Nanoparticle arrays and their applications in molecular detection

Abstract

A pattern of nanoparticles is proposed which offers the potential for developing new types of single molecule detectors. A multiple multipole method under development to obtain converged electrodynamics results is also introduced. Using these calculations, we have investigated the optical properties of nanoparticle arrays. Remarkably narrow (~meV or less) plasmon resonance spectra and exceptionally large electromagnetic field enhancements ($|\mathbf{E}|^2 > 10^7$) at specific locations are predicted in a one dimensional nanoparticle array. We propose that the performance of particle arrays will be improved dramatically if they are put into well defined subwavelength holes or slits where the local electric and magnetic fields are enhanced.

1. Background

Nanoparticles, especially nanoscale noble metal particles, have attracted extensive attention recently due to their applications in optical filters,[1] plasmonic waveguides[2], bio/chemosensors,[3-6] and substrates for surface-enhanced spectroscopies.[7-9] Recent advances in experimental techniques allow for the fabrication of nanoparticle arrays in different shapes, patterns, and distances,[10,11] but what is missing with these capabilities is an understanding of what are the optimal array structures for a given application. In an attempt to shed light on these problems we have been studying the optical properties of nanoparticle arrays by solving Maxwell's equations to determine extinction spectra and other properties. The theoretical solution of Maxwell's equation was presented 100 years ago by Mie and others[12-14] for isolated spherical particles of arbitrary size. Mie theory is still extremely useful, however, many of the nanoparticle structures being produced now require more sophisticated descriptions, including the ability to describe particles of arbitrary shape, and arrays of arbitrary arrangement.

To address these new challenges, researchers have developed several numerical methods to describe nanoparticle optical properties including the T-matrix method,[15,16] coupled dipole approximation (CD),[11,17] discrete dipole approximation (DDA),[18-20] multiple multipole methods(MMP),[21,22] and the finite difference time domain (FDTD) method.[23,24] Both T-matrix and CD methods can be used for arrays of particles with arbitrary positions. The T-matrix theory is an exact method which includes multipolar expansions around each particle. The most important limitation of the T-matrix method is that it is restricted to spherical particle arrays and is very time and memory consuming. As a result, it can only be used to describe the properties of hundreds of particles. The CD method considers dipole excitation only and thus is relatively efficient to use but often less accurate. It can be used to do calculations for thousands of particles and to describe arrays of particles of any shape provided that the particle polarizability tensor is known.

For nanoparticles of arbitrary shape, the DDA method is one of the most efficient numerical methods. It expresses the target particles as an array of point dipoles, with the fields of these dipoles determined self consistently. Each particle can be divided into a large number of polarizable cubes (point dipoles), and the electromagnetic scattering problem is solved essentially exactly as long as the cubes are small enough and subject to a model for the cube polarizability (lattice dispersion relation).

One reason for interest in the optical properties of gold and silver nanoparticles is because of their use in biosensors.[3,4] Here it is possible to take advantage of recent advances in the technology for fabricating nanoparticles with easily tuned optical properties that can be optimized for sensor applications. For example, in nanosphere lithography one creates homogeneous surface-confined nanotriangles of arbitrary width and height which enables one to tune the plasmon resonance wavelength anywhere in the visible and infrared.[10,25] Alternatively, electron beam lithography has been used to fabricate cylindrical and trigonal prism nanoparticles with similar optical tunability as shown in figure 1.[11] For applications to biosensors these particles need to have a sharp plasmon peak at a convenient wavelength. Several groups[11,26,27] have made progresses experimentally but the optimized structures have not been found yet. It is useful to use theory to determine plasmon wavelength as a function of particle shape, size, and interparticle distance to determine which particles to make.[17,28,29] To do this we have extended the DDA method using periodic boundary conditions, successfully simulating several recent experimental results.[29]

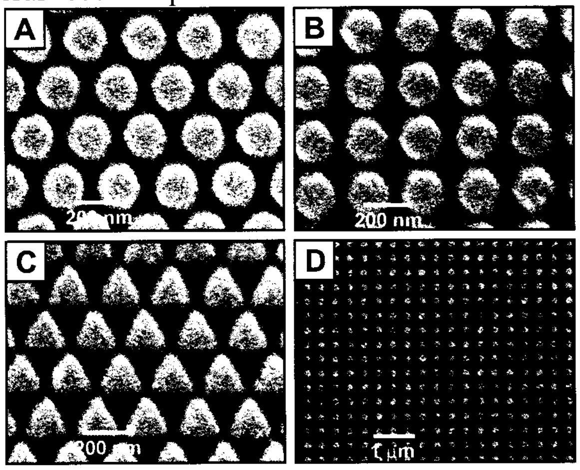


Fig 1. Scanning electron micrographs of representative nanoparticle arrays.

