UPS and DFT investigation of the electronic structure of gas-phase trimesic acid

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Abstract

Benzene-1,3,5-tricarboxylic acid (trimesic acid, TMA) molecules in gas-phase have been investigated by using valence band photoemission. The photoelectron spectrum in the binding energy region from 9 to 22 eV is interpreted by using density functional theory calculations. The electronic structure of TMA is compared with benzene and benzoic acid in order to demonstrate changes in molecular orbital energies induced by addition of carboxyl groups to benzene ring.

Keywords: trimesic acid, benzene-1,3,5-tricarboxylic acid, electronic structure, valence band photoemission

Introduction

During the last decade investigations of self-assembled supermolecular structures and their utilization as links between complex biomolecules, such as DNA and proteins, and surfaces [1] have been intensified [2]. Self-assembly of organic molecular structures on metal surfaces, stabilized by non-covalent bonding (e.g. hydrogen bonds, metal–ligand interactions, etc.), can be found in novel applications in catalysis, gas storage, selective ion exchange and data storage [3]. Furthermore self-organized molecules can be utilized to bind biomolecules to surfaces [1] in order to facilitate, for instance, manufacturing of solid-state biosensors for pathogen detection [4].

One of the promising self-organizing molecules is benzene-1,3,5-tricarboxylic acid (trimesic acid, TMA, $C_6H_3(COOH)_3$), which is composed of three peripheral carboxyl groups (-COOH) attached to central benzene ring. The symmetry and trigonal functionality of the TMA molecule facilitates formation of various arrangements on well-defined metallic substrates such as Cu [5], Au [6], but also to non-metallic substrate like graphene [7]. Scanning tunnelling microscopy has shown that below 280 K, TMA forms planar honeycomb structure at Cu(100) surface. This structure is driven by the carboxyl group dimerization and H-bond formation with the neighboring TMA molecules [8]. At temperatures above 300 K TMA forms upright-standing chains on Cu(100) surface, where TMA molecules bind to the Cu substrate via either one or two deprotonated carboxyl (i.e., carboxylate, COO−) groups, where the neighboring molecules are anchored to each other through H-bonds [8].

Although there are several investigations related to adsorbed TMA molecules [5],[7], no attention has been paid to electronic structure of gas-phase (not adsorbed) TMA molecule.

Investigation of free molecule enables better understanding of the interactions of the molecule and its complete electronic structure in quantum mechanical level.

In this study, we have utilized Ultraviolet Photoelectron Spectroscopy (UPS) and Density Functional Theory (DFT) to investigate and resolve valence band electronic structure of TMA. In order to gain insights into how one or three functional carboxyl groups influence the electronic structure of benzene, experimental and theoretical results obtained from TMA were compared with those of benzene [9] and its derivative benzoic acid (BA) [10]. The current investigation paves the way to comprehending the electronic structure of TMA and its interactions on different surfaces.

Experimental

In gas-phase experiments TMA (purity 98%), purchased from Alfa Aesar GmbH Co KG, Germany, was used without further treatments. Gas-phase experiments were carried out by evaporating the liquid from a quartz crucible of an effusion cell (MBE Komponenten NTEZ-40). TMA molecule has been depicted on Figure 1.

The UPS measurements of gas-phase TMA were carried out at beamline I411 [11] of the MAX II storage ring (Lund, Sweden). The beamline has an undulator source and covers the excitation photon energy range from 40 eV to about 1500 eV. Beamline I411 is equipped with a modified SX-700 plane grating monochromator with 1220 mm^{-1} grating and a plane-elliptical focusing mirror. UPS spectra were obtained using an electron energy analyzer (SCIENTA ~~SES-200~~ R-4000) in the fixed analyzer transmission mode with the pass energy of 20 eV. Spectral resolution was 80 meV, when measured as the full width at half maximum of the Ar $3p_{3/2}$ photoelectron line. UPS measurements were carried out in 10^{-7} mbar pressure. UPS spectrum was measured with excitation energy of 40 eV. Binding energies were calibrated according to Ar $3p_{3/2}$ (15.76 eV) and Ar $3p_{1/2}$ (15.94 eV) photoelectron lines [12]. Binding energies from experimental spectrum were obtained by CasaXPS software (version 2.3.13) [13]. TMA photoelectron peaks were fitted by symmetric Gaussian lineshapes.

