

论文题目：分子、团簇和凝聚体系中相互作用的计算研究

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摘 要

化学从十九世纪到二十世纪的飞跃，从本质上来说，是从十九世纪的在原子论、元素周期表的层次上定性、经验地认识和研究化学，进步到二十世纪的定量、基于物理原理地认识和研究化学。随着计算方法和计算条件的飞速进步，计算化学和计算物理将占有越来越重要的地位，代表了化学和物理未来发展的最重要方向之一。计算已经和实验与理论鼎足而三，成为一种基本的研究模式。分子和化学键是化学家认识世界的基本图象。在聚集的分子之间，可能具有化学键的强相互作用或者非键的弱相互作用。对这三种相互作用（分子内化学键、分子间化学键和分子间弱相互作用）的计算研究，构成了本论文的三部分内容。由于人们对这三种相互作用的理解程度的区别，相应的研究的近似程度也各自不同。我们可能直接对体系进行第一性原理计算，或者对模型进行第一性原理计算，或者只得采用唯象势能模型。计算化学和计算物理研究的目的不仅仅是获得数值结果，在许多情况下更重要的是获得对问题本质的一种理解的框架。比如定性分子轨道理论对于理解化学键就是极其重要的，其中常用的工具包括一阶与二阶 Jahn-Teller 效应、Walsh 图、等叶片性、晶体轨道重叠布居等。对于具体问题选择合适的计算方法、提高准确程度、以及理解计算结果，是计算化学与物理的艺术。

在第一章中，我们简要叙述了量子化学和电子密度泛函理论（DFT）的历史，介绍了传统量子化学中对电子相关能问题的处理方法，然后描述了密度泛函理论的基本框架和优点，并讨论了密度泛函理论中的一些概念问题。此后我们介绍了量子化学计算软件包 Gaussian 和 DMol 的性质和功能。这些理论与程序是我们处理分子内与分子间化学键的理论基础和计算工具。

在第二章中，我们对团簇和分子的电子和光谱性质进行了第一性原理计算研究。自从 1985 年 C₆₀ 的发现以来，以富勒烯为代表的碳基团簇分子以其新奇的电子和结构性质吸引了广泛的兴趣，开创了化学和材料科学的一大新兴领域。1998 年实验上成功地制备了 C₃₆ 的晶体，使人们的研究兴趣从 C₆₀ 以及更大的富勒烯分子转向较小的富勒烯分子。我们的计算表明，C₃₆ 分子具有 D_{2d} 和 D_{6h} 两种等能量的可能构型。为了解释固体中 C₃₆ 分子只具有 D_{6h} 对称性的实验事实，注意到合成固体时使用了弧光放电法，我们研究了两种构型的正负离子。结论是 D_{6h} 的负离子能量低于 D_{2d} 的负离子，而 D_{2d} 的正离子能量低于 D_{6h} 的正离子。我们假设放电中首先生成了负离子，然后负离子聚集为固体，在衬底上失去多余的电荷，从而提供了对此实验事实的第一种可能的解释。我们建议了首先产生正离子从而制备 D_{2d} 构型的 C₃₆ 分子、离子或固体的可能性。此外我们研究了两种构型的振动性质（频率、Jahn-Teller 效应）和电子性质（电离能、电子亲和能、能隙、态密度），并和可获得的实验结果进行了比较。此项工作发表在 J. Phys. Chem. A 上。1992 年发现的金属碳烯是另一类具有特别稳定性的团簇分子。经过长期的争论和研究，人们发现它的最稳定构型并不象富勒烯，而是四重

覆盖的四面体 T_d 结构。我们计算了一系列 T_d 构型的 M_8C_{12} 金属碳烯的电极化率。另一系列的工作是研究分子振动光谱的强度（与林海、王冬、何圣贵等同学合作）。分子光谱中的可观信息包括频率和强度。传统上，由于实验精度的限制，光谱研究的绝大部分集中于频率方面。随着实验和计算条件的进步，关于谱线强度的研究将占据越来越重要的地位。振动光谱的强度正比于 $|\langle v|M|0\rangle|^2$ ，其中 $\langle v|$ 和 $|0\rangle$ 是振动激发态和基态的波函数， M 是偶极矩函数。由于偶极矩的影响由其起伏决定（偶极矩变化一个常量不改变强度），所以要准确计算强度，对偶极矩的精度要求比对波函数的精度要求更高。我们使用第一性原理方法计算出分子在若干构型下的偶极矩，通过拟合给出偶极矩面的解析形式，并用谐振子或 Morse 振子表示振动波函数，从而以解析或数值积分得到相对强度。我们的第一个成功的例子是重现了硅烷的(3000)泛频比(4000)泛频更弱的“反常”（发表于 *Chem. Phys. Lett.*）。此后我们研究了一系列的体系（ $CHCl_3$, CH_3 , $CHBr_3$, SiH_3 , SiH_2F_2 等），论文发表在 *Chin. Phys. Lett.*, *J. Chem. Phys.*, *Chem. Phys. Lett.*, *J. Phys. Chem. A*, *Phys. Chem. Chem. Phys.* 等刊物上，开辟了一个长期的方向。

