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***Gas-Phase Molecular Dynamics: Theoretical Studies  
in Spectroscopy and Chemical Dynamics***

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## GAS-PHASE MOLECULAR DYNAMICS: THEORETICAL STUDIES IN SPECTROSCOPY AND CHEMICAL DYNAMICS

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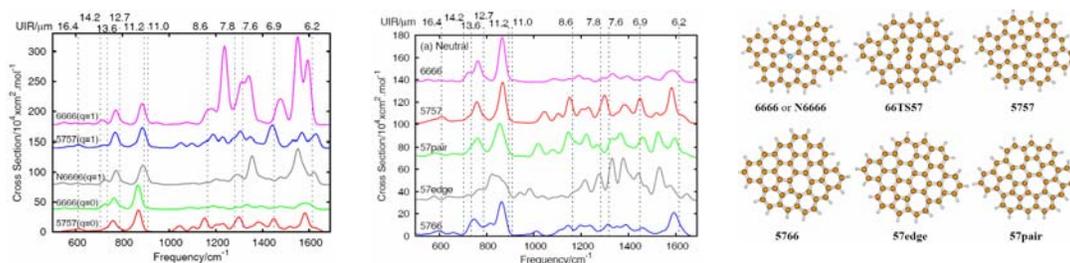
### Program Scope

The main goal of this program is the development and application of computational methods for studying chemical reaction dynamics and molecular spectroscopy in the gas phase. We are interested in developing rigorous quantum dynamics algorithms for small polyatomic systems and in implementing approximate approaches for complex ones. Particular focus is on the dynamics and kinetics of chemical reactions and on the rovibrational spectra of species involved in combustion processes. This research also explores the potential energy surfaces of these systems of interest using state-of-the-art quantum chemistry methods, and extends them to understand some important properties of materials in condensed phases and interstellar medium as well as in combustion environments.

### Recent Progress

#### Infrared and UV-visible spectra of Stone-Wales defected PAHs

We (with Nyman at Göteborg, Sweden) have investigated the infrared (IR) spectra of polycyclic aromatic hydrocarbons (PAHs, also called soot species) containing (5, 7)-member ring defects based on a  $C_{48}H_{18}$  model. Calculations are performed using the hybrid B3LYP density functional theory. The results show that the Stone-Wales defect in PAHs can yield a strong IR band at  $1448\text{ cm}^{-1}$  and a weak band at  $611\text{ cm}^{-1}$ , which may contribute to the UIR (unidentified infrared) bands at  $6.9\text{ }\mu\text{m}$  and  $16.4\text{ }\mu\text{m}$  observed in the interstellar medium, for instance, see Fig. 1. The charge effect on the IR spectra is discussed. The stability of the ring defected PAHs is also addressed by exploring the minimum energy pathway on the potential energy surface and through their UV-visible spectra, which are computed using a TDDFT method.



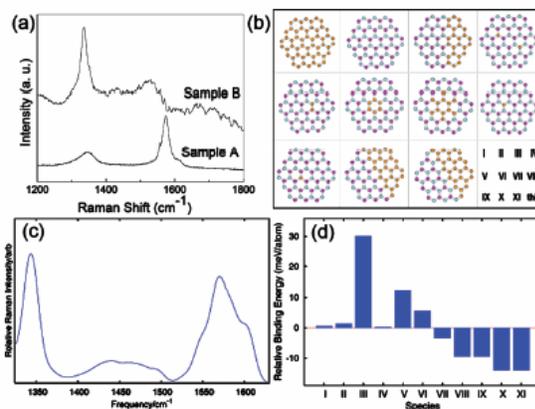
**Figure 1.** Theoretical IR spectra of some PAHs, and Stone-Wales defected PAHs, their cations, and one N-substituted PANH<sup>+</sup>. Some bands in  $\mu\text{m}$  are indicated by dashed lines.

Detailed investigations show that a peak near  $6.9\text{ }\mu\text{m}$  may be produced by SW defected PAHs that have both a 5-member ring close to a boundary carbon atom and (6,5,5,6)-member rings in a row with duo hydrogens at the edges. But those large PAHs with a deeply embedded SW defect can not produce a strong band at  $6.9\text{ }\mu\text{m}$ . In addition, the

SW-defected charged PAHs are less likely to contribute to the 6.9  $\mu\text{m}$  UIR band than 5757.