Ab initio DFT and Møller–Plesset perturbation theory (MP2) calculations were performed using Spartan 14 software [14]. The Gaussian basis sets 6-311G** (d,p-polarized basis set) and the hybrid B3LYP functional have been used in the calculations and the geometry of the molecule has been optimized for lowest energy. The density of states (DOS) type spectra shown in Figure 2 were obtained by convoluting the calculated discrete states with a Gaussian function under the assumption that the electron emission intensities from each orbital are the same and that the photoemission process is non-adiabatic, i.e. the emission process of the photoelectron is much faster than the rearrangement of the electron system after the absorption of the photon (the sudden approximation).

Results

The UPS spectrum of TMA (measured in binding energy range of 9 to 22 eV), BA and benzene together with theoretically calculated DOS is shown in Figure 2. Presented experimental TMA spectrum is obtained by subtracting background spectrum (acquired during the same experiment) from measured TMA spectrum. In the TMA spectrum 10 different photoelectron lines (in later discussion we refer them as regions) labelled from A to J were observed. It should be noted that the TMA photoelectron lines are convoluted with minor features related to background gases that were present during the experiments due to

the relatively low vapor density of TMA. In Figure 2a the intensity of spectral features between 15 and 17 eV (area from G-H) is slightly increased by a small contribution from overlapping N_2 photoelectron lines. This helps to explain why the experimental features are slightly more prominent than the theoretical lines (Figure 2d).

To attribute experimental photoelectron lines reliably to specific transitions, we have used DFT calculations. We have compared the experimental TMA spectrum with those of the benzene [9] and BA [15] from literature. Additionally, the spectra for BA and benzene were calculated (Figure 2e and Figure 2f) for comparison with TMA. The energies of the calculated orbitals were contracted to 80% of their original values and then shifted by 4 eV to higher binding energies since it is well known that DFT tends to underestimate binding energies [16]. It should be noted that a quantitative fit of the shape of the UPS spectra cannot be expected from DFT calculations because the intensities of the different spectroscopic methods do not depend on the density of states only [16], but also on the experimental geometry, electron analyzer transmission function, incident photon energy and photoemission cross sections among other parameters.

Before identifying the electronic structure of TMA and discussing the effect of adding carboxyl groups to benzene ring, let us consider electronic structure of benzene and benzoic acid. Benzene is the simplest aromatic hydrocarbon. It is a planar molecule of D_{6h} symmetry and has 30 valence electrons. In benzene, six p atomic orbitals from carbons form π bonding system. The electronic structure of benzene has been investigated by photoelectron spectroscopy [15] and identified by using theoretical methods [17]. According to these results three outer valence states of the benzene are $1E_g$, $3E_{2g}$ and $1A_{2u}$, where $1E_g$ and $1A_{2u}$ are π orbitals [18]. All other orbitals are σ orbitals.

BA, with lower symmetry (C_s [9]) than benzene, has one carboxyl group attached to benzene ring and it has 46 valence electrons. The electronic structure of BA has been investigated experimentally and theoretically [9],[10]. According to experiments, the HOMO is related to excitation of electrons from combination of π MO of benzene ring and lone electron pairs of oxygen in carboxyl group, where the benzene ring atoms exhibit higher electron density [10]. This is followed by excitation from atomic orbital related to oxygen in carboxyl group. Next excitation is from MOs, which are related to carbonyl group (π orbital). [9],[10]. MOs which has high binding energy have σ character, however MO at 15.10 eV has been identified as π orbital related to benzene ring.

TMA in its electronic ground state has C_{3h} symmetry and has 72 valence electrons. The irreducible representation of a C_{3h} molecule are E´, E´´, A´ and A´´. Its structure is demonstrated in Figure 1.

Fitted photoelectron peaks positions and calculated states are summarized in Table 1. All MO's that are not referred as π-bonding MOs are considered as σ-orbitals.