在第三章中，我们把目光转向化学吸附在表面的分子。由于其强大的单分子成像和操纵能力，扫描隧道显微镜（STM）大大推动了选键化学、表面科学和单分子化学与物理的发展。Wilson Ho 等人通过 STM 和非弹性电子隧穿谱（IETS）的结合，实现了单分子振动频率的测量，并首次生成了单个化学键。为了研究吸附分子的局域性质，我们采用团簇模型模拟表面吸附体系，使用电子密度泛函理论计算了体系的能量和构型，模拟了 STM 图象。尤其有意义的是，通过构造表面吸附分子的动力学矩阵，较为精确地得到了吸附分子的包括伸缩、弯折、受阻转动、受阻平动等各种内部和外部振动模式的频率。计算值不但和已有的实验值相当符合，而且可以用于预测大量实验上尚未测得的模式。对于吸附在 $Ag(110)$ 表面的 $M(CO)_n$ ($M=Fe, Co, Ni, Cu, Zn, Ag; n=1, 2$) 的研究表明，这六种金属元素可以按照其 d 轨道是否充满而分为两类，每一类显示一组特别的构型和振动频率。构型可以根据前线轨道理论得到理解。此项工作发表在 *Phys. Rev. B* 上。我们研究了吸附在 $Cu(001)$ 表面的乙炔及其演化产物。通过振动频率的实验值和计算值的比较，我们确认 1987 年在电子能量损失谱（EELS）实验中发现的乙炔的热演化产物并不是当时作者们指认的 CCH，而是 CCH_2 ，从而解决了该实验工作与 2000 年 Wilson Ho 等人对 CCH 的 STM-IETS 实验工作之间的矛盾。我们在指认的过程中也得到了实验上尚未给出的 CCH_2 的吸附取向，并发现在 $Cu(001)$ 表面 CCH_2 比乙炔更稳定。此项工作发表在 *J. Chem. Phys.* 上。

在第四章中，我们研究了一种典型的由分子间弱相互作用决定的新现象—二维 C_{60} 体系的取向畴结构。在三维 C_{60} 固体中，室温下分子相对自由地转动，晶格为面心立方，在 260K 发生分子取向有序化的一阶相变，晶格变为简单立方。中国科学技术大学结构分析开放实验室通过 STM 观察到，吸附在硫醇衬底上的二维单层 C_{60} 也可以发生取向无序到有序的转变。在一个低温取向畴中， C_{60} 分子具有晶格平移对称性，并且每个单胞（ 1×1 或 2×2 ）具有相同的取向结构。根据实验和模拟的 STM 图象之间的比较，可以确定 C_{60} 分子的取向。为了解释和预测实验现象，我们使用两种唯象分子间势模型，研究了取向有序情况下二维 C_{60} 晶体的各种取向畴结构，包括 1×1 晶格、 2×2 晶格和两种 1×1 取向畴之间的畴界。两种经验势中较为精细的 Lamoen-Michel 模型得到的结果令人满意。在 1×1 晶格的条件下，我们发现了三种取向势能面的局域极小，按照稳定性排序，分别以顶点、双键和六边形与衬底接触。以顶点和衬底接触的取向与出现最多的一种实验取向相当准确地吻合。把周期性边界条件放宽到 2×2 ，前两种局域极小仍然保持，第三种将发生畸变。我们发现了若干种非 1×1 的 2×2 局域极小，但它们的能量都高于以顶点接触衬底的 1×1 极小。这和绝大多数 STM

图象都属于 1×1 晶格的实验事实符合。在这些非 1×1 的 2×2 局域极小当中，有一种和实验观测到的 2×2 晶格 STM 图象符合得很好。此外，以顶点和双键接触衬底的两种 1×1 极小之间的畴界能为负值（能量稳定化），与实验观测的畴界的 STM 图象符合。最后，我们探讨了构造更精确的分子间势模型以及应用到一维 C60 体系中的可能性。这些工作发表在 Nature 和 J. Am. Chem. Soc. 上。

