

## IV.F.2 Capacitive Hydrogen Storage Systems: Molecular Design of Structured Dielectrics

R.P. Currier (Primary Contact), D.J. Devlin,  
N. Henson, S.J. Obrey, J.-M. Sansinena, Q. Wei,  
Y. Zhao

Los Alamos National Laboratory  
P.O. Box 1663; Mail Stop J567  
Los Alamos, NM 87545  
Phone: (505) 665-3601; Fax: (505) 667-0440  
E-mail: currier@lanl.gov

DOE Technology Development Manager:  
Carole Read

Phone: (202) 586-3152; Fax: (202) 586-9811  
E-mail: Carole.Read@ee.doe.gov

Project Start Date: October 1, 2008  
Project End Date: September 30, 2011

### Objectives

To develop storage materials that enable high H<sub>2</sub> loading under more economical temperature and pressure ranges; that have controllable uptake/release dynamics; and that have moderate thermal management requirements. By using electric field enhanced adsorption, we hope to:

- Address thermal management issues (10-15 kJ/mole electric-field effect expected).
- Ultimately meet hydrogen loading goals at more practical combinations of temperature and pressure.
- Establish better control over charge/discharge dynamics via field modulation.

### Technical Barriers

This project addresses the following technical barriers from the Storage section (part 3.3) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (C) Efficiency
- (E) Charging/Discharging Rates
- (J) Thermal Management
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

### Technical Targets

This project is conducting fundamental studies on hydrogen adsorption in porous adsorbents under the influence of externally applied electric fields. Electric field enhancement provides a new route towards the meeting the 2015 system capacity targets of 5.5 percent hydrogen by weight and 40 grams hydrogen per liter and the ultimate system targets of 7.5 percent hydrogen by weight and 70 grams hydrogen per liter. Electric-field enhancement of binding (i.e. capacitive storage) integrates well with electric drive systems and the insights gained from these studies will be applied toward the design and synthesis of storage materials that will be more likely meet the DOE hydrogen storage targets. Outcomes of this work are expected to include:

- New insights into H<sub>2</sub> physisorption/chemisorption at sites of high local polarizability.
- Improvements in net efficiency of storage systems, i.e. acceptable hydrogen wt% at more accessible temperature and pressure.
- Better control over hydrogen charge/discharge dynamics (field strength is now a control variable in addition to thermal and pressure modulation).

### Accomplishments

During year 1, the project team has:

- Initiated a series of ab initio computations to explore the effects of external fields on electron density in organic constituents typical of metal organic frameworks (MOFs). Baseline electronic structure calculations have also been performed on Cu-BTC MOF, with an external electric field to be imposed in the subsequent round of calculations.
- Fabricated and tested several capacitor designs for use in measuring sorption under action of an electric field. Sorption measurements are underway.
- Developed technique for densifying adsorbent material that avoids structural damage.
- Began characterizing dielectric properties of porous adsorbent materials using electrochemical impedance spectroscopy. Static dielectric constant, loss tangent, and the breakdown potential are all being measured.
- Completed initial design of a neutron diffraction cell for simultaneous static electric field application. Will ultimately provide insight into specific binding site locations.

Measured isosteric heats of sorption in MOFs are typically on the order of 10 kJ/mol or less. Our calculated value for hydrogen binding at the copper site in Cu-BTC is 8 kJ/mol. Simple thermodynamic calculations suggest that heats of the order of 15-25 kJ/mol will be required for an efficient hydrogen storage material. Thus 100-300% enhancement of binding over zero field must ultimately be achieved. This enhancement in binding can occur at either, or both, metal sites of polarizable organic sites (e.g. the organic linkers found within the MOFs).