Based on our DFT calculations, the region A (Figure 2a) features three distinctive MOs in a range 9.7 to 10 eV with three different symmetries E", E' and A'. HOMO (Table 1, 9.7 eV) with symmetry E" and ionization energy 9.72 eV, originates from benzene ring carbon p_z atomic orbitals (C1, C2, C4, C5 or C1, C3, C4, C6 atoms in benzene ring). HOMO has strong π character, we refer to it as $\pi_{3,2}$. However this MO has additionally low contribution from carboxyl group oxygens (O6 and O2). Next MO (9.9 eV) with symmetry E' originates mainly from p_x and p_y atomic orbitals of oxygens of all three carbonyl groups (C=O) but also from

carbons (C1, C5) of the benzene ring contribute. MO at 10 eV with symmetry of A' originates entirely from oxygen's p_x (O2, O6) and p_y (O2, O4) atomic orbitals of carbonyl group and carbon (C7, C8, C9) s orbitals.

The theoretical calculation has resolved the origin of the experimentally observed region B. Two MOs with A'' and E'' symmetries originate from oxygen p_z atomic orbitals of three carboxyl groups (O1-O6) and region B is therefore wholly due to π bonds (π_{CO}).

Region C contains two MOs with E' and A'' symmetry. First MO at 11.88 eV originates mostly from benzene ring carbons p_x (C1-C4, C6) and p_y (C2, C4-C6) atomic orbitals, however also hydrogen (H2, H4, H6) s atomic orbitals from benzene ring contribute. The second MO in region C originates from carbons (C1-C6) p_z atomic orbitals in benzene ring but also oxygen (-OH; O1, O3, O5) from carboxyl groups contributes. This orbital has a strong π character.

MOs at 12.59 eV and 12.66 eV explain region D. MO with E' symmetry originate from p_x (O3, O5), p_y (O1, O5) and s atomic orbitals of oxygen (-OH; O1, O3, O5) located at carboxyl groups, also there is contribution from carbon C2 of benzene ring. MO with A' symmetry at 12.66 eV originates only from p_x (O3, O4) and p_y (O1, O2) atomic orbitals of oxygen from two carboxyl groups.

Region E is positioned around 13.8 eV where calculations give three MOs with symmetries E'', A' and A''. The first one, at energy of 13.57 eV, consists of two overlapping MOs. The peak has strong π character and it originates from p_z atomic orbital of oxygen (O1-O6) and carbon (C7-C9) from carboxyl groups. MO at energy 13.69 eV with symmetry A' originates from p_x (C1, C6) and p_y-orbitals (C2, C5) of carbons in the benzene ring. Third MO (13.77 eV) with symmetry A'' is combination of p_z orbital of all the oxygens (O1-O6) from three carboxyl groups and p_z orbitals of carbon (C2, C4, C6) from the benzene ring.

Region F contains four MOs with symmetries A' and E'. All states in region F are delocalized and therefore their decomposition is not trivial. Here, the most probable origins of MOs are given according to calculations. First MO at energy 14.12 eV with a symmetry group A' originates from s atomic orbital of carbons in the benzene ring (C2, C4, C6). The second MO at binding energy 14.14 eV forms two σ-bonds. The first one originates from oxygen (O2, O4) and carbon (C5, C7) s atomic orbitals and oxygen (O2) p_y-atomic orbital. The second one originates from s orbital of oxygen (O4, O6) and from s orbital of carboxyl group carbon (C9). The third MO with energy 14.32 eV and symmetry E' forms also two σ-bonds. One of them originates from oxygen s (O1, O2, O4) and p_y-orbitals (O1) from two carboxyl groups. The other originates from oxygen p_x (O3), p_y (O6) and s (O6) orbitals.

Region G contains MO with symmetries A', at the energy 15.78 eV and originates from carbon p_x (C5), p_y (C1, C3) and s (C2, C4, C6 of benzene and C7, C8, C9 of carboxyl groups) orbitals.

Region H contains one MO (16.59 eV) with symmetry E' and originates from oxygen's and carbon's p_x (O5), p_y (O3) and s (C2, C3, C5, C8) atomic orbitals.

Region I contains two MOs with the symmetry A' and E'. The first one of them, at energy of 18.3 eV, originates only from carbon s orbitals (C7-C9) of the carboxyl groups. The second

with symmetry E' and energy 18.43 eV originates mostly from carbon (C2, C4, C6-C9) s atomic orbitals but also has contribution from oxygen p_y (O3) atomic orbital.