### Raman spectra and structures of boron nitride-carbon sheets

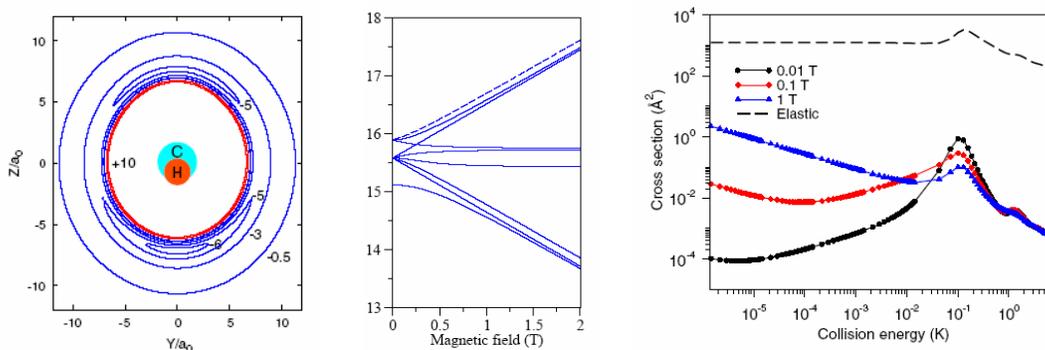
Boron nitride sheet is isoelectronic to graphene sheet but they have dramatically different electronic properties. The mixed BN-C sheets might have band gap engineered applications in electronics and optics. In this work, we (with Han at CFN, BNL) did a combined experimental and theoretical study to understand the structures of carbon units in BN sheets. The theoretical calculations were done using the B3LYP DFT method, based on a circumcoronene-like model. The Raman spectra, structures, and their relative stability are displayed in Fig.2. Results clearly demonstrated that the most stable BN-C sheet is **III** with an armchair linked C-B/N structure. In other words, the armchair linked structure is energetically preferable so that there is relatively large fraction in BN-C sheets, or higher Raman intensities as shown in Fig.2 (a) and (c). Furthermore, Fig. 2(d) shows that the occurrence of embedded C<sub>2</sub> and benzene C<sub>6</sub> units is likely. This finding does support the experimental observations by Krivanek et al. (O.L. Krivanek et al. *Nature* (London) 464 (2010) 571) and Ci et al. (L. Ci et al. *Nature Mater.* 9 (2010) 430). Indeed, the finding of the armchair connection of graphene fragments to BN can be understood by the fact that graphene sheets with armchair edges are metallic. In addition, the weaker C-B and C-N bond strengths relative to C-C are consistent with the redshift of the Raman peak around 1580  $\text{cm}^{-1}$ .



**Figure 2.** (a) Experimental Raman spectra of BN-C sheets; (b) the C (brown), B (purple), and N (blue) skeletons of circumcoronene-like sheets studied in this work, their labeling map is given in the right-bottom panel; (c) simulated Raman spectrum of the armchair-connected BN-C species (**III**); (d) calculated relative stability of the BN-C sheets among the group in (b).

### Quantum dynamics calculations of cold collisions of methylene radicals with S-state atoms in a magnetic field

A rigorous quantum dynamics study has been performed for the low-temperature collisions of polyatomic molecular radicals with  $^1\text{S}_0$  atoms in the presence of an external magnetic field using the CCSD(T) *ab initio* and scaled potential energy surfaces. Results are shown in Fig.3. The He-CH<sub>2</sub>(X<sup>3</sup>B<sub>1</sub>) interaction potential is weakly isotropic. Quantum scattering calculations show that collision-induced spin relaxation of the prototypical methylene molecule CH<sub>2</sub>(X<sup>3</sup>B<sub>1</sub>) and nine other triatomic radicals in cold  $^3\text{He}$  gas occurs at a slow rate, demonstrating that cryogenic buffer-gas cooling and magnetic trapping of those molecules is feasible with current technology. The calculations also suggest that it may be possible to create ultracold gases of polyatomic molecules by sympathetic cooling with alkaline-earth atoms in a magnetic trap. This work was done in collaboration with Tscherbul and Dalgarno at Harvard.