## Introduction

The concept of capacitive storage involves establishing an electric field across a porous dielectric material specifically designed to adsorb hydrogen. The field then acts on localized regions of high polarizability to enhance hydrogen binding within the cavities of the porous network through induction and dispersion forces. Upon discharge of the “capacitor,” the electric field is removed, and in turn, the induced electrostatic moment required to stabilize hydrogen dissipates. Thus the thermodynamic driving force for binding can in principle be switched on and off at will. As a consequence, the uptake/release dynamics are no longer solely dependent on thermal diffusion processes as much of the energy required to bind and release hydrogen is reversibly introduced into the system in the form of an electric field. Two critical operational issues associated with hydrogen storage are potentially addressed with capacitive storage – hydrogen density and thermal management. Electric field-mediated storage has the ability to enhance the density of stored hydrogen at accessible temperatures and pressures. By applying and releasing the molecular binding energy in the form of voltage (i.e. via the field), the requirements for thermal management of hydrogen uptake and release are lessened. Operating over the range  $-40$  to  $60^{\circ}\text{C}$  should become less onerous since the system is no longer critically dependent on externally supplied thermal flux. Charging and discharging, system cycling, and transient system response now involve field modulation as opposed to just direct heat exchange through the entire bed. The other outstanding issues detailed in the On-Board Hydrogen Storage System Technical Targets, such as delivery pressure, charging/discharging kinetics, and system fill time may also benefit.

The interaction between hydrogen and a porous dielectric host under action of an electric field arises from a number of terms. First, one can consider “static” terms, that are not a function of the field. These represent a baseline and include van der Waals interactions and permanent charge-quadrupole terms. Alone these appear to be insufficient to produce a good hydrogen storage material. Then there are terms that

are a function of electric field, but not of the dielectric substrate. These include the interaction between the field and the permanent  $\text{H}_2$  quadrupole. Finally, are the terms that are a function of field and the substrate. These are interactions that we can hopefully tune via structural modification. The simplest of the many possible terms here is the induced dipole-induced dipole term (e.g. an field-induced dipole within a MOF structural element and an induced dipole in the hydrogen). The magnitude of the induced dipoles is proportional to local field and the polarizability tensor. The interaction between the two dipoles, which falls off as  $r^{-3}$ , can then be calculated. By tuning the polarizable structural elements to have the highest polarizability in the direction of interaction with hydrogen, we can increase this term. Our manipulation strategy is based on the proportional relationship between polarizability and the volume of electron density (which depends in turn on the radius of the local structural moiety). The polarizability can then be related to the proximity of excited state and local chemical bonding (e.g. lowest unoccupied molecular orbital - highest occupied molecular orbital or band gaps). The molecular-level properties can then be mapped to bulk dielectric response using classical electrostatics (e.g. the Debye equation).

## Approach

It is known that manipulation of temperature and pressure provides benefits in hydrogen storage, however, it appears that combinations of these two intensive variables alone will not likely yield the desired end result, namely, high loading under moderate (and economically attractive) conditions. As an alternative, we are examining the effects of also introducing an electric field to enhance hydrogen uptake in porous dielectric substrates. This materials discovery effort is based on the idea that local regions of high electron polarizability will respond strongly to an applied external field. In doing so, the expectation is that the resulting redistribution of electron density will enhance hydrogen binding. This may involve a combination of lower binding energies, creation of new binding sites and/or formation of hydrogen clusters (as is reported in clathrate-hydrate cages [1]). The key challenge then is to localize polarizability within porous adsorbents in order to produce a high dielectric response adjacent to, or within, sub-structures (e.g. cavities) favorable to gas uptake through adsorption or molecular clustering.

Electrostatic stabilizing forces can be locally enhanced by judiciously increasing the polarization of the host substrate at specific sites. The MOFs will serve as one starting point for developing the new dielectric materials [2]. MOFs are composed of metal ions with coordinated organic ligands, where the nature of metal-to-organic ligand coordination provides

versatility in the design and control of chemical and physical characteristics (e.g. local polarizability). Thus in addition to being high surface area structures (up to 3,000 m<sup>2</sup>/g) MOFs can be chemically tailored by changing the organic links between metal centers. This can be done through introduction of more polarizable atoms and functional groups, tuning the band gap, and/or varying core metal electronic properties. Other related materials such as the zeolitic imidazolate frameworks (ZIFs) will also be considered as candidate adsorbents. Other candidate adsorbents include composites constructed by distributing small metal or semi-conducting clusters in porous structures (e.g. xero- or aero-gels) as another means of producing inorganic materials with extreme dielectric properties [3]. These metal-loaded gels consist of open pore structures that can be impregnated with small metal or semi-conducting clusters to just below the percolation threshold (at the percolation threshold, an electrical short would then develop). The resulting cluster-loaded gels should be insulator-conductor composites capable of large space charge polarization and thus high dielectric response, since they possess ample free electrons within the clusters to readily react to an imposed electric field. Our approach to developing these materials (structured dielectrics) combines both computational guidance and experimental probes.