Last region J located at 20.95 eV, contains only one MO which has E' symmetry and originates entirely from benzene ring carbon (C2, C3, C5 and C1, C4 and C6) s atomic orbitals.

Discussion

The correlation diagram for the MO energies of benzene, TMA and BA is shown in Figure 3. In all cases HOMO is related to p_z atomic orbitals of carbons in benzene ring. The addition of three carboxylic groups to the benzene ring increases the binding energy of TMA $\pi_{3,2}$ HOMO as compared to that of benzene and BA. Main reason is that the increase in the binding energy of TMA and BA is correlated with the multiple oxygen states that also contribute to the formation of the HOMO. In case of BA smaller shift has been observed [9] compared to TMA, where HOMO is formed from combination of π MOs of the benzene ring and oxygen atoms [10]. Similarly aldehyde group addition to benzene leads to increase of ionization potential of HOMO [9],[19].

In TMA excitation from atomic orbitals of oxygens in the carboxyl group is not distinguished, like in BA [9,10]. In BA experimental spectrum (Figure 2) the second photoelectron line is related to excitation from atomic orbital related to oxygens in carboxyl group. In comparison to BA, in simple carboxylic acids like formic acid (HCOOH) and acetic acid (CH₃COOH), two highest filled MOs arise from the p atomic orbitals on C, O and OH. Hartree-Fock calculations demonstrates that binding energy of electrons in the oxygen atomic orbital is HOMO [20],[21]. According to the DFT calculations, a related MO A´ in TMA (Figure ~~4~~ **3**) is convoluted into the first photoelectron peak (region A) observed at 10.04 eV.

Band B in measured photoelectron spectrum arises from oxygen p_z atomic orbitals of carbonyl and hydroxyl group. In comparison to the MO of BA (Figure ~~3~~ **2**e, Figure ~~4~~ **3**), which has similar origin, there is energetically a major binding energy difference, approximately 1 eV. Formation of 1 eV energy shift between BA and TMA MO is related to addition of three carboxyl groups to the benzene ring, however the reason remains unclear and needs further investigations.

In Figure ~~4~~ **3** MO at 11.9 eV originates only from benzene's ring carbon π orbitals (π_1). The binding energy of electrons from current orbital has higher binding energy than in benzene. Main reason is multiple oxygen states that also contribute to the formation of the MO. Same tendensy exists when aldehyde group is attached with benzene ring [19].

In TMA region E, the first MOs with symmetry E´´ and binding energy 13.57 eV has a strong π character. It originates from p_z atomic orbital of oxygen (O1-O6) and carbon (C7-C9) from carboxyl groups. We have assigned it to the carboxyl group π orbital (π_{COO}). Our assignment of the TMA MO at 13.57 eV is supported by observations in acetic acid, where MOs with 2a´´ and 12a´´ symmetry originates from carboxyl group. MO 2a´´ has π character [22].

In case of TMA all MOs which have ionization potential above 14 eV have σ character.

Conclusions

In the current study outer valence band electronic structure of benzene-1,3,5-tricarboxylic acid was interpreted. Furthermore, experimental and calculated TMA spectrum were compared to ones of benzene and BA. *Ab initio* DFT calculations are in good accordance with experimental binding energies. It is shown that similarities between MO energies and shapes of benzene and TMA exists. It is demonstrated that the addition of carboxyl groups to the benzene ring clearly correlates with increasing binding energy.

Acknowledgements

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Captions of the illustrations

Figure 1: TMA molecule in the ground state.

Figure 2: Experimental UPS spectrum of TMA (a) and calculated spectrum of TMA (d), BA (e) and benzene (f). Experimental spectrum of BA (b) [9] and benzene (c) [15] are reproduced with permission.

Figure ~~4~~ **3**. Binding energies of benzene (experimental) [15], BA [10] (calculated) and TMA (experimental and calculated).