In addition, we found a silver array structure that produces extremely narrow peaks, less than one nm in width.[30] We also described special silver nanoparticle array structures that lead to exceptionally large electromagnetic field enhancements ($|\mathbf{E}|^2 > 10^7$) at specific locations in the structure, thus providing a purely electromagnetic mechanism for producing single molecule surface enhanced Raman scattering (SMSERS) enhancements $>10^{13}$ that are as large or larger than has been found in experiments.[9]

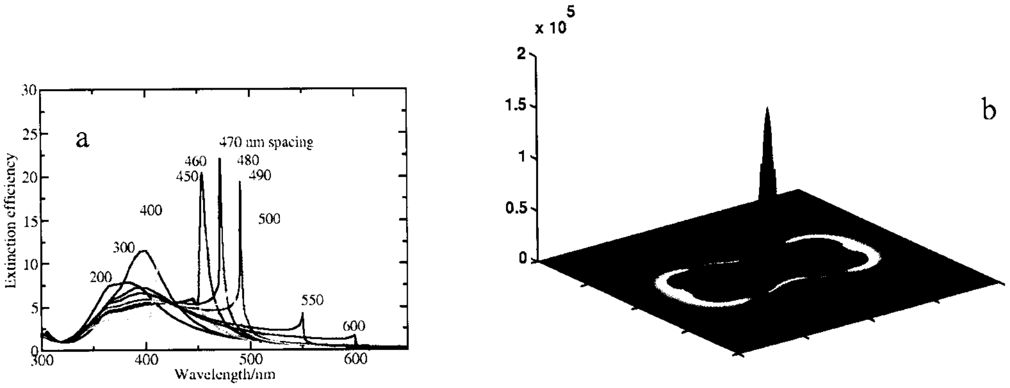


Fig. 2 (a) Extinction spectra of nanoparticle arrays, (b) Enhanced electric field near the particle dimer.

Another issue for sensing is the influence of adsorbate molecules on the plasmon resonance wavelengths. Here we have found that both long range and short range distance effects can be important for the surface plasmon resonances of these nanoparticles, and that by understanding these effects we can determine which kinds of particles are suitable for the detection of small biomolecules and which kinds are better for the big ones. By changing the DDA code, we have learned how to deal with particles of arbitrary shape covered by multilayers of analyte, including the calculation of extinction, adsorption, scattering cross sections, and near and far electric field properties. Figure 3 shows the electric field around the particle surface and field change at different locations on the particle surface as function of adsorbate layer thickness. Perfect agreement between the experimental data and calculation results is obtained.

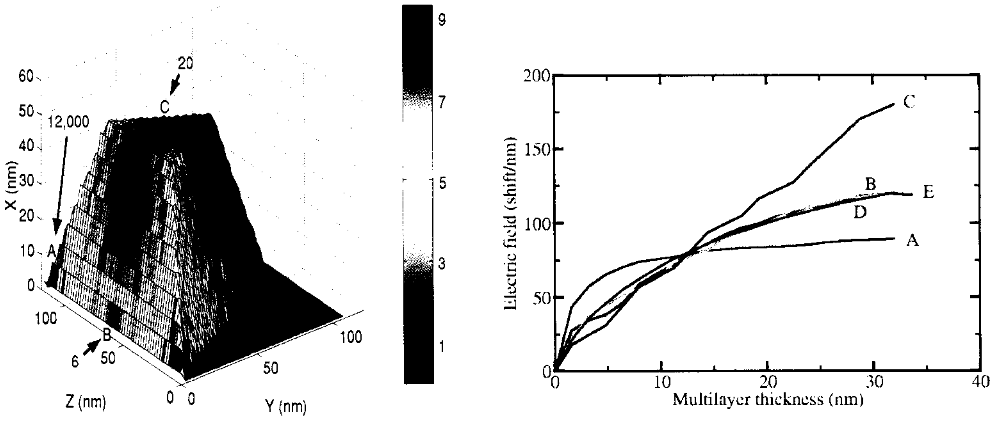


Fig. 3 (a) Plots of the logarithm of the square of the electric field averaged over distance between 0 to 2.0 nm from the surface (b) Integrated electric field change as function of layer thickness of adsorbate. (A, B, and C) the electric field at the points A, B, and C of the nanoparticle; (D) the averaged electric field; (E) the experimental LSPR shift.

2. Future work

Not only for particles, surface plasmon modes are also observed on highly conducting surfaces perforated by holes. [31-33] We are proposing to use the surface plasmon modes generated by these holes to excite the plasmon resonances of nanoparticles synthesized inside the holes. Since the electric and magnetic fields inside each hole are enhanced, the final electric and magnetic fields caused by the nanoparticles can be augmented another 10 or 100 times, so the sensitivity of SMSERS will be increased as a consequence. A schematic representation of the proposed structure is presented in Fig. 4. Odom' group [34] have been successful in growing the individual nanocrystals in each wells of an array of hemispherical nanowells. This indicates that our proposal is experimentally relevant. We are planning to study the excitation mode of the aperture array and its variation with different size, spacing and arrangement. This part can be finished approximately by using the DDA code with periodic boundary conditions. After the first step, monomers or dimers of particles will be introduced into the system and the final optimized structure will be determined. The ultimate goal of the project will be to add target molecules into the system to detect a change in extinction spectra or enhanced Raman scattering spectra for target molecules that are adsorbed on the particle.

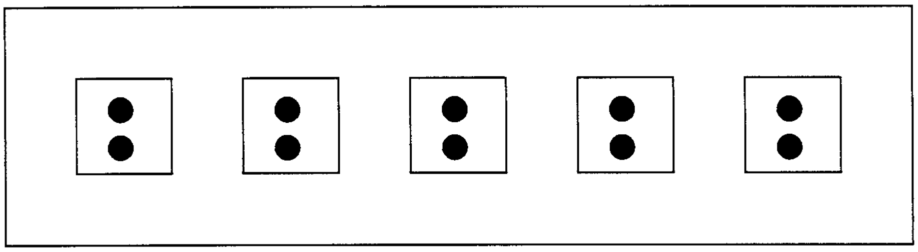


Fig. 4 schematic representation of particles in an array of holes.

