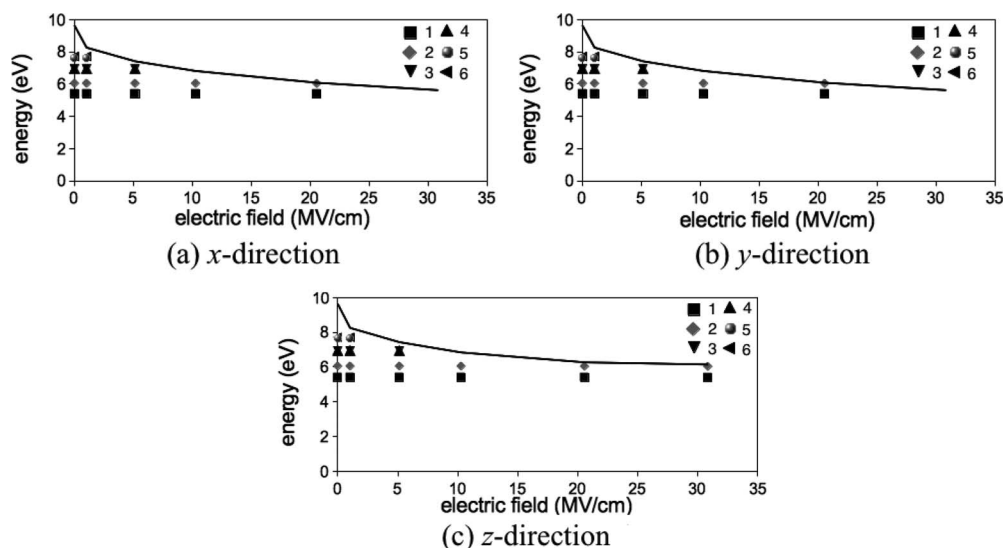


FIG. 2. The IP and excitation energies (eV) in the (a) x , (b) y , and (c) z direction of the electric field for benzene. The solid line is the IP and the dots are excitation energies.

liquids either as base liquids or as additives. The IP and excitation energies in different directions of the electric field are studied for benzene (aromatic), cyclohexane and n -tridecane (alkanes), propylene carbonate and methyl butyrate (esters), benzil, 4,4'-dihydroxybenzil, 2,3-heptanedione and p -benzoquinone (diketones). The excitations that remain at higher fields are investigated in more detail. The reported experimental IPs are adiabatic, whereas the calculated IPs are vertical.

A. Benzene

The presence of polyaromatics in transformer oil affects the streamer behavior. For example, 2-methyl naphthalene can speed up both negative and positive streamers in Marcol-70, even at very low concentrations.¹³ Benzene is included as the simplest aromatic molecule. The calculated zero-field vertical IP for benzene is 9.63 eV compared to the adiabatic experimental IP of 9.24 eV.³⁷ The result is in good agreement with a focal point analysis giving a vertical IP around 9.45 eV.³⁸ In the focal point analysis, the Hartree-Fock (HF) energy is converged with respect to the completeness of the basis set (cc-pV ∞ Z) and a correlation correction to the HF energy (coupled-cluster with single and double and perturbative triple excitations CCSD(T)) at the basis set limit.³⁸ The lowest excitation energy is from the π to π^* orbital with the energy 5.41 eV, which is in good agreement with results from the HCTH functional,³⁹ using various augmented basis sets (5.32–5.44 eV).⁴⁰ Figure 2 shows the IP and excitation energies in different directions of the field. The x - and y -directions are the in-plane and z is the out-of-plane electric field, respectively (Figure 1). The center of benzene ring is the origin of the coordinate system. The field-dependent IP calculated here is in good agreement with the point-charge model.¹ While the IP is decreasing with increasing electric field, the π to π^* excitation energies remain almost constant in the field. A few excitations have energies at or above the IP. Since we use different methods for calculating the IP and the excitation energies, it could be that some of the excitations just below the IP should instead be interpreted as ionized states just above the IP.

B. Alkanes: Cyclohexane and n -tridecane

Alkanes are the major components of mineral oils.²⁷ Cyclohexane and n -tridecane are chosen because of earlier experimental studies of liquid cyclohexane^{9,10,41–43} and n -tridecane^{44,45} with different additives, and also to find out whether the CDFT method can be applied on longer chains. The electric field in x - and y -directions are through the ring of the chair conformation of cyclohexane

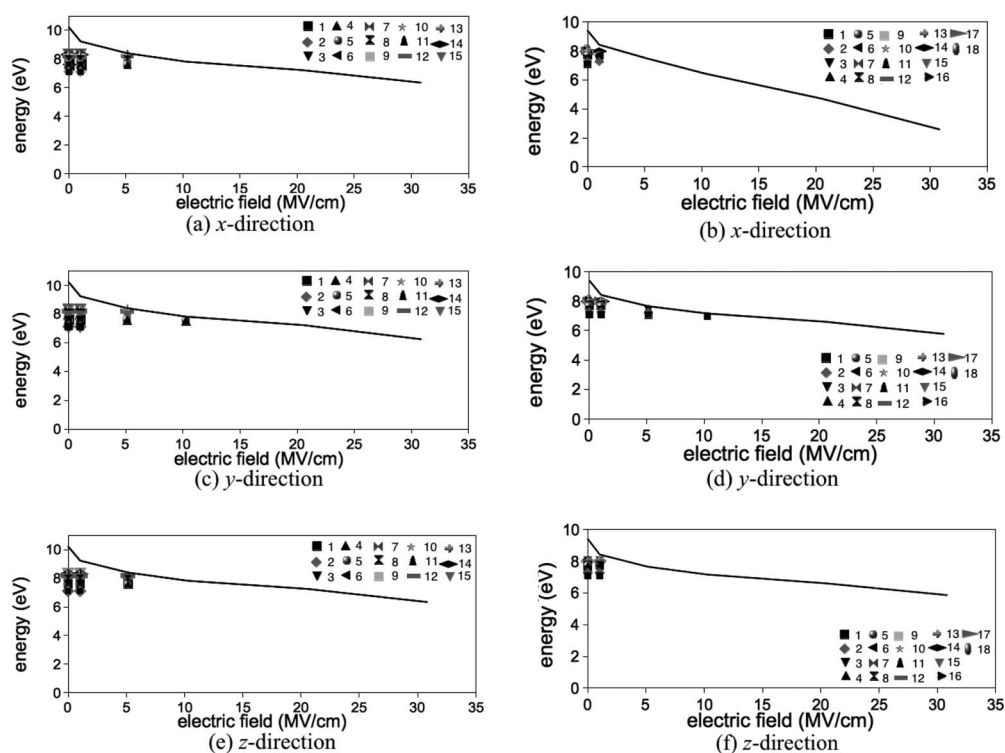


FIG. 3. The IP and excitation energies (eV) in the (a) and (b) x, (c) and (d) y, (e) and (f) z direction of the electric field for cyclohexane (left) and *n*-tridecane (right). The solid line is the IP and the dots are excitation energies.