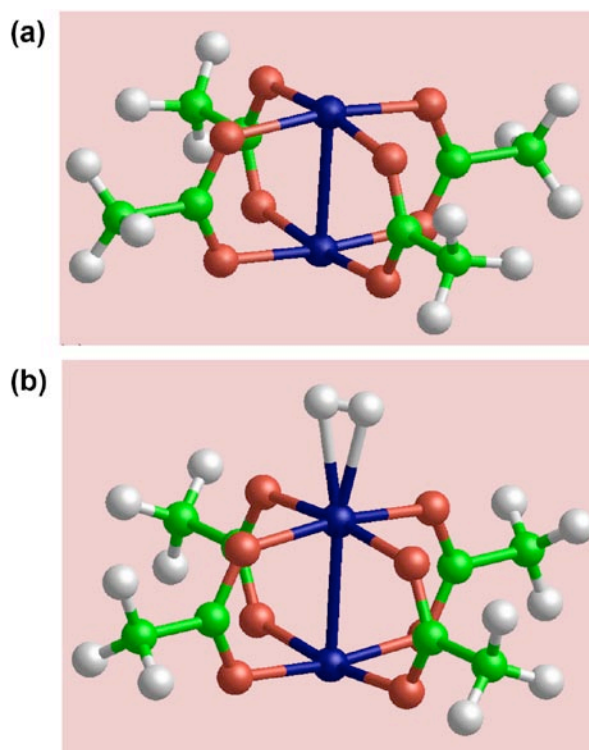
## Results

Static polarization calculations were the first of the computational exercises used as guidance. Several simple substituted benzene molecules (often found in MOF organic linkages) were examined to assess which functionalities are the most promising with regards their charge polarization properties under an applied electric field. These calculations were performed using the Gaussian03 software. Preliminary results suggested that there was little dependence of the calculated dipole polarizability on whether electron withdrawing or electron donating substituents are present. Rather, trends indicated that the stronger effect is that of how many substituents are present (i.e. the total number of electrons in the system) and hence the volume of electron density that is available to respond (be polarized) under action of the field. Reductions in the hydrogen binding energy were indicated, provided the electron density and field strength were both high.

Building on this initial work with simple molecular models of substituted benzenes interacting with a hydrogen molecule in an electric field, we expanded the computational study to now consider molecular fragments of MOF structures. Previously, we have performed calculations on the binding site geometry and thermodynamics of hydrogen in the Cu-BTC MOF structure. The crystal structure of Cu(II) acetate provides a useful starting point for the construction

of a molecular model containing a structural unit from the Cu-BTC structure (Figure 1a). Cu-BTC has several predicted binding sites for the hydrogen molecule in the absence of an electric field, including at the open-coordination Cu(II) site and in the vicinity of the organic spacer. Our initial calculations place the hydrogen molecule at the metal site in a side-on geometry as shown in Figure 1b. Calculations are now being performed using the MP2 perturbation method (MP2/6-31G for ligands and LANL2DZ for the Cu) within the Gaussian03 software, since our initial calculations showed the importance of including electron correlation in the calculation to account for weak dispersion interactions. We are also considering both the singlet and triplet spin states for the Cu(II)-Cu(II) unit. Full geometry optimization of all the models is being performed with basis set superposition error to calculate the binding sites and binding energies. Once these calculations are completed, an electric field will be applied along the Cu-Cu vector to assess the enhancement of the binding energy.

Dielectric material synthesis efforts were initiated. A laboratory was configured for the preparation of analytical test samples (initially these will include inorganic zeolites, MOFs, ZIFs, and porous carbonaceous materials) for baseline testing activities.



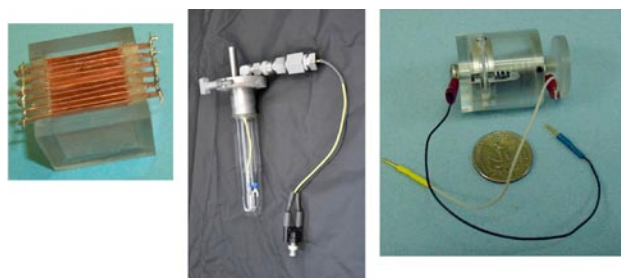
**FIGURE 1.** Models used in initial Cu-BTC calculations. (a) Simplified molecular model for structural building unit in Cu-BTC. (b) Calculated binding site for H<sub>2</sub> at Cu(II) center.