Because of the large dimension faced in describing particles, well converged spectra and near electric fields of the holes and particles are still a big challenge for the DDA program. We are planning to develop a new program based on the multiple multipole (MMP) method. This method is different from other conventional ones in that all vector spherical harmonics (VSH) are inside the particle instead of being located in another domain as used in the conventional method. The strategy of the new multiple multipole method is introduced in the following paragraph.

For a cluster of particles with arbitrary shapes, the incident, scattering and internal electric and magnetic fields may be expanded in an infinite series of vector spherical harmonics which include the spherical Bessel functions, associated Legendre functions and $e^{im\phi}$ functions in spherical polar coordinates. The expansion coefficients will be determined by applying boundary conditions at matching points:

$$(E_{inc} + E_{scat} + E_{ret} - E_{\text{int}}) \times \hat{e}_n = (H_{inc} + H_{scat} + H_{ret} - H_{\text{int}}) \times \hat{e}_n = 0, \qquad (1)$$

where E and H represent the electric and magnetic fields, subscripts inc, scat, and ret, int, represent the incident, scattering, retarded, and internal fields, respectively. $\hat{e}_n$ is the normal vector to each matching point.

For a cluster of N particles with arbitrary shape and multiple layers, K VSH functions are used to expand the fields for each particle. The extinction cross section can be expressed as:

$$C_{sca} = \frac{2\pi}{k^2}\sum_{i=1}^{N}\sum_{j=1}^{K}\sum_{n=1}^{\infty}\sum_{m=-l}^{l}\sum_{q=1}^{2} \mathrm{Re}\left(p^{ij*}_{mnq} a^{ij}_{mnq}\right), \qquad (2)$$

where n, and m specify the degree and order of the VSH functions, the index q denotes the modes of the scattered field, with q=1 referring to transverse magnetic modes(TM) and q=2 to transverse electric modes. $k = \frac{2\pi}{\lambda}$ is the wave number of the incident radiation having wavelength λ. p^{ij}_{mnq} and a^{ij}_{mnq} are expansion coefficients of incident and scattering light, respectively.

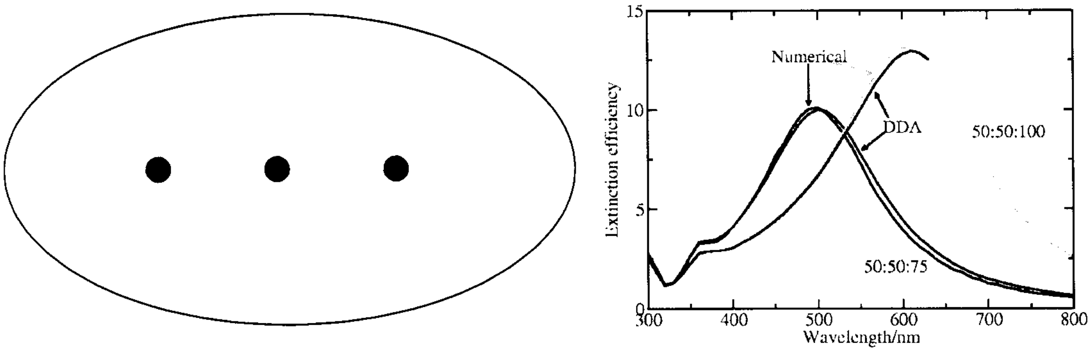


Fig.5. (a) Schematic representation of the particle, (b) Comparison of spectra for the DDA and MMP methods.

Fig 5 presents the preliminary results for the new MMP program and comparison with the results from the DDA method. They agree with each other very well while the new MMP method needs less function terms and computer time. For 50:50:75 (ellipse radiuses in nm) particle, 5 origins are used with excitation orders of VSH functions up to 2, and 120 matching points. For 50:50:100 particle, 7 origins are used with excitation orders up to 2, and 440 matching points. For the DDA method, the dipole number used is 98,000, and 130,000 respectively.

The results show that the new MMP method is more flexible than the DDA method, since it allows for the expansion of the electric field with a higher order for a given point. As a consequence, only very few multipole expansion terms are needed to obtain the converged results compared with the DDA method. Ultimately, the MMP method will be further improved to study more complicated systems.

References:

(1) Dirix, Y.; Bastiaansen, C.; Caseri, W.; Smith, P. *Adv. Mater.* **1999**, *11*, 223.

(2) Knoll, W. *Annu. Rev. Phys. Chem.* **1998**, *49*, 569.

(3) Storhoff, J. J.; Elghanian, R.; Mucic, R. C.; Mirkin, C. A.; Letsinger, R. L. *J. Am. Chem. Soc.* **1998**, *120*, 1959.

(4) Haes, A.; Voges, E.; Van Duyne, R. P. *J. Am. Chem. Soc.* **2002**, *124*, 10596.

(5) Haes, A.; Zou, S.; Schatz, G. C.; Van Duyne, R. P. *J. Phys. Chem. B* **2004**, *108*, 109.

(6) Haes, A.; Zou, S.; Schatz, G. C.; Van Duyne, R. P. *J. Phys. Chem. B* **2004**, *108*, 6961.

(7) Kahl, M.; Voges, E.; Kostrewa, S.; Viets, C.; Hill, W. *Sens. Actuators B* **1998**, *51*, 285.