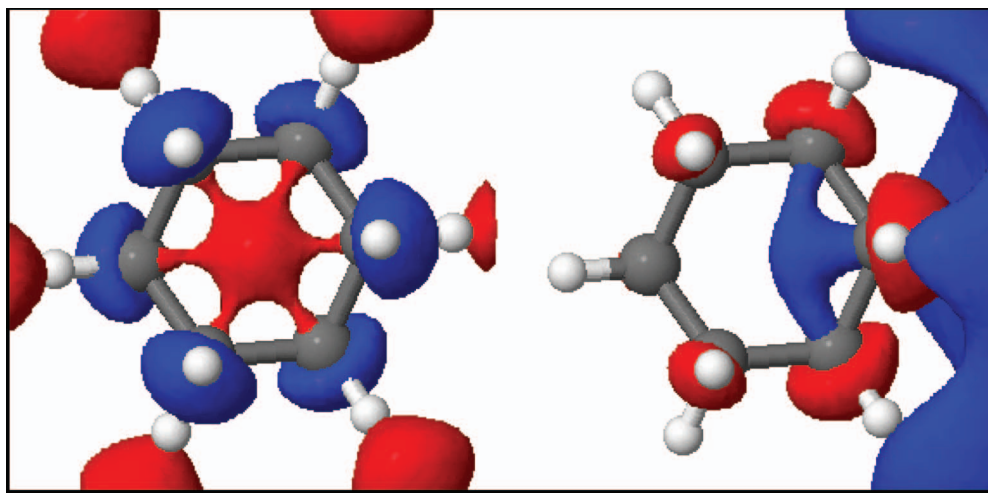


FIG. 4. The σ^* orbital of carbon-carbon bonds (LUMO) in zero-field (left) and 10 MV/cm (right) in x-direction of the electric field for cyclohexane.

and z is perpendicular to the ring (see Figure 1). The center of the ring is the origin of the coordinate system. The experimental IP is around 9.8 eV^{37,46} and the calculated zero-field IP is 10.22 eV, which is in good agreement with the result of the B3P86 functional of 10.0 eV.⁴⁶ The lowest excitation energy of cyclohexane is 7.11 eV, in good accordance to the experimental value around 7.0 eV.⁴⁷ Figure 3 (left) shows that the excited states vanish at fields higher than 5 MV/cm except in the y-direction where excitation energies remain close to the IP and should possibly be interpreted as ionized states. Figure 4 shows the lowest unoccupied molecular orbital (LUMO) in zero-field and

the corresponding ionized orbital in 10 MV/cm in the x -direction, which clearly demonstrates the general effect of increasing the field, that an unoccupied orbital changes from a bound to an ionized state. The two lowest excitations in cyclohexane are from carbon σ orbitals to σ^* orbitals.

The calculated zero-field IP for n -tridecane is 9.41 eV, in good agreement with the B3P86 functional, 9.42 eV⁴⁶ and the experimental value of 9.72 eV.⁴⁶ The lowest excitation energy is 7.08 eV. In the field calculations of the IP, the origin of the coordinate system is located on the middle of the carbon chain. The x -direction of the field is along the chain and the y - and z -directions are perpendicular to the chain, respectively (see Figure 1). The excited states become ionized already at fields close to 1 MV/cm except in the y -direction (perpendicular to the chain) where the first excited state remains up to 10 MV/cm (see Figure 3(d)). This excited state should probably be regarded as an ionized state, since its energy is very close to the IP at 10 MV/cm.

n -tridecane and cyclohexane are alkanes with higher IPs and excitation energies as compared to molecules with π -systems, as for example benzene discussed in the previous section, since their excitations are from low-lying σ orbitals to high-lying σ^* orbitals. All the excited states vanish at a relatively low electric field for both molecules. The difference between the two molecules is that n -tridecane is more influenced by the direction of the electric field along the alkane chain. Figure 3(b) shows that the decrease in the IP is around 70% in the field along the chain comparing zero field with 30 MV/cm, whereas it is around 40% in the field perpendicular to the chain as shown in Figure 3 (right). Consequently, the direction of the field is important for relatively long linear alkanes, such as n -tridecane and also 9,10-dimethyl octadecane as in our previous study.² The field-dependent IPs of cyclohexane and n -tridecane calculated by CDFT method are in good agreement with the earlier study using the point-charge model.¹

In general, the excited states of alkanes vanish at lower fields as compared to other molecules in the study, and for the linear alkanes the direction of the electric field becomes important. Alkanes have fewer number of excited states in the field compared to esters, diketones and quinones as will be discussed here. Therefore, alkanes have a reduced ability to be excited at a high electric field. The light emission from the streamers in cyclohexane is experimentally difficult to detect,^{48–50} which maybe explained by that the excited states of cyclohexane vanish already at an electric field around 5 MV/cm.

C. Esters: Propylene carbonate and methyl butyrate

Propylene carbonate and methyl butyrate are chosen as model compound for ester molecules. Ester-based oils are more biodegradable and have lower volatility and higher flash points than mineral oils,^{29,51} and are investigated intensively as a replacement for mineral oils in electrically insulating devices. Propylene carbonate is a carbonate ester that is mainly used as a polar solvent with a high dielectric constant of 66 at 293 K.³⁷ The ionic conduction of chloride ions in propylene carbonate has been studied to understand conduction mechanisms in dielectric liquids.⁵²

The optimized geometry of propylene carbonate is in good agreement with the obtained geometry using BLYP/DNP method.⁵³ The calculated zero-field IP for propylene carbonate is 10.81 eV compared to the experimental adiabatic IP of 10.52 eV and the vertical IP of 10.71 eV,⁵⁴ respectively. Figure 5 (left) shows the IP and excitation energies in a field. The center of the ring is the origin of the coordinate system. The x - and y -directions are through the ring, with the y -direction parallel to the carbonyl bond, and z -direction is perpendicular to the ring, respectively (see Figure 1). The decrease in the IP with increasing field is not dependent on the direction of the field. The lowest excitation energy for propylene carbonate is 6.97 eV and it is the only excitation that survives at 30 MV/cm. The three lowest excitations are from oxygen lone pairs, n orbitals, to π_{CO}^* orbitals.