Table

Table 1: Experimental and calculated binding energies and MO characters for TMA
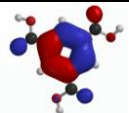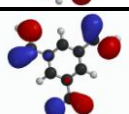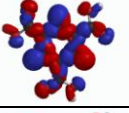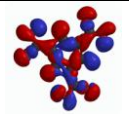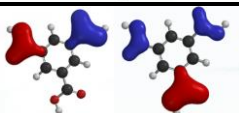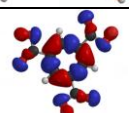
Experiment		Calculation			MO character
Photoelectron regions	Fitted bands (eV)	Calculated MO energy (eV)	Symmetry	MO shape	
A	10.0	9.72	E"		$\pi_{2,3}$
		9.89	E'		
		10.04	A'		
B	10.8	10.79	A"		π_{CO}
		10.87	E"		
C	12.0	11.88	E'		
		11.97	A"		π_1
D	12.7	12.59	E'		
		12.66	A'		
E	13.8	13.57	E"		π_{COO}
		13.69	A'		
		13.77	A"		π
F	14.2	14.12	A'		
		14.14	E'		
		14.32	E'		
		14.89	A'		
G	15.5	15.78	A'		
H	16.8	16.59	E'		
I	18.9	18.30	A'		
		18.43	E'		
J	20.6	20.95	E'		