(8) Freeman, R. G.; Grabar, K. C.; Allison, K. J.; Bright, R. M.; Davis, J. A.; Guthric, A. P.; Hommer, M. B.; Jackson, M. A.; Smith, P. C.; Walter, D. G.; Natan, M. J. *Science* **1995**, *267*, 1629.

(9) Zou, S.; Schatz, G. C. *Submitted to Phys. Rev. Lett.* **2004**.

(10) Haynes, C. L.; Van Duyne, R. P. *J. Phys. Chem. B* **2001**, *105*, 5599.

(11) Haynes, C. L.; McFarland, A. D.; Zhao, L.; Van Duyne, R. P.; Schatz, G. C.; Gunnarsson, L.; Prikulis, J.; Kasemo, B.; Kall, M. *J. Phys. Chem. B* **2003**, *107*, 7337.

(12) Mie, G. *Ann. Phys.* **1908**, *25*, 377.

(13) Kerker, M. *The Scattering of Light and Other Electromagnetic Radiation; Academic: New York,1969.*

(14) Bohren, C. F.; Huffman, D. R. *Absorption and Scattering of Light by Small Particles; Wiley Interscience: New York, 1983.*

(15) Barber, P. W.; Hill, S. C. *Light Scattering by Particles: Computational Methods; World Scientific: Singapore, 1990.*

(16) Mackowski, D. W. *J. Opt. Soc. Am. A* **1994**, *11*, 2851.

(17) Zhao, L.; Kelly, K. L.; Schatz, G. C. *J. Phys. Chem. B* **2003**, *107*, 7343.

(18) Draine, B. T.; Flatau, P. J. *J. Opt. Soc. Am. A* **1994**, *11*, 1491.

(19) Schatz, G. C. *Rev. Mod. Phys.* **1989**, *61*, 669.

(20) Schatz, G. C. *TheoChem* **2001**, *573*, 73.

(21) Novotny, L.; Pohl, D. W.; Hecht, B. *Opt. Lett.* **1995**, *20*, 970.

(22) Novotny, L.; Bian, R. X.; Xie, X. S. *Phys. Rev. Lett.* **1997**, *79*, 645.

(23) Bian, R. X.; Dunn, R. C.; Xie, X. S.; Leung, P. T. *Phys. Rev. Lett.* **1995**, *75*, 4772.

(24) Taflove, A. *Artech House, Boston* **1995**, 599.

(25) Hulteen, J. C.; Van Duyne, R. P. *J. Vac. Sci. Technol. A* **1995**, *13*, 1553.

(26) Huang, W.; Qian, W.; El-Sayed, M. A. *Nano Lett.* **2004**, *4*, 1741.

(27) Moran, C. E.; Steele, J. M.; Halas, N. J. *Nano Lett.* **2004**, *4*, 1497.

(28) Kelly, K. L.; Coronado, E.; Zhao, L.; Schatz, G. C. *J. Phys. Chem. B* **2003**, *107*, 668.

(29) Zou, S.; Zhao, L.; Schatz, G. C. *SPIE proceeding* **2003**, *5221*, 174.

(30) Zou, S.; Janel, N.; Schatz, G. C. *J. Chem. Phys.* **2004**, *120*, 10871.

(31) Barnes, W. L.; Dereux, A.; Ebbesen, T. W. *Nature* **2003**, *424*, 824.

(32) Pendry, J. B.; Martin-Moreno, L.; Garcia-Vidal, F. J. *Science* **2004**, *305*, 847.

(33) Lezec, H. J.; Degiron, A.; Devaux, E.; Linke, R. A.; Martin-Moreno, L.; Garcia-Vidal, F. J.; Ebbesen, T. W. *Science* **2002**, *297*, 820.

(34) Barton, J. E.; Odom, T. W. *Nano Lett.* **2004**, *4*, 1525.

Self-assembly of supermolecules into designed structures and molecular dynamics of small molecules

Abstract

The self-assembly of molecules composed of hundreds of atoms into nanocapsules will be studied using a newly developed program package. The parallel program, which contains subroutines to carry out molecular dynamics, Monte Carlo, and energy minimization calculations, will be finished and optimized. New algorithms to speed up the calculations will also be developed. The mechanisms of reactions between small molecules are also of the interest, and can be studied with the same methods.

(A) Self-assembly of supermolecules

1. Background

Cells synthesize and assemble molecules to produce a variety and complexity of cellular function. Could man-made molecules mimic those in the cell? The answer is yes according to the recently published Nature article by Dennis E. Discher and Randall D. Kamien,[1] who summarized the recent progress in this area. Kellermann *et al.*[2] reported a highly ordered example of a persistent spherical micelle in their amphiphilic dendrocalixarenes. Yoo, Y. et al. [3] generated nanocapsules by the self-assembling of molecular trees consisting of octa-p-phenylene as a stem segment and oligoether dendrons as a flexible head. Not only the spherical shape, but other structures like the highly stable cylindrical morphologies[4] are also reported.

Self-assembled nanostructures composed of super-molecule precursors also offer great potential for nanofabrication of materials. Recently, super molecules have been used to generate periodic patterned structures[5-7], electronic materials,[8] and molecular computing systems.[9,10] Functional materials[11,12] based on self-assembly of polymeric supermolecules and functionalization of carbon nanotube surface[13] are also discovered.