The calculated zero-field IP for methyl butyrate is 10.13 eV and the experimental IP is 10.07 eV.³⁷ The origin of the coordinate system is located on the center of the carbon-carbon bond adjacent to the carboxylate group. The x -direction is along the carbon-carbon bonds, y -direction is parallel to the carbonyl bond and z -direction is perpendicular to the central carbon-carbon bond, respectively (see Figure 1). For methyl butyrate the IP is also independent of the direction of the field (Figure 5 (right)). As shown in Figure 5 (right), the lowest excitation energy is 5.88 eV and it

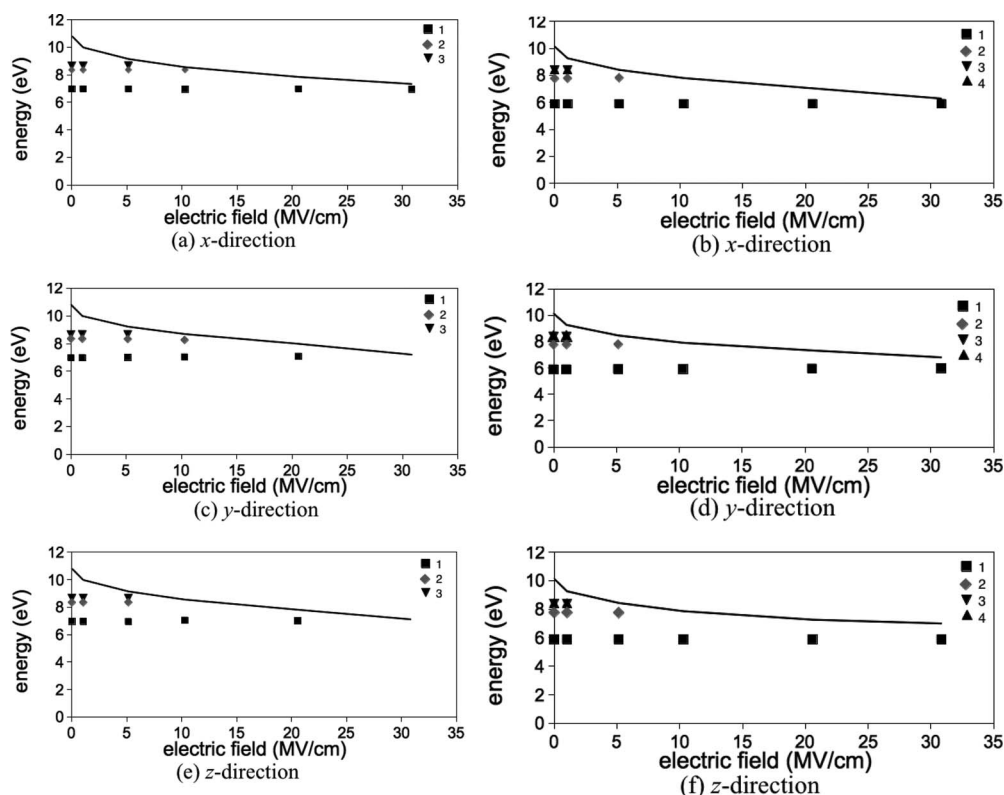


FIG. 5. The IP and excitation energies (eV) in the (a) and (b) x , (c) and (d) y , (e) and (f) z direction of the electric field for propylene carbonate (left) and methyl butyrate (right). The solid line is the IP and the dots are excitation energies.

survives at 30 MV/cm. The excitations are from n orbitals of oxygen atoms to π_{CO}^* orbital similar to propylene carbonate.

For the ester molecules included in this study, there are few excited states in the field, but the lowest excited state survives at 30 MV/cm. The results do not depend on the direction of the electric field. For larger ester molecules such as glyceryltributyrate,² there are a larger number of excited states in the field but they have all vanished at fields higher than 30 MV/cm. Also the IP is more influenced by the electric field than for the small ester molecules studied here. Glyceryltributyrate is sensitive to the direction of the field and the molecular orbitals involved in some of the excitations change in the field which results in an increase or decrease in their energies with increasing field.²

D. Diketones: Benzil, 4,4'-dihydroxybenzil, 2,3-heptanedione and p -benzoquinone

Benzil is a typical aromatic α -diketone molecule that has been the subject of many spectroscopic investigations.⁵⁵⁻⁵⁸ Benzil and 4,4'-dihydroxybenzil have been evaluated as voltage stabilizer to resist electrical treeing in polymer dielectrics used for high-voltage cable applications.⁵⁹ The most stable gas phase structure of benzil is *cis*-skew with the calculated torsion angle of 125° , in good agreement with the RHF (121°) method and the BLYP (123°) functional.⁶⁰ The experimental torsion angle is 108° for the crystal phase⁶¹ and 117° for the gas phase,⁶² respectively. The bond lengths and angles are in good agreement with the X-ray data⁶¹ and calculated data.⁶⁰ The long central carbon-carbon bond is 1.54 \AA resulting in a non-conjugated structure which gives the molecule some specific features.

Figure 6 (left) shows the IP and excitation energies for the *cis*-skew configuration of benzil in different directions of the electric field. The center of the central carbon-carbon bond is the origin of the coordinate system. The x -direction is through one of the phenyl rings, the y -direction is along one of the central carbonyl bonds and the z -direction is perpendicular to the central carbon-carbon bond,