Figure 1
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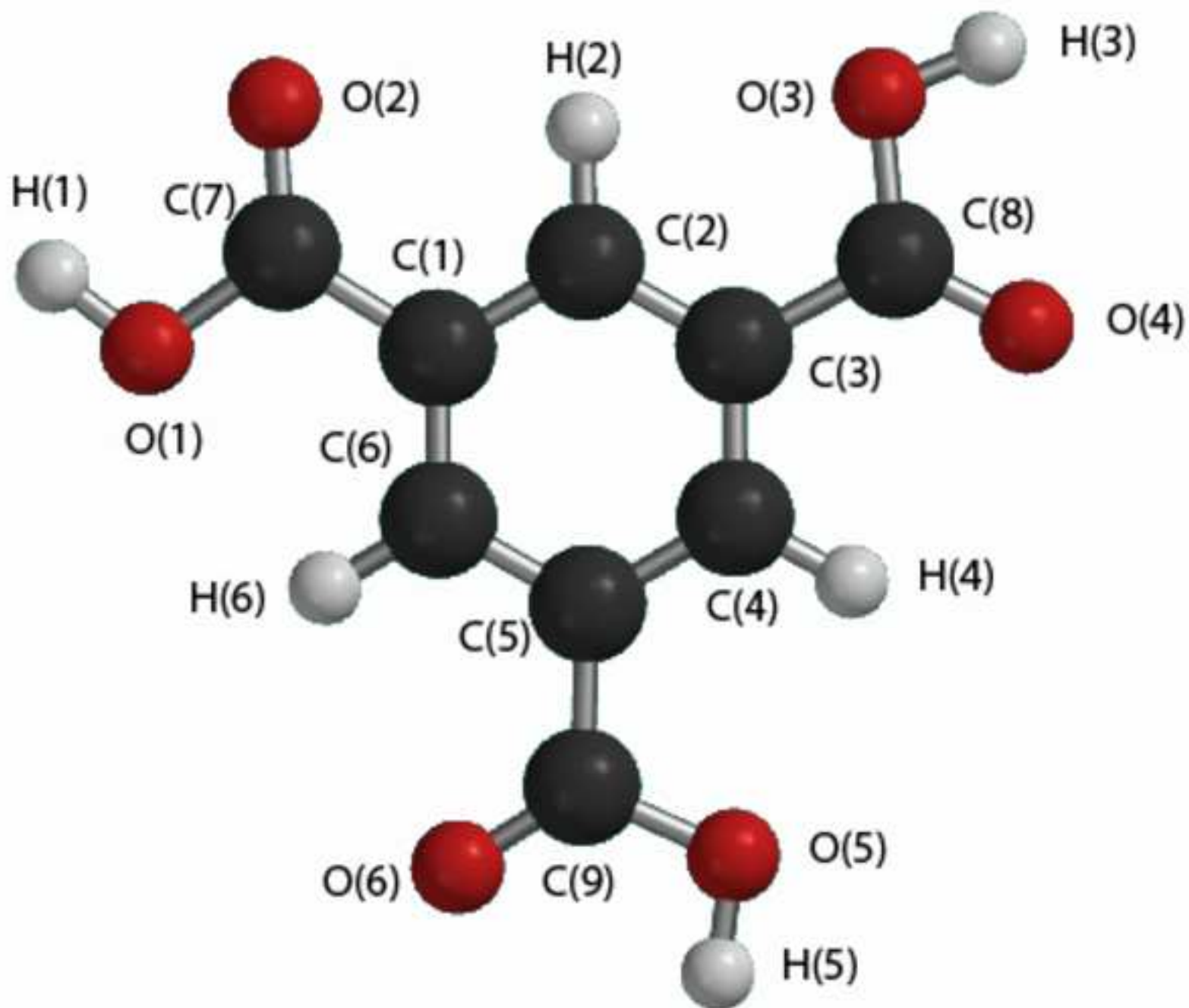
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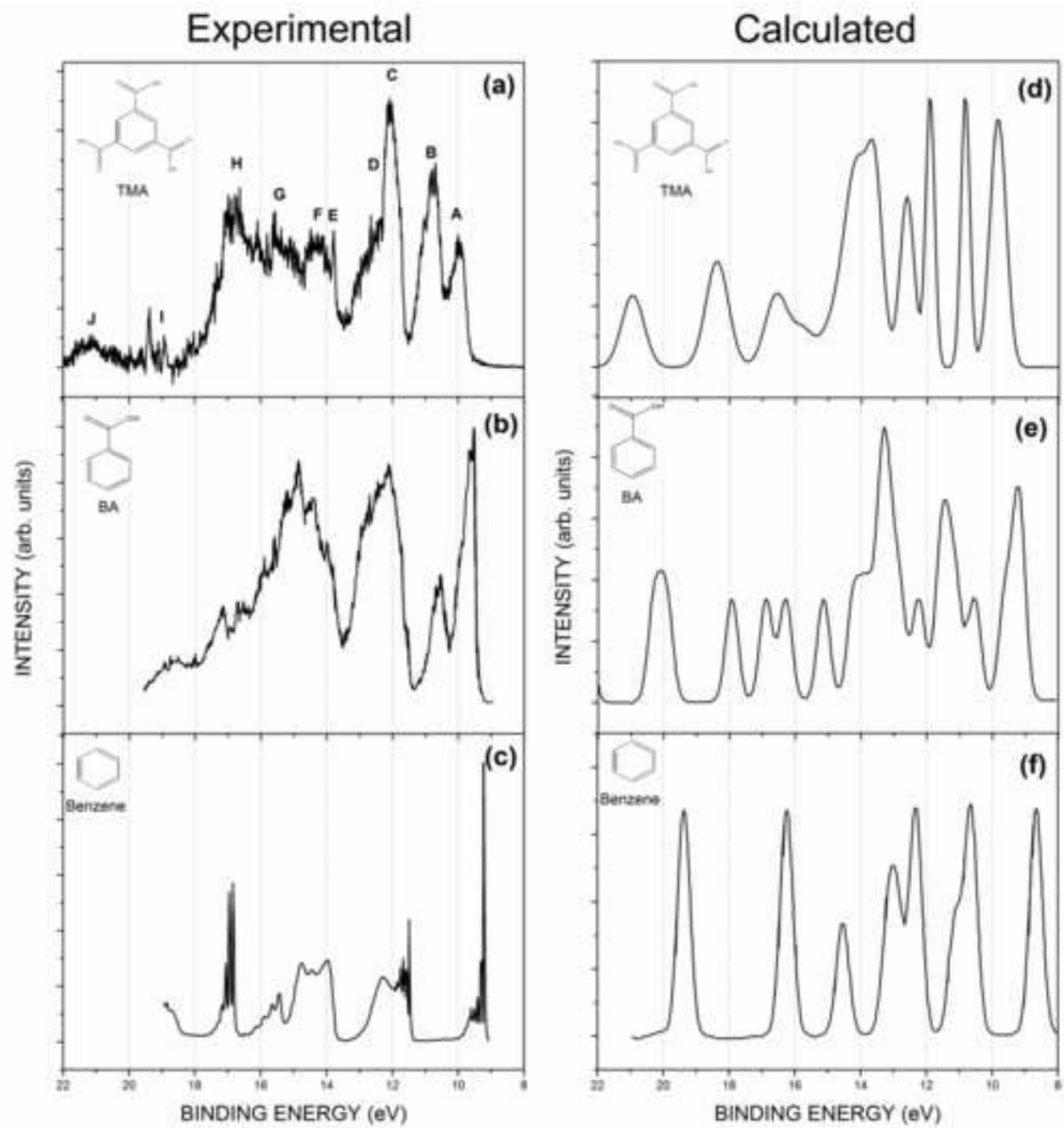