**Figure 3.** (a) A contour plot of the CCSD(T) potential energy surface for the He-CH<sub>2</sub>(X) interactions; (b) The lowest Zeeman energy levels in cm<sup>-1</sup> of *p*-CH<sub>2</sub>; (c) Cross sections for elastic scattering (dashed line) and spin relaxation in He + CH<sub>2</sub> collisions plotted vs collision energy for different magnetic field strengths.

## Future Plans

### Kinetics and dynamics study of combustion-related reactions

We will continue to study some important combustion reactions using the direct *ab initio* molecular dynamics program. An interesting direction will focus on the kinetics and dynamics of cyclic, N- and O-containing fuel molecules. The concentration of cyclic compounds in diesels and other future transportation fuels, produced largely from non-traditional sources such as oil shales and sand oils, are much higher than those in current fuels. There are only limited kinetics data on cyclic fuel molecules, yet they are required to design future internal combustion engines using such fuels. A new unique step in the chemistry is the ring-opening processes resulting in, for example cyclopentoxy (cyc-C<sub>5</sub>H<sub>9</sub>O) radicals discussed by us before. Such radicals may well contribute to enhanced formation of soot without a ring-opening reaction. In this work, we will start this project with the reactions of morpholine (1-oxa-4-aza-cyclohexane, i.e. cyclic -OCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>-) and its derivatives with small radicals such as O<sub>2</sub>, HO<sub>2</sub> and OH. Westmoreland et al. have recently demonstrated that morpholine is an ideal compound for modeling those hydrocarbon, oxygenated and N-containing fuels.

Recently, we have investigated the energies, geometries, and vibrational frequencies of the stationary points on the ground-state surfaces of the morpholinyl radicals with oxygen molecule using DFT and CCSD(T) methods. The ring-opening mechanism of morpholinyl radicals was fully explored. In near future, their dynamics will be carried out using the DualOrthGT program, together with variational RRKM theory.

### Vibronic spectrum calculations of CH<sub>2</sub> and its interactions with He

In our GPMD group, Sears and Hall have observed rich and complicated rovibronic levels of CH<sub>2</sub> near the C + H<sub>2</sub> and CH + H dissociation limits. They provide a challenge for multiple surface dynamics theory, with relevance to the reactive system as well as CH<sub>2</sub> spectroscopy. We have calculated five low-lying electronic potential energy surfaces of CH<sub>2</sub> using a multireference CI (MRCI) method. The adiabatic surfaces will be transformed into a set of diabatic ones using the quasi-adiabatic approximation of Koppel et al. Full-dimensional quantum dynamics will then be performed on the five

coupled surfaces. The principal interest is in the energy levels and non-adiabatic coupling effects, for detailed comparison with experimental observations. In addition, we have calculated the singlet and triplet potential energy surfaces of the He-CH<sub>2</sub> (X/A) interaction system using the CCSD(T)/aug-cc-pVQZ level of theory. The surfaces will be used for investigating the dynamics of singlet and triplet states of CH<sub>2</sub> in collaboration with Tscherbul at Toronto/Harvard

### **Non-adiabatic molecular dynamics studies of polyatomic molecular reactions**

Electronically excited species such as <sup>1</sup>CH<sub>2</sub> also play an important role in combustion chemistry. However, the studies of their reactivity are rather limited, partially due to the non-adiabatic dynamics effects because those reactions often occur on multiple potential energy surfaces. In this research, we will extend the surface hopping direct *ab initio* molecular dynamics algorithm, developed for the SECH MD studies, to simulate the bimolecular reactions and the photo-dissociation chemistry. The first application would be the photodissociation dynamics of acetone at 193-230 nm. This system has been investigated by Suits et al. using a universal ion imaging technique. The photon excited acetones produce two major types of products: CH<sub>3</sub>CO + CH<sub>3</sub> and CO + 2CH<sub>3</sub>. The latter products result from poorly understood dissociation mechanisms. Here we will attempt to explore the dissociation pathways of acetone on its three low-lying electronic states.

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