The laboratory enables us to synthesize of new ligands with the aim of altering framework polarizability. To date, 12 different materials from four material classifications have been prepared and are ready for electrochemical and storage testing. A small metal-insulator-metal capacitor bank was also constructed as the first-generation capacitor test rig. A series of thin copper sheets were used as the capacitor plates, as shown in Figure 2. Once loaded (e.g. with a MOF), the capacitor bank can be inserted into a pressure vessel that provides a small headspace and fitted with temperature probes, high accuracy pressure gauges. The stainless steel pressure containment vessel is also equipped with high voltage electrical leads. Several other test capacitors were also designed and fabricated (see Figure 2).

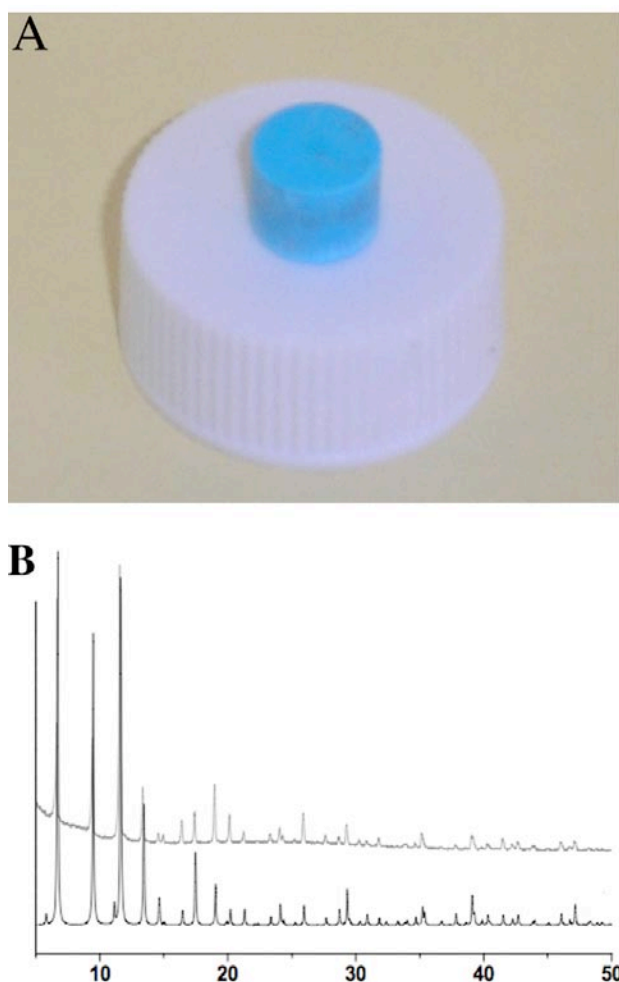
Early experiments involving the metal-insulator-metal capacitor made use of as-synthesized MOF powders. Packing and granular flow problems during loading of the capacitors led to a lack of reproducibility in tests using powders. Thus, formation of higher density, and reproducibility, was pursued. However, a natural question was the following. Are these candidate materials, which involve rather wispy frameworks, mechanically robust enough to withstand pelletizing as part of a testing protocol? Initial tests suggest that MOF structures do maintain their crystalline nature following pressing into pellets, as shown in Figure 3. Dielectric materials testing is now performed using pressed materials that provide higher density and avoid the granular packing issues.

Gas adsorption experiments are underway using these capacitor test rigs. The effect due to the electrostatic moment in the gas is also being explored by examining adsorption of nitrogen and carbon dioxide, which have significantly different electrostatic moments than hydrogen (e.g. the relative quadrupole moments are:  $\text{CO}_2$  - 4.3 electrostatic unit of charge, esu;  $\text{H}_2$  - 0.662 esu [4]). Based on the initial screening results, the chemical composition, packing density and physical properties (pore size/volume) of the adsorbent appear to be important, as expected, along with the dielectric response of both the substrate and gaseous species. One potentially important issue we hope to resolve is the relative importance of the crystallographic orientation of the solid adsorbent. One would expect that if the adsorbent has an ample supply of mobile electrons capable of responding to the imposed field, that crystallographic orientation would not govern the net response. Additional work is needed to establish this. Also, by year's end, we expect to have an initial quantitative assessment of the electric field enhancement on hydrogen adsorption in selected MOFs.