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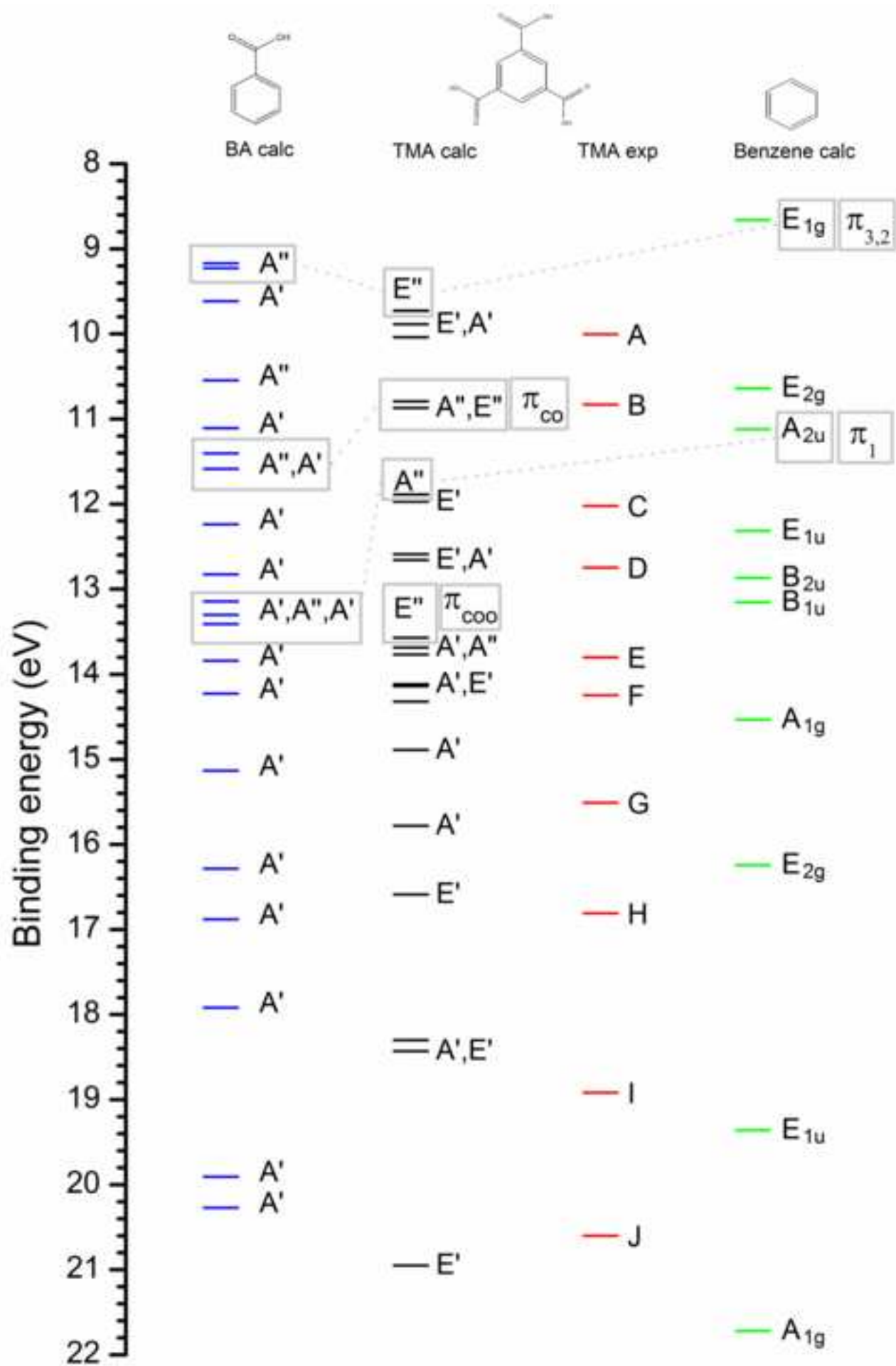
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