The application of computer-based models has been an increasingly powerful tool with the advances in computer speed and the development of analytical potential energy functions, like CHARMM,[14] AMBER[15] etc. which are based on simple ab initio calculations. Our future work will be concerned with developing parallel program packages which are especially efficient for supermolecular dynamics simulations, and which use a more accurate and general force field. These could include the force field of a specific supermolecule, or the interactions between carbohydrate and metallic atoms.

2. Future work

The immediate goal of the project will be to finish a parallel Fortran program which is used for the simulation of the self-assembly of super molecules. Using the AMBER force field, we have finished a program package from scratch which includes molecular dynamics, energy minimization, and Monte Carlo methods. The program had been tested and examined carefully by comparing our results with those from the Amber program package. The example molecule is a tree-shaped molecule consisting of octa-p-phenylene as a stem segment and oligoether dendrons as a flexible head which had been studied experimentally by Yoo Y. et al. [3] The schematic representation of formation of the nanocapsule of the molecules is presented in Fig. 1.

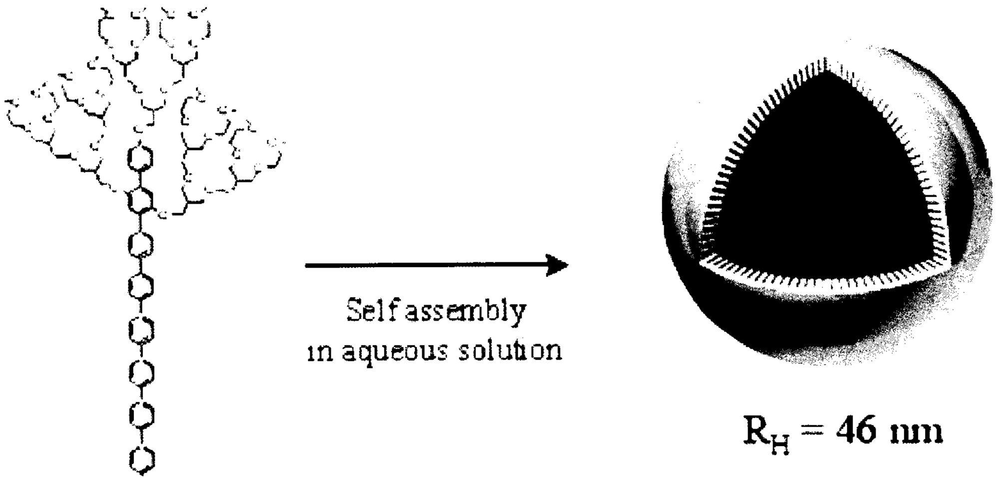


Fig. 1 Schematic representation of formation of the nanocapsule in solution state

The charges of the atoms are obtained from GAMESS and programs available in the AMBER program packages. The stable structure of the single molecule is shown in Fig.2 (a), Fig. 2(b) is the stable structure produced by self-assembly of four molecules. In the self-assembly project the four molecules are initially put into a plane parallel to each other but allowed to rotate along its backbone freely. The diagonal matrix and conjugate gradient methods are used to locate the stable structure of the cluster. To find the global minimum instead of a local well on the potential surface, a Monte Carlo method is also used in the simulation process. Though we use only four molecules in the simulations, Fig. 2(b) clearly indicates the conical pattern of the cluster which will eventually evolve into a spherical micelle when more molecules are included in the simulations.

The immediate goal of the project will be to parallelize the program. The development of new strategies which are efficient in finding global minima will also be a focus of the next step so that the simulation with hundreds of molecules will be possible. To speed up the calculation, we will use a dipole to approximately represent one molecule in considering the electronic static and Van der Waals interactions between two molecules when the distance between them is pretty large.

In addition to self-assembly of super-molecules, another theme is based on DNA, RNA recognition. DNA is composed of two antiparallel strands which wind about a common axis to form a double helix. In a DNA molecule, adenine always pairs with thymine, while cytosine always pairs with guanine. Thus, one DNA strand directs the synthesis of the other strand. We will fix one DNA strand and simulate the synthesis of the other strand using the molecular dynamics method.