In order to characterize the dielectric properties of the adsorbents and ultimately correlate with adsorptive capacity under an applied voltage, dielectric properties are being measured over a wide frequency bandwidth



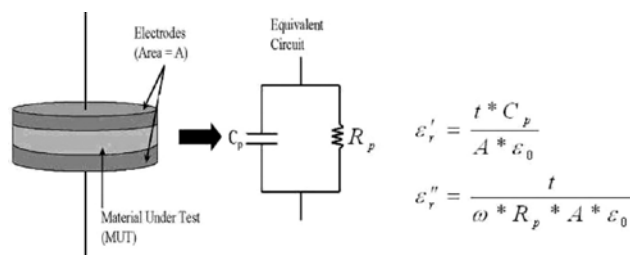
**FIGURE 2.** Capacitor cells for testing electric field enhanced adsorption. A metal-insulator-metal capacitor (left); glass cell with internal parallel plate capacitor designed to fit Brunauer-Emmett-Teller apparatus (middle); a custom designed spring-loaded cell to hold pressed pellets during adsorption and dielectric measurements (right).



**FIGURE 3.** A pressed (densified) copper-based MOF (blue pellet; 1/4" diameter). (A) Optical photograph of a pellet of HKUST-1 MOF compressed at 1,000 psi. Three-dimensional tomography of the pellet also showed good uniformity. However, some small bright spots seen in the pellet via tomography may represent free copper and copper oxide particles (which may ultimately provide a conduit for dielectric break-down). Image (B) shows intensity (arbitrary units) versus diffraction angle theta for a powder X-ray diffraction of HKUST-1 pressed MOF (upper diffraction pattern). This is compared to unpressed powder (lower diffraction pattern) showing crystallinity is largely maintained through processing/pressing. It was found that with enough applied force the crystallinity could ultimately be destroyed.

(1Hz - 10<sup>4</sup>Hz). A parallel plate capacitor structure is being used for these measurements. The electric response of the capacitor is analyzed by electrochemical impedance spectroscopy (EIS) using an equivalent circuit model which includes a parallel capacitor-resistor configuration. The directly-measured capacitance ( $C_p$ ) is used to calculate the real part of the dielectric constant ( $\epsilon_r'$ ). Moreover, the measured resistance of the resistor portion of the circuit ( $R_p$ ), is directly related to the current leakage in the capacitor and is thus used to calculate the imaginary part of the dielectric constant ( $\epsilon_r''$ ). The basic relationship between the variables is highlighted in Figure 4. The real and imaginary parts of the dielectric constant define the loss tangent ( $\tan \delta = \epsilon_r''/\epsilon_r'$ ), which is a dielectric parameter that quantifies its inherent dissipation of electromagnetic energy. It will ultimately enable us to estimate the “losses” over a charge/discharge cycle. Different experimental configurations and procedures have been designed and tested in order to perform accurate measurements of dielectric properties. The first approach was based on a capacitor configuration that included two parallel copper blocks separated by a compartment that was then filled with a sample of powder. Measurement reproducibility issues were initially encountered due to problems controlling powder packing and uniformity (granular flow/packing problems). Now, specified weights of powder are pelletized under controlled pressure. Then, a capacitor is formed by placing the material pellet between two metal plates connected to a potentiostat/galvanostat capable of performing the required EIS measurements accurately. Dielectric constants and loss tangents have been measured for several MOFs and MOFs impregnated with polarizable constituents such as ferrocene.

We are also currently designing an electric charge/discharge device (capacitor) capable of being inserted into a high-pressure gas loading system. The device is intended for ultimate use in in situ neutron diffraction experiments to determine precisely how MOF crystals (and related structures) respond as the electric field varies. Such probes will also ultimately allow us to monitor hydrogen adsorption at specific internal sites. Hydrogen bonding sites will be refined from the neutron



**FIGURE 4.** Schematic of test cell assembly for determining dielectric properties, the equivalent circuit and relationship between key variables.

diffraction data and used to improve the next iteration in materials design.

