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13. ABSTRACT (Maximum 200 words)

This report results from a contract tasking J. Heyrovsky Institute of Physical Chemistry & Electrochemistry as follows: The contractor will improve upon an existing computer code modeling the classical dynamics of a molecular structure within a solid (intramolecular bonding and vibrations, intermolecular collisions, and electrostatic interactions). The new program will be used to explore computationally a variety of possible structures for the synthesis of new materials capable acquiring significant internal mechanical angular momentum along a well defined macroscopic axis due to the rotation of nanoscale internal constituents (molecular propellers) at microwave frequencies. Two possible mechanisms for driving the internal rotation will be investigated, as well as latice-induced loss mechanisms and inter-rotor interactions.

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Final Report to European Office of Aerospace Research and Development

Contract number: F61775-98-WE043
Contract title:

Computer simulations of molecular propellers

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INTRODUCTION:

It is believed that it will ultimately be possible to assemble new highly organized nanostructured materials of sturdy molecular connectors and rods. Such materials would posses unique and potentially useful features and functions. In our research coordinated by Prof. Josef Michl of Boulder, CO we concentrate on theoretical investigation of properties of these hypothetical materials usually consisting of ultra thin molecular layers with mounted mobile groups (molecular rotors, propellers etc.). We hope that these computational studies prior to experimental investigation may be helpful in directing the synthetic effort by eliminating structures predicted to be of limited interest and thus may reduce the cost of synthetic preparation. In the case of recently prepared molecular rotors mounted on quartz (cf. our interim report) our simulations may also be useful in interpreting the experimental results.

In our investigations we use molecular dynamics (MD) simulations to study theoretically the properties of propeller shaped groups (molecular rotors) mounted on a suitable solid. We have shown before[1] (by means of MD) that molecular propellers would rotate in a flow of rare gas. During the period of support from EOARD we were mainly investigating the behavior of molecular rotors driven by rotating electric field. A publication on this issue is almost finished.[2] New force field for carboranes was parameterized and three new rotor structures were built.

The results of our simulations will be presented on the first EL.B.A. – Foresight Conference on Nanotechnology in Rome (April 1999).

TECHNICAL REPORT:

Code Development. During the year of support new features were added to the TINK program. It is now capable of running MD simulations of molecules consisting of virtually any elements from the periodic table both in the flow of rare gas atoms (to study the rotation induced by gas flow) and in an external rotating electric field. For the evaluation of the simulations in the rotating electric field dipole moment vector of the rotor (rather than position of charged groups) is now used to calculate the relative orientation of the electric intensity vector and the rotor. Time averaged lag angle, mean angle lag per turn, average rotational frequency of the rotor, and other features are evaluated to judge the performance of the molecular rotor.[2] The code also calculates the average polarization and torque in the system rotating with the field. It is also capable of automatic calculation of the rotational barriers and rotational decay times. In order to estimate the rotational decay times the code averages angular momentum decay of many trajectories following an initial rotation excitation. The latest feature implemented is an automated algorithm to perform several simulations in electric field of a given frequency and different amplitude, reducing the human involvement required. This feature was added specifically for the temperature dependence calculations.

The work on implementing the polarization energy term into the force field has just barely begun. Routines for self-consistent polarization energy evaluation were obtained from the University of Lund. Routines to calculate the derivatives of the polarization energy are to be programmed yet. The simulations in the electric field performed up to now appeared so expensive, however, that the calculations using polarization force field (expected to be 5-10 times slower) may not be feasible in the next couple of years.

Simulations of Molecular Propellers in Electric Field. Most of our effort was oriented in the direction of investigating the behavior of molecular rotors in rotating electric field. We felt that this subject needed to be addressed first. Many trajectories of our originally designed molecular rotor (described in ref. 1) mounted on a rectangular grid in an external rotating electric field were calculated and analyzed. All trajectories were run at 150 K. For various field strengths and frequencies the performance of the rotor was judged based on the mean lag per turn and other characteristics. For each frequency investigated a ”critical” field strength E_{crit} was estimated. For fields higher than E_{crit} the rotor follows the field almost without missing any turns, i.e. synchronously. The expected “asynchronous” region below the critical field line has two subregions; the regular asynchronous region and the thermal asynchronous region. In the regular asynchronous region the rotor still behaves more or less like a macroscopic rotor but it misses most of the turns of the rotating field. The efficiency of the rotor decreases with increasing distance from the E_{crit} line. When the field strength decreases under ckT, (we estimated $c \sim 1.3$), however, the thermal fluctuations overwhelm the response to the field. This behavior has no equivalent in the macroscopic world. A paper on this subject is almost ready for submitting.[2] We are now trying to fit phenomenological theories to our data and to extract characteristics like the friction constant of the rotor from the simulations. The latest draft of the paper (without figures) is attached to this report.

Simulations designed to address more quantitatively the temperature dependence of the rotor behavior are in progress. Much more data are needed for this task, since we have to perform same simulations as before (at the temperature of 150 K) but now at a range of different temperatures. Therefore we have designed our program to run these simulations with small user intervention.