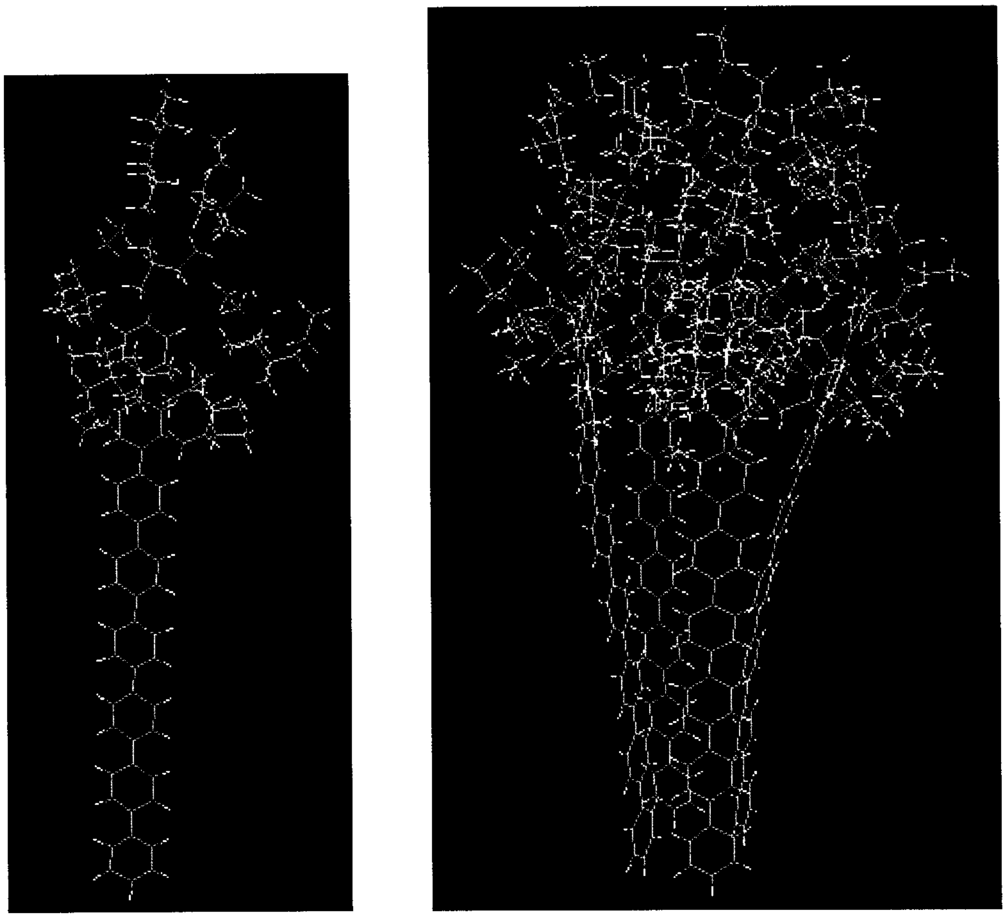


Fig. 2. (a) The stable structure of a single molecule, (b) the stable structure of four molecules.

(b) Molecular dynamics of small molecules

The self-assembly of the super molecules is a very interesting topic, however, the detailed information about the interactions between nearby atoms still requires simulations for small molecule dynamics. Using reduced and full dimensionality quantum method, we are able to study the reaction of small molecules.[16,17] Also, in classical trajectory methods, we solve the equations of motion to study the dynamics of small molecules. We will use the program packages mentioned above to do molecular dynamics studies of small molecules. To do this, accurate analytical potential functions of the molecules will be constructed.

Even though construction of an accurate potential of a tetra-atomic molecule is doable, construction of analytical global potential functions with high accuracy is very difficult for molecules with more than five atoms. Using direct dynamics,[18] we can obtain the potential directly from an ab initio program. This allows us to do the dynamics calculations with more atoms. However this is very time consuming because we need to calculate the potential and its derivative at every step of the trajectory. This eliminates our usage of higher order ab initio methods. Using a local interpolation method,[19] we may fit the potential locally which will save time for the next trajectory when it passes the same region as before and not lose much accuracy. Liu's group[20] recently measured the velocity distribution of a state-selected CD_3 product in the reaction $F + CD_4 \rightarrow DF + CD_3$ which opened up a new way to unravel the complexity of a polyatomic reaction. We will be interested in reproducing these results theoretically.

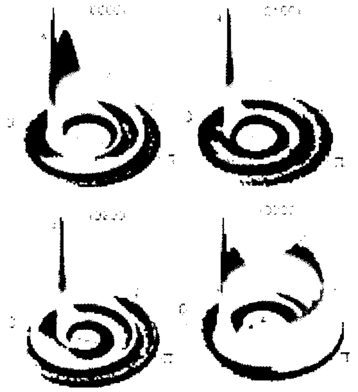


Fig. 3 CD_3 product state-resolved flux-velocity contour maps

References:

(1) Discher, D. E.; Kamien, R. D. *Nature* **2004**, *430*, 519.

(2) Kellermann, M.; Bauer, W.; Hirsch, A.; Schade, B.; K., L.; Bottcher, C. *Angew. Chem. Int. Edn* **2004**, *43*, 2959.

(3) Yoo, Y.; J., C.; Song, J.; Oh, N.; Zin, W.; Park, S.; Chang, T.; Lee, M. *J. Am. Chem. Soc.* **2004**, *126*, 6294.

(4) Harterink, J. D.; Beniash, S.; Stupp, E. *Science* **2001**, *294*, 1684.

(5) Jenekhe, S. A.; Chen, X. L. *Science* **1999**, *283*, 372.

(6) Seeman, N. C. *Nature* **2003**, *421*, 427.

(7) Yan, H.; Park, S. H.; Finkelstein, G.; Reif, J. H.; Labean, T. H. *Science* **2003**, *301*, 1882.

(8) Percec, V.; Glodde, M.; Bera, T. K.; Miura, Y.; Shiyanovskaya, I.; Singer, K. D.; Balagurusamy, V. S. K.; Heiney, P. A.; Schinell, I.; Papp, A.; Spiess, H. W.; Hudson, S. D.; Duan, H. *Nature* **2002**, *419*, 384.

(9) Adleman, L. M. *Science* **1994**, *266*, 1021.

(10) Braich, R. S.; Chelyapov, N.; Johnson, C.; Rothemund, P. W. K.; Adleman, L. *Science* **2002**, *296*, 499.

(11) Ikkala, O.; Brinke, G. *Science* **2002**, *295*, 2407.

(12) Percec, V.; Dulcey, A. E.; Balagurusamy, V. S. K.; Miura, Y.; Smidrkal, J.; Peterca, M.; Nummelin, S.; Edlund, U.; Hudson, S. D.; Heiney, P. A.; Duan, H.; Magonov, S. N.; Vinogradov, S. A. *Nature* **2004**, *430*, 764.