Abstract

The leap of chemistry from the 19th century to the 20th century is, in essence, the advance from studying chemistry qualitatively and empirically at the level of atomic theory and the element periodical table in the 19th century to studying chemistry quantitatively and based on physical principles in the 20th century. Along with the rapid progress of the computational methods and resources, computational chemistry and computational physics will become more and more crucial, and are among the most important developing directions of chemistry and physics. Calculation has paralleled experiment and theory to be a fundamental research mode. For chemists, the molecule and the chemical bond is the basic paradigm to understand the world. Between aggregated molecules, there may exist strong interactions of chemical bonding or nonbonding weak interactions. The computational investigations for the three types of interactions (intramolecular chemical bond, intermolecular chemical bond, and intermolecular weak interaction) compose the three parts of this dissertation. Because people understand these three interactions in different depths, the degree of approximation for the researches are correspondingly distinct. We could directly conduct first-principles calculations for the system, or do first-principles calculations for a model, or have to use empirical potential model. The aims of computational chemistry and physics researches are not only to obtain the numerical results; in many cases the more important is to get an understanding framework for the essence of the problem. For example, the qualitative molecular orbital theory is extremely valuable to understand the chemical bond, where some tools in common use are first- and second-order Jahn-Teller effects, Walsh diagram, isolobality, and crystal orbital overlap population (COOP). To a given topic, selecting appropriate calculation scheme, improving computation accuracy, and understanding results are the arts of computational chemistry and physics.

In Chapter 1, we briefly describe the history of quantum chemistry and density functional theory (DFT), introduce the conventional quantum chemistry methods to deal with the electronic correlation problem, then describe the framework and merits of DFT, and discuss some conceptual issues of DFT. Then we introduce the properties and functions of the quantum chemistry computational software packages Gaussian and DMol. These theories and programs are our theoretical foundations and computational implements to handle the intramolecular and intermolecular chemical bonds.

In Chapter 2, we investigate electronic and spectroscopic properties of clusters and molecules using first-principles calculations. Since the discovery of C₆₀ in 1985, the carbon-based clusters, with the fullerenes as their representatives, have attracted extensive interests, and a novel field of chemistry and materials sciences was originated. The experimental making of C₃₆ crystals in 1998 turned people's research interests from C₆₀ and the larger fullerenes to the smaller fullerenes. Our calculations show that there are two kinds of isoenergetic geometries (D_{2d} and D_{6h}) of C₃₆ molecule. To explain the experimental fact that only the D_{6h} isomers exist in C₃₆ solids, noticing the use of arc discharge method in the synthesis of solids, we study the anions and cations of the two geometries. The result is that the D_{6h} anion is lower in energy than the D_{2d} anion, while the D_{2d} cation is more stable than the D_{6h}- cation. We suppose that anions are

made at first in the discharge, then they assemble to form solids, and the excessive charges are lost to the substrates. Thus we give the first likely explanation for this experimental fact. We propose the possibility of producing the D2d molecules, ions, or solids by first making cations. Besides, we study the vibrational (frequencies, Jahn-Teller effect) and electronic (ionization potential, electron affinity, gap, density of states) properties of the two isomers, and compare them with available experimental data. This work was published in J. Phys. Chem. A. The metallocarbonhederenes (met-cars) discovered in 1992 are another family of especially stable clusters. After long-term controversy and research, the most stable geometry of the met-cars had been found as not fullerene like, but tetracapped tetrahedron with Td symmetry. We calculate the electric polarizabilities of a series of Td M8C12 met-cars. Another series of works are on molecular vibrational spectroscopic intensities (cooperating with Doctors Hai Lin, Dong Wang, and Sheng-Gui He, et al.). The observable information in molecular spectrum includes frequencies and intensities. Traditionally, due to limitation of experimental precision, most of the spectroscopic researches were concentrated on frequencies. Along with the progress of experimental and computational conditions, the intensity is becoming more and more important a topic. The vibrational spectroscopic intensity is proportional to $|\langle v|M|0\rangle|^2$, where $\langle v|$ and $|0\rangle$ are the wave functions of the vibrational excited and ground states, and M is the dipole moment function. Because the influence of dipole moment is determined by its fluctuation (varying M by a constant does not change the intensity), the accuracy of dipole moment function is more crucial than the accuracy of wave functions to calculate intensity quantitatively. We obtain the molecular dipole moments at many geometries by first-principles computations, get the analytical form of dipole moment function by fitting, and describe vibrational wave functions in terms of harmonic or Morse oscillators, then calculate the intensities by analytical or numerical calculations. Our first successful example is to reproduce the "anomaly" that for SiH4 the (3000) overtone is weaker than the (4000) overtone (published in Chem. Phys. Lett.). Afterwards we investigate a series of systems (CHCl3, CHI3, CHBr3, SiHD3, SiHF-3, etc.), with papers published in Chin. Phys. Lett., J. Chem. Phys., Chem. Phys. Lett., J. Phys. Chem. A, Phys. Chem. Chem. Phys. etc., making a long term direction.