Force Field Development. The new force field for carboranes was parameterized within the framework of the universal force field (UFF), based on *ab initio* calculated geometries (MP2/6-31G*) and energies. The relative energies calculated using this force field deviate from those calculated *ab initio* by less than 0.5 kcal/mol (for *ab initio* relative energies ranging from 0.9 to 14 kcal/mol). We are still trying to optimize the force field further, but it may not be possible within the UFF concept. We think that the structure of UFF should be preserved, if possible.

Simulations of New Rotors. Three new structures were prepared in the computer and preliminary calculations were performed. Thorough investigation of their behavior will need to be done in the future, though.

(1) New “cobalt based” (cyclopentadiene - Co - cyclobutadiene sandwich) rotors (see our interim report for picture) were built in the computer and prepared for the calculations. They appear to have too high rotational barrier, however, to be simulated successfully at room temperature using MD (they only may rotate at much lower frequencies than we can simulate). More data is needed to address this issue and possibly direct the synthesis to more promising

structures (e.g. having smaller groups on the cyclobutadiene). The quartz glass to which these rotors are to be mounted has also been prepared. We plan to enlarge that piece of glass yet, to make our simulations more accurate. The UFF charge model may not be suitable for estimating the charges on the charged groups of this rotor. We plan to develop RESP[3] charges for these groups prior to running definitive calculations.

(2) The proposed porphyrin - shishkhabab rotor was built in the computer and preliminary simulations were performed. We would like to start data production MD runs after we finish the electric field simulations on the old rotor, which are in progress now.

(3) Finally, the promising five – fold carborane rotor (cf. Fig. 1) was constructed using the new force field for carboranes developed. It will yet be needed to calculate the atomic charges on charged groups of the blades more accurately (using RESP[3]) and to attach the rotor to the molecular grids (one above and one under the rotor). The blades will be shortened (with respect to those shown in Fig. 1) by one C_6 ring to be synthetically more realistic.

References:

1. Vacek, J.; Michl, J. *New J. Chem.* **1997**, 21, 1259.
2. Vacek, J.; Michl, J. *A Molecular "Tinkertoy" Construction Kit: Computer Simulation of a Molecular Dipolar Rotor in a Rotating Electric Field*, in preparation.

   The most recent draft of this paper (without figures) is attached to this report.
3. Bayly, C. I.; Cieplak, P.; Cornell, W. D.; Kollman, P. A. *J. Phys. Chem.* **1993**, *97*, 10269.

Figures.

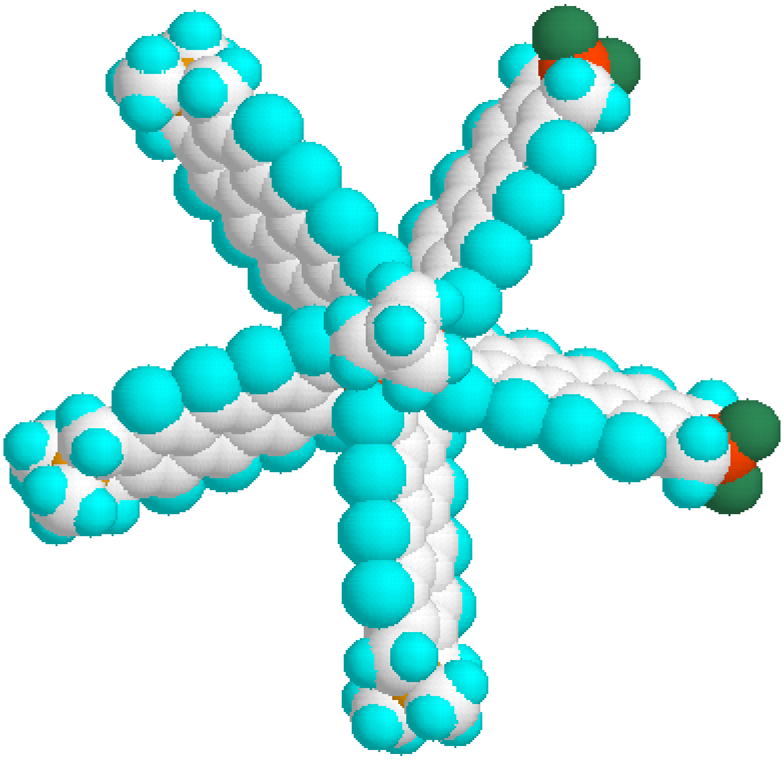

Fig. 1. Five – fold molecular propeller. Top view. The aromatic blades are mounted on a 12 – vertex carborane CB_{11}^{-}. There are two blades with a negatively charged group and three with a positively charged group, so that the whole structure is neutral. The charged groups are of the following kind: – $N(CH_3)_3^{+}$ and – $BCH_3F_2^{-}$. There is one cyclopentadien on the top of the carborane and one under the carborane (on the rotational axis).