(13) Richard, C.; Balavoine, F.; Schultz, P.; Ebbesen, T. W.; Mioskowski, C. *Science* **2003**, *300*, 775.

(14) MacKerell, A. D. J.; Brooks, B.; Brooks, C. L.; Nilsson, I., L.; Rous, B.; Won, Y.; Karplus, M. *The Encyclopedia of Computational Chemistry* **1998**, *1*, 271.

(15) Cornell, W. D.; Cieplak, P.; Bayly, C. I.; R., C. I.; Merz, K. M. J.; Ferguson, D. M.; Spellmeyer, D. C.; Fox, T.; Caldwell, J. W.; Kollman, P. A. *J. Am. Chem. Soc.* **1995**, *117*, 5179.

(16) Skokov, S.; Zou, S.; Bowman, J. M. *J. Phys. Chem. A* **2001**, *105*, 2298.

(17) Zou, S.; Bowman, J. M.; Brown, A. *J. Chem. Phys.* **2003**, *118*, 10012.

(18) Hase, W. L.; Song, K. H.; Gordon, M. S. *Computing in Science & Engineering* **2003**, *5*, 36.

(19) Christoffel, K. M.; Bowman, J. M.; Braams, B. J. *J. Chem. Phys.* **2001**, *115*, 11021.

(20) Liu, J. J.; Zhou, J.; Shiu, W.; Liu, K. *Science* **2003**, *300*, 966.

Vibrational spectra of small and big molecules

Abstract

Using the quantum mechanics and molecular mechanics, we are interested in the vibrational spectra of both small and big molecules. The small molecules include the triatomic and tetraatomic molecules and large ones can be extended to DNA and RNA molecules.

1. Background

In the last 20 years there has been considerable interest in calculating vibrational spectra, including IR and Raman intensities, by ab initio methods. Until recently, most of the reported studies were concerned with relatively small molecules. However, the advancement in technology requires the calculations of vibrational spectra for relatively large molecules. In 1997, Nie et. al [1] developed a strategy to detect the single molecule using surface-enhanced Raman scattering spectra. Using a Raman tag as a narrow-band spectroscopic fingerprint, Cao et. al. [2] reported a new experimental method to detect DNA and RNA. To identify the detected molecules, we need to be able to predict the vibrational spectra of the target molecules.

In small molecules, the vibrational modes of the molecules are well defined and predictable. Using reduced and full dimensionality quantum methods, we are able to study the vibrational energy and dissociation of small molecules. The vibrational spectra of small molecules like C_2H_2[3-5] had been studied up to the isomerization energy threshold using a full dimensionality quantum method developed during my Ph.D program. The calculated photodetachment spectra agree with the experimental results[6] very well.

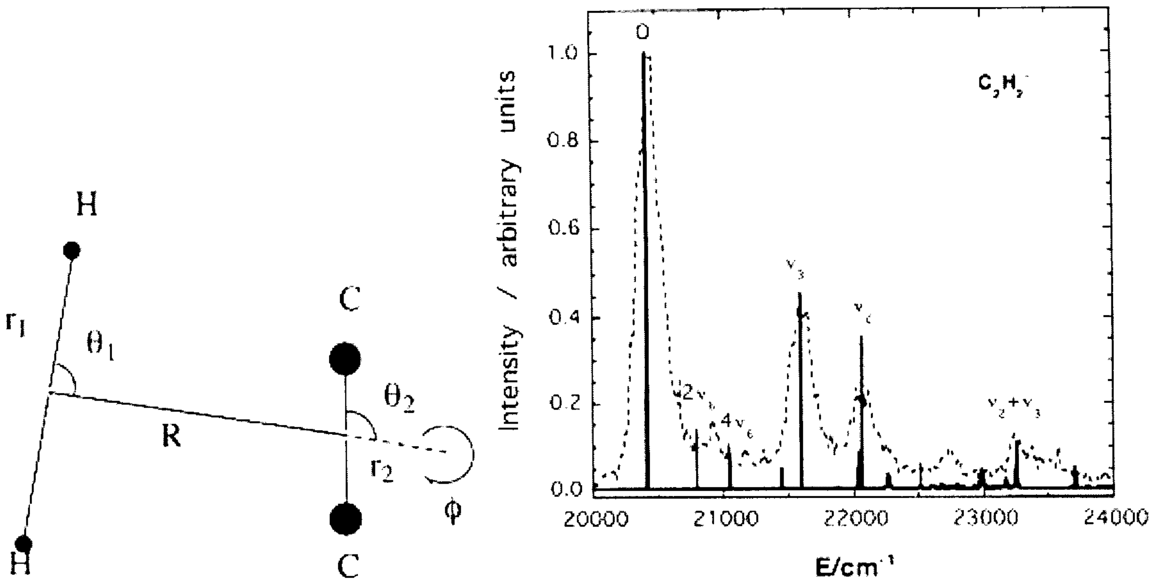


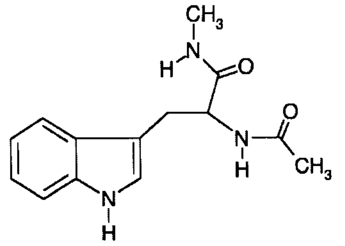
Fig1. (a) Diatom–diatom Jacobi coordinates of C_2H_2

(b)Franck–Condon factors for the vinylidene anion with molecular eigenstates of acetylene–vinylidene (C_2H_2) vs the energy of the neutral and comparison with the experimental photoelectron

2. Future work

Vibrational spectra of small molecules can be calculated accurately using quantum methods. Once the molecules become larger, predicting the vibrational modes becomes more complex. However, because different groups of the molecule have certain spectral features at characteristic frequencies, the infrared spectrum still often can be used for identification. Since proteins and DNA are built from repeating units, their vibrational spectra will reflect these repeating units, allowing assignments of the individual vibrational bands.