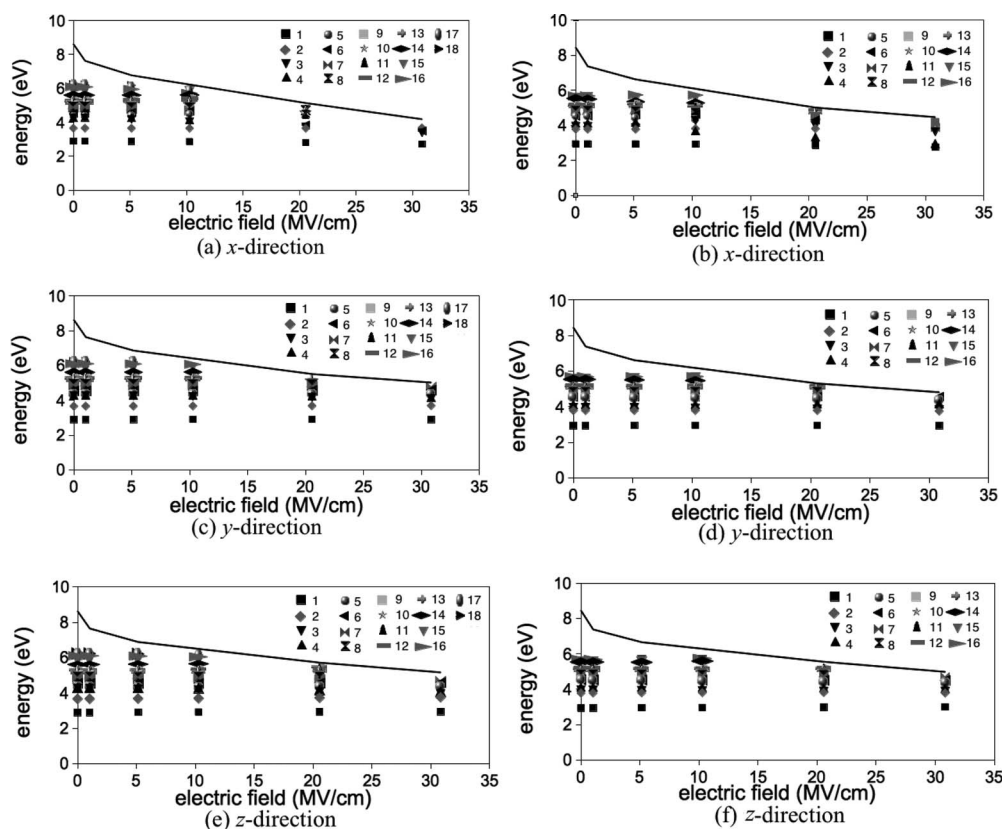


FIG. 6. The IP and excitation energies (eV) in the (a) and (b) x, (c) and (d) y, (e) and (f) z direction of the electric field for the *cis*-skew configuration of benzil (left) and the *cis*-skew configuration of 4,4'-dihydroxybenzil (right). The solid line is the IP and the dots are excitation energies.

respectively. The calculated zero-field IP is 8.62 eV and the experimental IP is 8.68 eV.⁶³ The lowest excitation energy is 2.89 eV and it is from the lone pairs of oxygen atoms, n , to π^* orbital of benzoyl groups, π_{CO+CC}^* . The experimental value is around 3.34 eV.⁶⁴ The deviation from the experimental value is because of the photoisomerization of benzil molecule. After absorption of light, the excited molecule rearranges from *cis*-skew into a *trans*-planar configuration,^{65,66} and by computations it has been found that the first singlet and triplet excited states of benzil are *trans*-planar,⁶⁷ while in this work, the calculated vertical excitation energy is for the same configuration as the ground state (*cis*-skew).

The *trans*-planar configuration of benzil has also been investigated and according to our calculations, the *cis*-skew configuration is 0.20 eV more stable than the *trans*-planar configuration. The calculated IP of the *trans*-planar configuration is around 8.49 eV and the excitation energy is around 2.38 eV. The field-dependent IP is similar for the two configurations.

The calculated zero-field IP for the *cis*-skew configuration of 4,4'-dihydroxybenzil is 8.43 eV and the lowest excitation energy is 2.93 eV. The ground state configuration of this molecule is *cis*-skew. The IP and excitation energy of the *trans*-planar configuration are 8.15 and 2.46 eV, respectively. Comparing benzil and 4,4'-dihydroxybenzil shows that the two hydroxyl groups cause blue shifts of around 0.04 and 0.13 eV, respectively, for the two lowest excitations, which both are n to π_{CO+CC}^* excitations. Figure 6 (right) shows the IP and excitation energies in different directions of the field for *cis*-skew 4,4'-dihydroxybenzil. The directions of the field are the same as in benzil. A few of the excitations decrease substantially with increasing field. For example, the fourth excitation in 4,4'-dihydroxybenzil which is similar to the sixth excitation in benzil decreases with increasing field. This excitation energy in zero-field is 4.11 eV for 4,4'-dihydroxybenzil and 4.53 eV for benzil, respectively, and decreases to 2.96 eV for 4,4'-dihydroxybenzil and 3.50 eV for benzil at 30 MV/cm,

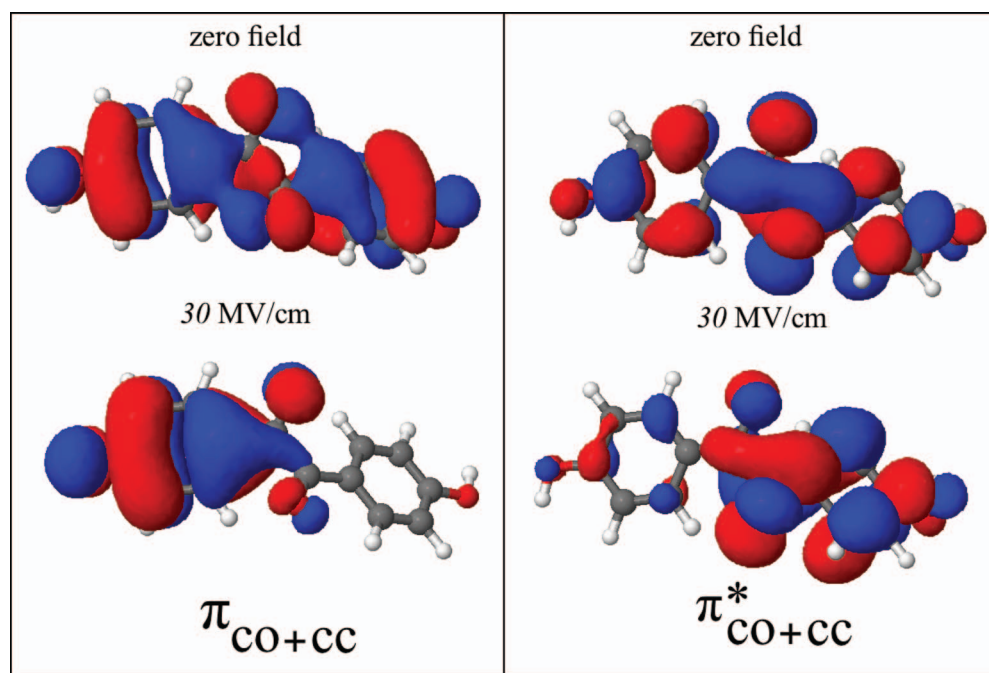


FIG. 7. The molecular orbitals (π_{CO+CC} to the left and π_{CO+CC}^* to the right) that are involved in the fourth excitation for 4,4'-dihydroxybenzil in zero-field (top) and 30 MV/cm (bottom) in the x -direction of the electric field.

respectively. The excitation is from π_{CO+CC} to π_{CO+CC}^* of benzoyl groups as shown in Figure 7. The molecular orbitals in zero-field and 30 MV/cm are shown in Figure 7. In zero-field, the molecular orbital is localized on the two benzoyl groups. As the field increases, the molecular orbital of one of the benzoyl groups gradually disappears until at 30 MV/cm is localized on one of the benzoyl groups. The excitations that remain in the higher fields have the same characteristics as in benzil and are from n to π_{CO+CC}^* , phenyl π orbitals, π_{CC} , to π_{CO+CC}^* and π_{CO+CC} to π_{CO+CC}^* , respectively.