## Conclusions and Future Directions

As this Fiscal Year 2009 new start project completes the first year, the following statements can be made:

- Capacitive storage under electric fields offers a practical means of enhancing hydrogen storage (that can be used in conjunction with manipulation of temperature and storage). The energy used to establish the field can largely be recovered upon discharge (less the dielectric losses, which we will quantify).
- The approach is expected to result in more economical combinations of temperature and pressure in hydrogen storage systems. Higher efficiencies and better control over the charge/discharge dynamics are expected (via proper modulation of the field).

Work in progress includes:

- Completing quantitative demonstration of enhanced hydrogen loading in the presence of an electric field.
- Assess H<sub>2</sub>/substrate compatibility under dielectric breakdown.
- Identifying of best porous frameworks to employ as adsorbent substrates - e.g. MOFs; ZIFs; semiconductor composites.

While this is a materials discover project, we expect to compare measured loadings with On-Board Hydrogen Storage System Technical Targets storage targets as data is obtained, with continuous down-selection of materials for subsequent performance testing in integrated storage systems. This is an ambitious materials design endeavor and it is recognized that there will be practical limits on the applied voltages, e.g. a break-down potential across the dielectric will always be lurking. However, success will define a new, and needed, direction in the stabilization of molecular hydrogen.

## Special Recognitions & Awards/Patents Issued

1. A Provisional US Patent Application was prepared and submitted in 2009: “Apparatus and Method for Gas Storage and Separation” Agent Docket Number: S-112,957. R.P. Currier, S.J. Obrey, J.-M. Sansiñena, and D.J. Devlin.

## FY 2009 Publications/Presentations

1. “Capacitive Storage of Gases in Porous Dielectric Materials” R.P. Currier, D.J. Devlin, N. Henson, S.J. Obrey, B.M. Patterson, J.-M. Sansiñena (presenter), Q. Wei, Y. Zhao. Presented at the 11<sup>th</sup> Annual *ELECTRIC POWER Conference & Exhibition*, Chicago, IL May (2009).

2. “Capacitive Hydrogen Storage Systems: Molecular Design of Structured Dielectrics” poster presentation. R.P. Currier, D.J. Devlin, N. Henson, S.J. Obrey, B.M. Patterson, J.-M. Sansinena, Q. Wei, Y. Zhao. Presented at the DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting, Washington, May (2009).
3. “Metal-Organic Aerogels: A New Class of Aerogels Composed of Metal Clusters and Organic Ligands” Q. Wei, H. Kim, D. Yang, K.A. Obrey, G. Zou, P. Chupas, Z. Lin, R. Zou, Y. Wang, S.J. Obrey, R.P. Currier, T.E. Proffen, H. Xu and Y. Zhao. Submitted to *Science* (2009).
4. “Kinetic Hysteresis Adsorption Behavior in MOFs with Zig-Zag Channels” Q. Wei, S.J. Obrey, R.P. Currier, H. Xu and Y. Zhao. In Preparation (2009).

## References

1. Lokshin, K.A. et al., “Structure and Dynamics of Hydrogen Molecules in the Novel Clathrate Hydrate by High Pressure Neutron Diffraction” *Phys. Rev. Lett* 93(12): 125503 (2004).
2. “Hydrogen Sorption in Functionalized Metal-Organic Frameworks” J.L.C. Rowsell, et al. *J. Am. Chem. Soc.* 126: 5666-5667 (2004).
3. (a) Valant, M., Dakskobler, A.; Ambrozic, M.; Kosmac, T. “Giant permittivity phenomena in layered BaTiO<sub>3</sub>-Ni composites” *J. Euro. Ceramic Soc.* 26: 891 (2006); (b) Abdurakhmanov, U.; Sharipov, S.; Rakhimova, Y.; Karabaeva M.; and Baydjanov, M. “Conductivity and Permittivity of Nickel-Nanoparticle-Containing Ceramic Materials in the Vicinity of Percolation Threshold” *J. Am. Ceramic Soc.* 89(9): 2946 (2006).
4. Hanna, M. W. “Bonding in donor-acceptor complexes. I. Electrostatic contributions to the ground-state properties of benzene-halogen complexes” *J. Am. Chem. Soc.* 90:285 (1968).