We start from the dipeptide, *N*-acetyl-tryptophan methyl amide (NATMA) whose vibrational spectra have been recorded by Dian et al. [7] to experimentally study the mechanisms and dynamics of conformational isomerization in flexible molecules. The structure of the molecule is presented in Fig. 2.



N-acetyl-tryptophan methyl amide, NATMA

Fig. 2 Structure of the NATMA molecule.

The AMBER force field will be first used to examine precise structural features of the peptide and normal mode analysis will be carried out at several of the most stable structures of the molecule. Density functional theory with a small basis will then be used to compare the results from ab initio calculations and those from the analytical potential functions. New parameters of the force field will be developed based on the ab initio calculations so that they are more precise to the specific molecule. The new force field will also be used in the molecular dynamics simulations to study the three dimensional structures and vibrational frequencies of the big molecules.

With increase in atomic number, the normal mode analysis using the Hessian matrix becomes more and more difficult. A new method called "A driven molecular-dynamics approach"[8] was developed recently in Dr. Bowman's group to do the normal mode analysis of molecules without using a Hessian and was successfully applied to the molecules of HOD and $H_5O_2^+$. I will be very interested in developing this method and other new methods to the calculations of vibrational spectra of big molecules. No doubt, the development of the accurate potential surface of the system is still a big challenge.

References:

(1) Nie, S.; Emory, S. R. *Science* **1997**, *275*, 1102.
(2) Cao, Y. W. C.; Jin, R. C.; Mirkin, C. A. *Science* **2002**, *297*, 1536.
(3) Zou, S.; Bowman, J. M. *J. Chem. Phys.* **2002**, *116*, 6667.
(4) Zou, S.; Bowman, J. M. *J. Chem. Phys.* **2003**, *117*, 5507.
(5) Zou, S.; Bowman, J. M.; Brown, A. *J. Chem. Phys.* **2003**, *118*, 10012.
(6) Ervin, K. M.; Ho, J.; Lineberger, W. C. *J. Chem. Phys.* **1989**, *91*, 5974.
(7) Dian, B. C.; Longarte, A.; Zwier, T. S. *Science* **2002**, *296*, 2369.
(8) Bowman, J. M.; Zhang, X.; Brown, A. *J. Chem. Phys.* **2003**, *119*, 646.

Teaching Philosophy

Shengli Zou

Learning is a process of discovery, not memorization. Although major and introductory science courses obviously require different teaching strategies and goals, they share a common purpose, which is the students' achieving a new or broader perspective on the universe. One must understand the difference between learning and memorization. The later implies that one can call up facts; whereas, the former implies that one must not only know the facts but also how to make use of them in problem solving and in new situations. I strongly believe that in chemistry the understanding of concepts and the ability to solve problems should be emphasized over memorization. Memorization can not be totally eliminated but it could be modified.

As a teacher I must be aware of what students know when they come into the classroom as well as how to tap into that knowledge and build on it. On the first day of class I ask students to fill out a science questionnaire. Their answers provide me a baseline of their knowledge in the field. I aim to maximize the learning of a subject, and challenge the students how to learn.

To be effective, learning must occur actively, rather than passively. Teachers should enable students to become responsible for their own learning. The goal of education is learning, not teaching. I believe that students should be stimulated to think on their own. Students will learn and understand more if they are given an opportunity to become creators rather than merely consumers of knowledge

I actively seek to create a relaxed, open, and encouraging attitude in the classroom where students participate in directing their objectives, and I act as a guide, working side-by-side with my students. I encourage my students to take an active role in the classroom, guiding classroom discussions and curriculum choices, and discovering and using their new knowledge. I believe that by creating and sustaining a constructive classroom, teachers will enable students to become responsible for their own learning. My function is to spark intellectual curiosity, introduce the subject, respond to difficulties by interacting with the class, stimulate creativity, and monitor student progress.

When I teach, I enter each class period ready with a well-prepared, organized lecture. I am always looking for ways to bring clarity and organization to my lectures. I begin each lecture by briefly reviewing the previous one. This seems to ease students' attention into the classroom by addressing students' questions. Chemistry can be a complicated subject for many students due in part to confusing symbols and notation. When preparing each lecture, I am constantly looking for better examples to illustrate difficult concepts and new ways of presenting complex models.

It is necessary for a teacher to truly care about his or her students. Teachers must respect students; we must believe that students have something to contribute, and that students may bring new insights to a subject. A good teacher will recognize that there is as much to be learned from students as there is to be taught to them

The time spent in office hours allows me to get to know my students, their backgrounds, strengths and weaknesses, and their goals. I encourage students to utilize office hours to discuss questions or difficulties they face in the class and attempt to maintain a friendly office hour so students will be encouraged to come. Homework is also an important teaching tool and grading it serves as a diagnostic into how well students understand the material.