Another diketone, 2,3-heptanedione, is included in this study to be compared with benzil since it has alkyl chains in its structure instead of the two phenyl rings as in benzil. The calculated IP is 9.03 eV, larger than for benzil (8.62 eV) and 4,4'-dihydroxybenzil (8.43 eV). The reason is that the ion is more stabilized in benzil and 4,4'-dihydroxybenzil due to the π systems of the two phenyl rings as compared to 2,3-heptanedione. The lowest excitation energy is 2.69 eV, lower than for benzil (2.89 eV) and 4,4'-dihydroxybenzil (2.93 eV). Figure 8 shows the IP and excitation energies in the field for this molecule. The origin of the coordinate system is on the carbon of the carbonyl bond connected to the butyl chain. The x -direction is along the carbon chain, the y -direction is along one of the carbonyl bonds and the z -direction is perpendicular to the carbonyl bond, respectively (Figure 1). The first two excitations are from n orbitals to π_{CO}^* which remains up to 30 MV/cm. The other excitations are from σ_{CH} , σ_{CC} and π_{CO} to π_{CO}^* , respectively. There are fewer excited states in the field for 2,3-heptanedione compared to benzil and 4,4'-dihydroxybenzil since the π to π^* excitations contribute to many excited states for the benzil molecules.

Quinone derivatives are conjugated diketone cyclic structures that are widely used as color pigments,^{68,69} and are well-known as electron acceptors in many charge-transfer type organic conductors.⁷⁰ Among the quinones, p -benzoquinone is selected as a reference molecule in studying the IP and excitation energies since it has been used as an electron-attaching additive to study its effect on the propagation of streamer in liquid cyclohexane.⁹ The calculated molecular structure is close to the structure obtained from X-ray diffraction.⁷¹ The calculated zero-field IP is 9.84 eV compared to the experimental IP of 9.99 eV.⁷² The calculated energies of the four lowest excitations are 2.51, 2.74, 3.88 and 4.95 eV compared to the experimental values of 2.49, 2.52, 4.07 and 5.12 eV, respectively.^{71,73} Figure 9 shows the IP and excitation energies in different directions of

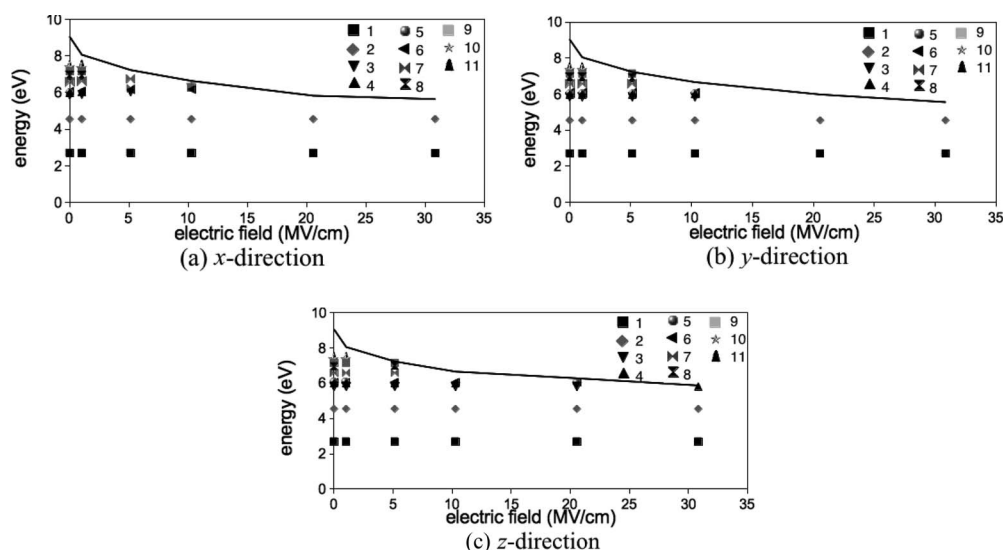


FIG. 8. The IP and excitation energies (eV) in the (a) *x*, (b) *y*, and (c) *z* direction of the electric field for 2,3-heptanedione. The solid line is the IP and the dots are excitation energies.

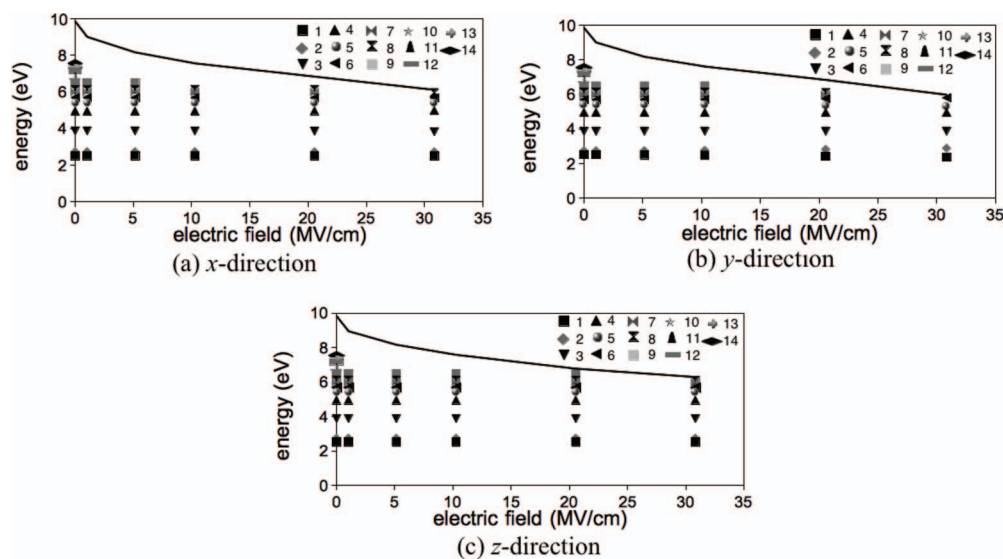


FIG. 9. The IP and excitation energies (eV) in the (a) *x*, (b) *y*, and (c) *z* direction of the electric field for *p*-benzoquinone. The solid line is the IP and the dots are excitation energies.

the field. The *x*- and *y*-directions are through the ring, with the *y*-direction along the carbonyl bonds and the *z*-direction is perpendicular to the ring, respectively (see Figure 1). The center of the ring is the origin of the coordinate system. The lowest two singlet-singlet excitations are from *n* orbitals to the delocalized π_{CO+CC}^* orbital, the third and fourth excitations are from π_{CC} and π_{CO+CC} orbitals to π_{CO+CC}^* orbital, respectively. Several semiempirical^{74–76} and ab-initio^{77–79} studies on the excited states of *p*-benzoquinone show that the first two excitations have $n \rightarrow \pi^*$ character followed by two $\pi \rightarrow \pi^*$ excitations. These excitations survive in the field up to 30 MV/cm. The two additional excitations at 30 MV/cm are from oxygen *n* orbitals to π_{CC}^* orbital.