In Chapter 3, we turn our sight to chemisorbed molecules. In virtue of its powerful abilities for single molecule imaging and manipulation, the scanning tunneling microscope (STM) has greatly impeded the developments of bond selective chemistry, surface science, and single molecule chemistry and physics. By combining STM with the inelastic electronic tunneling spectroscopy (IETS), Wilson Ho et al. realized the measurements of single molecule vibration frequencies and the formation of single chemical bond. In order to study local properties of the adsorbate molecules, we model the adsorption systems as clusters, calculate their energetics and geometries using DFT, and simulate the STM images. Especially meaningfully, by constructing the dynamic matrices of the adsorbate molecules, we obtain relatively accurate frequencies of the internal and external modes such as stretch, bending, frustrated rotation, and frustrated translation. With available experimental values our calculated frequencies have good agreement, and we can predict many modes not experimentally observed. Our investigations for M(CO)n (M=Fe, Co, Ni, Cu, Zn, and Ag; n=1, 2) on Ag(110) show that the six metals can be sorted to two classes, each of which exhibits a set of special geometries and frequencies, according to whether its d orbitals are fully occupied or not. The adsorbate geometries are understood in the light of

the frontier orbital theory. This work was published in Phys. Rev. B. Then we study acetylene and its evolution products on Cu(001). Via comparison between the experimental and calculated vibrational frequencies, we conclude that the thermal evolution product of acetylene discovered in the 1987 electronic energy loss spectrum (EELS) experiment is not CCH (assigned by the then authors), but CCH₂, thus solve the contradiction between the EELS work and the 2000 STM-IETS work for CCH by Wilson Ho et al.. In the course of this assignment, we predict the adsorbate orientation of CCH₂, which was not given by experiments, and we find that on Cu(001) CCH₂ is more stable than C₂H₂. This work was published in J. Chem. Phys..

In Chapter 4, we study a novel typical phenomenon determined by intermolecular weak interactions, i.e., the orientational domain structure of two-dimensional (2D) C₆₀ systems. In three-dimensional (3D) C₆₀ solids, at room temperature the molecules rotate relatively freely, and the lattice is face-centered cubic (fcc). At 260 K, C₆₀ solids undergo a first-order phase transition triggered by the orientational ordering of molecules, and the lattice becomes simple cubic (sc). Via STM observations, the structure research laboratory at USTC finds that there is also orientational ordering transition for 2D C₆₀ monolayer adsorbed on thiol substrate. In a low temperature orientational domain, there is lattice translational symmetry among the C₆₀ molecules, and every unit cell (1'1 or 2'2) has the same orientatioanl structure. By comparing the experimental and simulated STM images of C₆₀, we can determine its orientation. To explain and predict the experimental phenomonon, we employ two kinds of semi-empirical intermolecular potential models to investigate the various orientational domain structures of low temperature 2D C₆₀, including the 1×1 and 2×2 lattices, and the domain boundary between two 1×1 lattices. The results by the more refined Lamoen-Michel (LM) model are satisfactory. Under the limitation of 1×1 lattice, we find three kinds of local minima on the orientational potential energy surface. From the lowest to the highest in energy, molecules at these three orientations contact with the substrate by a vertex, a double bond, and a hexagon, respectively. The vertex-contacting orientation agrees very accurately with the experimental orientation appearing the most frequently. Relaxing the periodic boundary to 2×2, the former two kinds of 1×1 orientations keep local minima, but the last one will be distorted. Several 2×2 local minima other than the 1×1 ones are found, but their energies are all higher than that of vertex-contacting 1×1 minima, which is consistent with the experimental fact that the most STM images are of 1×1. A kind of non-1×1 2×2 structure is found to agree well with an experimental 2×2 STM image. The domain boundary energy between the vertex-contacting and the double-bond-contacting 1×1 orientations is negative (stabilizing), in accordance with the experimental STM image of domain boundary. Finally, we discuss the possibility of constructing more precise intermolecular potential and extending the research to one-dimensional C₆₀. These works were published in Nature and J. Am. Chem. Soc..