In general, for diketones there is a large gap between the IP and the lowest excitation energy which results in a larger number of excited states at higher fields. This behavior was also found for *trans*-azobenzene.² The lowest excitation which is from the lone pairs of nitrogen atoms to the π^* orbital of azo bond can survive in the field up to 100 MV/cm.² In addition to the ester and

diketone molecules included in this study, the excitation of the type n to π^* in N,N-dimethylaniline, tetrakis-(dimethylamino)ethylene, glyceryltributyrate in our previous work² can remain in the field of 30 MV/cm. Consequently, n to π^* excitations have the ability to survive at higher fields.

IV. CONCLUSION

The constrained DFT method is demonstrated as an efficient method for calculating the field-dependent IP of different types of molecules. The strong decrease of the IP with increasing electric field causes a reduction in the number of available excited states at high electric fields. At a threshold field, different for each molecule, all the excited states have vanished. The threshold field value is much lower for alkanes compared to esters and diketones, i.e. the excitations of the alkanes vanish at lower fields as compared to the other types of molecules included in our studies. The direction of the electric field is important for linear alkanes. The ester molecules included in this work have fewer excited states in high fields compared to the color dyes, but the lowest excitation which is from n to π^* survives at 30 MV/cm. Diketones have a higher number of excited states in the field since the n to π^* excitation has a relatively low energy compared to the field-dependent IP. Therefore, diketones are more likely to become excited, whereas alkanes become ionized with increasing field. A general conclusion is that n to π^* excitations can survive at higher fields, while σ to σ^* excitations vanish at relatively low fields.

ACKNOWLEDGMENTS

We would like to acknowledge a research grant “Modeling of electrical pre-breakdown and breakdown phenomena in insulating liquids” (200631/560) from the Norwegian Research Council, ABB and Statnett and a grant of computer time (account nn2920k) from the NOTUR project.

- ¹H. S. Smalø, Ø. Hestad, S. Ingebrigtsen, and P.-O. Åstrand, “Field dependence on the molecular ionization potential and excitation energies compared to conductivity models for insulation materials at high electrical fields,” *J. Appl. Phys.* **109**, 073306 (2011).
- ²N. Davari, P.-O. Åstrand, S. Ingebrigtsen, and M. Unge, “Excitation energies and ionization potentials at high electric fields for molecules relevant for electrically insulating liquids,” *J. Appl. Phys.* **113**, 143707 (2013).
- ³J. Jadidian, M. Zahn, N. Lavesson, O. Widlund, and K. Borg, “Effect of impulse voltage polarity, peak amplitude, and rise time on streamers initiated from a needle electrode in transformer oil,” *IEEE Trans. Plasma Sci.* **40**, 909 (2012).
- ⁴J. Jadidian, M. Zahn, N. Lavesson, O. Widlund, and K. Borg, “Stochastic and deterministic causes of streamer branching in liquid dielectrics,” *J. Appl. Phys.* **114**, 063301 (2013).
- ⁵J. Jadidian and M. Zahn, “Charge transport analysis in two-phase composite dielectric systems,” *IEEE Trans. Plasma Sci.* **41**, 2464 (2013).
- ⁶Y. Nakao, H. Itoh, S. Hoshino, Y. Sakai, and T. Hagashira, “Effects of additives on prebreakdown phenomena in n -hexane,” *IEEE Trans. Dielect. Elect. Insul.* **1**, 383 (1994).
- ⁷L. Angerer, “Effect of organic additives on electrical breakdown in transformer oil and liquid paraffin,” *Proc. IEE* **112**, 1025 (1965).
- ⁸N. V. Dung, H. K. Høidalen, D. Linhjell, L. E. Lundgaard, and M. Unge, “Influence of impurities and additives on positive streamers in paraffinic model oil,” *IEEE Trans. Dielect. Elect. Insul.* **19**, 1593 (2012).
- ⁹S. Ingebrigtsen, H. S. Smalø, P.-O. Åstrand, and L. E. Lundgaard, “Effects of electron-attaching and electron-releasing additives on streamers in liquid cyclohexane,” *IEEE Trans. Dielect. Elect. Insul.* **16**, 1524 (2009).
- ¹⁰O. Lesaint and M. Jung, “On the relationship between streamer branching and propagation in liquids: influence of pyrene in cyclohexane,” *J. Phys. D: Appl. Phys.* **33**, 1360 (2000).
- ¹¹A. Beroual and R. Tobazeon, “Prebreakdown phenomena in liquid dielectrics,” *IEEE Trans. Dielect. Elect. Insul.* **21**, 613 (1986).
- ¹²W. G. Chadband and T. Sufian, “Experimental support for a model of positive streamer propagation in liquid insulation,” *IEEE Trans. Elect. Insul.* **20**, 239 (1985).
- ¹³J. C. Devins, S. J. Rzad, and R. J. Schwabe, “Breakdown and prebreakdown phenomena in liquids,” *J. Appl. Phys.* **52**, 4531 (1981).
- ¹⁴N. V. Dung, H. K. Høidalen, D. Linhjell, L. E. Lundgaard, and M. Unge, “Effects of reduced pressure and additives on streamers in white oil in long point-plane gap,” *J. Phys. D: Appl. Phys.* **46**, 255501 (2013).
- ¹⁵M. Unge, S. Singha, N. V. Dung, D. Linhjell, S. Ingebrigtsen, and L. E. Lundgaard, “Enhancements in the lightning impulse breakdown characteristics of natural ester dielectric liquids,” *Appl. Phys. Lett.* **102**, 172905 (2013).
- ¹⁶K. Burke, “Perspective on density functional theory,” *J. Chem. Phys.* **136**, 150901 (2012).
- ¹⁷N. Davari, P.-O. Åstrand, and T. Van Voorhis, “Field-dependent ionisation potential by constrained density functional theory,” *Mol. Phys.* **111**, 1456 (2013).

- ¹⁸ Q. Wu and T. Van Voorhis, "Direct optimization method to study constrained systems within density-functional theory," *Phys. Rev. A* **72**, 024502 (2005).
- ¹⁹ B. Kaduk, T. Kowalczyk, and T. Van Voorhis, "Constrained density functional theory," *Chem. Rev.* **112**, 321 (2012).
- ²⁰ Q. Wu and T. Van Voorhis, "Constrained density functional theory and its application in long-range electron transfer," *J. Chem. Theory Comput.* **2**, 765 (2006).
- ²¹ T. Kowalczyk, Z. Lin, and T. Van Voorhis, "Fluorescence quenching by photoinduced electron transfer in the Zn²⁺ sensor Zinpyr-1: A computational investigation," *J. Phys. Chem. A* **114**, 10427 (2010).
- ²² I. Rudra, Q. Wu, and T. Van Voorhis, "Predicting exchange coupling constants in frustrated molecular magnets using density functional theory," *Inorg. Chem.* **46**, 10539 (2007).
- ²³ Q. Wu, B. Kaduk, and T. Van Voorhis, "Constrained density functional theory based configuration interaction improves the prediction of reaction barrier heights," *J. Chem. Phys.* **130**, 034109 (2009).
- ²⁴ H. Oberhofer and J. Blumberger, "Charge constrained density functional molecular dynamics for simulation of condensed phase electron transfer reactions," *J. Chem. Phys.* **131**, 064101 (2009).
- ²⁵ Y. Lu, R. Quardokus, C. S. Lent, F. Justaud, C. Lapinte, and S. A. Kande, "Charge localization in isolated mixed-valence complexes: An STM and theoretical study," *J. Am. Chem. Soc.* **132**, 13519 (2010).
- ²⁶ T. Van Voorhis, T. Kowalczyk, B. Kaduk, L.-P. Wang, C.-L. Cheng, and Q. Wu, "The diabatic picture of electron transfer, reaction barriers, and molecular dynamics," *Ann. Rev. Phys. Chem.* **61**, 149 (2010).
- ²⁷ M. Nishimatsu, T. Miyamoto, and T. Suzuki, *Liquid Insulation* (Wiley Encyclopedia of Electrical and Electronics Engineering, 1999) John Wiley & Sons.
- ²⁸ N. Berger, M. Randoux, G. Ottmann, and P. Vuarchex, "Review on insulating liquids," *Electra* **171**, 33 (1997).
- ²⁹ L. Rongsheng, C. Törnkvist, V. Chandramouli, O. Giralanda, and L. A. A. Pettersson, "Ester fluids as alternative for mineral oil: The difference in streamer velocity and LI breakdown voltage," in *IEEE Conf. Elect. Insul. Dielect. Phenomena* (2009) pp. 543–548.
- ³⁰ A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange," *J. Chem. Phys.* **98**, 5648 (1993).
- ³¹ C. Lee, W. Yang, and R. G. Parr, "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density," *Phys. Rev. B* **37**, 785 (1988).
- ³² T. H. Dunning, Jr., "Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen," *J. Chem. Phys.* **90**, 1007 (1989).
- ³³ P.-O. Löwdin, "On the nonorthogonality problem connected with the use of atomic wave functions in the theory of molecules and crystals," *J. Chem. Phys.* **18**, 365 (1950).
- ³⁴ G. Zhang and C. B. Musgrave, "Comparison of DFT methods for molecular orbital eigenvalue calculations," *J. Phys. Chem. A* **111**, 1554 (2007).
- ³⁵ R. A. Kendall, T. H. Dunning, and R. J. Harrison, "Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions," *J. Chem. Phys.* **96**, 6796 (1992).
- ³⁶ M. Valiev, E. J. Bylaska, N. Govind, K. Kowalski, T. P. Straatsma, H. J. J. van Dam, D. Wang, J. Nieplocha, E. Apra, T. L. Windus, and W. A. de Jong, "NWChem: a comprehensive and scalable open-source solution for large scale molecular simulations," *Comput. Phys. Commun.* **181**, 1477 (2010).
- ³⁷ D. R. Lide, *Handbook of Chemistry and Physics*, 84th ed. (FL: CRC Press, Boca Raton, 2004).
- ³⁸ M. S. Deleuze, L. Claes, E. S. Kryachko, and J.-P. François, "Benchmark theoretical study of the ionization threshold of benzene and oligoacenes," *J. Chem. Phys.* **119**, 3106 (2003).
- ³⁹ F. A. Hamprecht, A. J. Cohen, D. J. Tozer, and N. C. Handy, "Development and assessment of new exchange-correlation functionals," *J. Chem. Phys.* **109**, 6264 (1998).
- ⁴⁰ N. C. Handy and D. J. Tozer, "Excitation energies of benzene from Kohn-Sham theory," *J. Comput. Chem.* **20**, 106 (1999).
- ⁴¹ A. Denat, J. P. Gosse, and B. Gosse, "Electrical conduction of purified cyclohexane in a divergent electric field," *IEEE Trans. Elect. Insul.* **23**, 545 (1988).
- ⁴² S. Ingebrigtsen, L. E. Lundgaard, and P.-O. Åstrand, "Effects of additives on prebreakdown phenomena in liquid cyclohexane: II. streamer propagation," *J. Phys. D: Appl. Phys.* **40**, 5624 (2007).
- ⁴³ S. Ingebrigtsen, L. E. Lundgaard, and P.-O. Åstrand, "Effects of additives on prebreakdown phenomena in liquid cyclohexane: I. streamer initiation," *J. Phys. D: Appl. Phys.* **40**, 5161 (2007).
- ⁴⁴ Ø. Hestad, H. S. Smalø, P.-O. Åstrand, S. Ingebrigtsen, and L. E. Lundgaard, "Effects of N,N-dimethylaniline and trichloroethene on prebreakdown phenomena in liquid and solid *n*-tridecane," *IEEE Trans. Dielect. Elect. Insul.* **18**, 1886 (2011).
- ⁴⁵ Ø. L. Hestad, P.-O. Åstrand, and L. E. Lundgaard, "*n*-tridecane as a model system for polyethylene: Comparison of pre-breakdown phenomena in liquid and solid phase stressed by fast transient," *IEEE Trans. Dielect. Elect. Insul.* **18**, 1929 (2011).
- ⁴⁶ Z. Zhou, L. Zhang, M. Xie, Z. Wang, D. Chen, and F. Qi, "Determination of absolute photoionization cross-sections of alkanes and cyclo-alkanes," *Rapid Commun. Mass Spectrom.* **24**, 1335 (2010).
- ⁴⁷ L. W. Pickett, M. Muntz, and E. M. McPherson, "Vacuum ultraviolet absorption spectra of cyclic compounds. I. cyclohexane, cyclohexene, cyclopentane, cyclopentene and benzene," *J. Am. Chem. Soc.* **73**, 4862 (1951).
- ⁴⁸ N. Bonifaci and A. Denat, "Spectral analysis of light emitted by prebreakdown phenomena in non-polar liquids and gases," *IEEE Trans. Elect. Insul.* **26**, 610 (1991).
- ⁴⁹ S. Ingebrigtsen, N. Bonifaci, A. Denat, and O. Lesaint, "Spectral analysis of the light emitted from streamers in chlorinated alkane and alkene liquids," *J. Phys. D: Appl. Phys.* **41**, 235204 (2008).
- ⁵⁰ D. Linhjell, S. Ingebrigtsen, L. E. Lundgaard, and M. Unge, "Streamers in long point-plane gaps in cyclohexane with and without additives under step voltage," in *IEEE International Conference on Dielectric Liquids (ICDL)* (Trondheim, Norway, 2011).
- ⁵¹ T. V. Oomen, "Vegetable oils for liquid-filled transformers," *IEEE Electric. Insul. Mag.* **18**, 6 (2002).
- ⁵² J. P. Gosse, "Electric conduction in dielectric liquids," *NATO ASI Series* **193**, 503 (1989).

- ⁵³ R. Chen, F. Wu, L. Li, Y. Guan, X. Qiu, S. Chen, Y. Li, and S. Wu, "Butylene sulfite as a film-forming additive to propylene carbonate-based electrolytes for lithium ion batteries," *J. Phys. Chem. B* **11**, 395 (2007).
- ⁵⁴ Y. Yokoyama and M. Jinno, "Identification of accidentally degenerate bands in UV and propylene photoelectron spectra carbonate," *J. Electron Spectrosc. Rel. Phen.* **5**, 1095 (1974).
- ⁵⁵ S. C. Bera, R. Mukherjee, and M. Chowdhury, "Spectra of benzil," *J. Chem. Phys.* **51**, 754 (1969).
- ⁵⁶ J. Arnett and S. P. McGlynn, "Phototautomerism of aromatic α -dicarbonyls," *J. Phys. Chem.* **79**, 626 (1975).
- ⁵⁷ S. Lopes, A. Gómez-Zavaglia, L. Lapinski, N. Chattopadhyay, and R. Fausto, "Matrix-isolation FTIR spectroscopy of benzil: Probing the flexibility of the C-C torsional coordinate," *J. Phys. Chem. A* **108**, 8256 (2004).
- ⁵⁸ A. Singh, D. K. Palit, and J. P. Mittal, "Conformational relaxation dynamics in the excited electronic states of benzil in solution," *Chem. Phys. Lett.* **360**, 443 (2002).
- ⁵⁹ M. Jarvid, A. Johansson, V. Englund, S. Gubanski, and M. R. Andersson, "Electrical tree inhibition by voltage stabilizers," in *IEEE Conference on Electrical Insulation and Dielectric Phenomena, (CEIDP)* (Montreal, Canada, 2012) pp. 605–608.
- ⁶⁰ T. M. Kolev and B. A. Stamboliyska, "Vibrational spectra and structure of benzil and its 18O and d10-labelled derivatives: a quantum chemical and experimental study," *Spectrochim. Acta A* **58**, 3127 (2002).
- ⁶¹ C. Brown and R. Sadanaga, "The crystal structure of benzil," *Acta Cryst.* **18**, 158 (1965).
- ⁶² Q. Shen and K. Hagen, "Gas-phase molecular structure and conformation of benzil as determined by electron diffraction," *J. Phys. Chem.* **91**, 1357 (1987).
- ⁶³ A. V. Polevoi, V. M. Matyuk, G. A. Grigoréva, and V. K. Potapov, "Formation of intermediate products during the resonance stepwise polarization of dibenzyl ketone and benzil molecules," *J. Phys. Chem.* **21**, 12 (1987).
- ⁶⁴ W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, "Mechanisms of photochemical reactions in solution. XXVIII. ¹ Values of triplet excitation energies of selected sensitizers," *J. Am. Chem. Soc.* **86**, 4537 (1964).
- ⁶⁵ D. J. Morantz and A. J. C. Wright, "Structures of the excited states of benzil and related dicarbonyl molecules," *J. Chem. Phys.* **54**, 692 (1971).
- ⁶⁶ A. Chakrabarty, P. Purkayastha, and N. Chattopadhyay, "Laser induced optacoustic spectroscopy of benzil: Evaluation of structural volume change upon photoisomerization," *J. Photochem. Photobiol. A: Chem.* **198**, 256 (2008).
- ⁶⁷ K. K. Das and D. Majumdar, "Ground and excited states of benzil: A theoretical study," *J. Mol. Struct. (THEOCHEM)* **288**, 55 (1993).
- ⁶⁸ K. Venkataraman, ed., *The Chemistry of Synthetic Dyes* (Academic press, New York, 1971).
- ⁶⁹ M. Matsuoka, *Infrared Absorbing Dyes* (Plenum Press, New York, USA, 1990).
- ⁷⁰ V. Khodorkovsky and J. Y. Becker, *In Organic Conductors: Fundamentals and Applications*. (Matcel Dekker, New York, 1994).
- ⁷¹ H. P. Trommsdorff, "Electronic states and spectra of *p*-benzoquinone," *J. Chem. Phys.* **56**, 5358 (1972).
- ⁷² L. Åsbrink, G. Bieri, C. Fridh, E. Lindholm, and D. P. Chong, "Spectra of *p*-benzoquinone, studied with HAM/3," *Chem. Phys.* **43**, 189 (1979).
- ⁷³ H. Yasushi, H. Masahiko, E. Masahiro, and N. Hiroshi, "Excited and ionized states of *p*-benzoquinone and its anion radical: SAC-CI theoretical study," *J. Phys. Chem. A* **106**, 3838 (2002).
- ⁷⁴ P. Jacques, J. Faure, O. Chalvet, and H. H. Jaffe, "A reexamination of the oxygen parameters in the CNDO/S method. Application to UV and photoelectron spectra of *p*-benzoquinone," *J. Phys. Chem.* **85**, 473 (1981).
- ⁷⁵ A. Kuboyama, Y. Kozima, and J. Maeda, "The CNDO/S-CI calculations of the singlet $n\pi^*$ and $\pi\pi^*$ levels of quinones," *Bull. Chem. Soc (Jpn)* **55**, 3635 (1982).
- ⁷⁶ A. A. Meier and G. H. Wagnière, "The long-wavelength MCD of some quinones and its interpretation by semi-empirical MO methods," *Chem. Phys.* **113**, 287 (1987).
- ⁷⁷ S. Coriani, P. Jørgensen, A. Rizzo, K. Ruud, and J. Olsen, "Ab initio determinations of magnetic circular dichroism," *Chem. Phys. Lett.* **300**, 61 (1999).
- ⁷⁸ R. Broer and W. Nieuwpoort, "Hole localization and symmetry breaking," *J. Mol. Struct. (THEOCHEM)* **458**, 19 (1999).
- ⁷⁹ J. Weber, K. Malsch, and G. Hohlneicher, "Excited electronic states of *p*-benzoquinone," *Chem. Phys.* **264**, 275 (2001).