

Molecular Machines: Rotational Motion, Molecular Impellers, and an Operational Nanovalve

Jeffrey I. Zink

Department of Chemistry and Biochemistry
University of California
Los Angeles, CA 90095

A machine is a system consisting of moving parts attached to a solid support that accomplishes a specific objective. The moving parts in a molecular machine consist of molecules that undergo large amplitude motion in response to photo- or electrical stimulus. The first part of this talk focuses on photo-induced molecular motion. Nano-structured frameworks for molecular machines are then presented briefly, followed by a discussion of three types of operational molecular machines.

Excited State Distortions and Photo-Induced Molecular Motion. Molecular Electronic emission and absorption spectroscopy, resonance Raman spectroscopy, and time-dependent theory are used to determine excited state bond length and bond angle changes in the lowest electronic excited states of large molecules in condensed media.¹ These results provide information about the excited state potential surfaces. Theoretical and experimental methods are introduced and applied to two categories of molecules: transition metal compounds that undergo simple bond lengthening,² and molecules in which the lowest excited state exhibits mixed valency.³ The latter requires interpretation in terms of coupled potential energy surfaces. The time-dependent theory of electronic and resonance Raman spectroscopy is used to interpret the spectra. These examples are representative of “normal” amplitude molecular motion where bond length changes are typically less than ten percent of the ground state bond length.

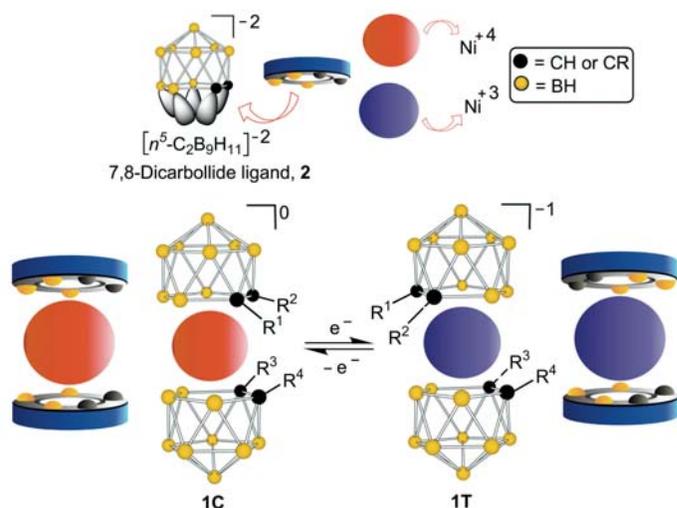
The second part of the talk will examine large amplitude molecular motion that is utilized to design and operate functional molecular machines. Two of the examples that are discussed are rotary motion in a metallocarborane complex and linear motion in a supramolecular rotaxane.

Rotational Motion: a Rotary Motor.⁴ The rotary motion, intramolecular rotation of a carborane cage ligand (7,8-dicarbollide) around a nickel axle, is controlled by simple electron transfer processes and by photoexcitation. The Ni(III) metallocarborane structure is a *transoid*-sandwich with two pairs of carbon vertices related by a center of symmetry, but that of the Ni(IV) species is *cisoid*. The

interconversion of the two provides the basis for controlled rotational oscillatory motion.

Direct spectroscopic evidence for photon-driven rotation is provided by resonance Raman spectroscopy. The largest distortions are associated with the very intense low frequency bands at 63 cm^{-1} and 198 cm^{-1} . Based on density functional theory (DFT) calculations, the 63 cm^{-1} band is associated with the rotational motion, i.e., a dicarbollide-dicarbollide torsional normal coordinate, and the 198 cm^{-1} band is assigned as a metal-dicarbollide elongation, i.e., a symmetric stretch along the ligand-metal-ligand normal coordinate. These distortions, excited by populating the

lowest energy excited electronic state, produce a “corkscrew” motion that simultaneously rotates the ligands and elongates the metal-ligand bonds. The luminescence spectrum provides further supporting evidence for the photon-driven rotation. The emission band is red-shifted dramatically from the corresponding absorption band and contains a large ($> 2000\text{ cm}^{-1}$) energy gap, consistent with a process

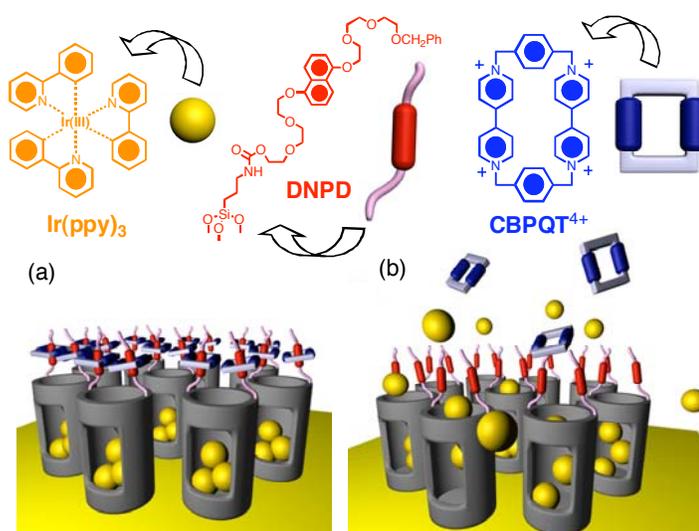


wherein the molecule absorbs a photon, relaxes to its minimum energy configuration in the excited state by rotating, and then emits from this new configuration.

To understand the rotatory operation of the molecule, DFT was used to calculate the molecular and orbital energies as a function of the rotational angle. Time-dependent DFT is used to compute the vertical electronic excitation. The Ni(IV) species has a stable *cisoid* position (144°) and a maximum at the *transoid* position (0°), while Ni(III) is stable at the *transoid* configuration (0°). Upon excitation of Ni(IV), the excited state potential has a minimum at 0° . A large average torque of $8 \times 10^3 \text{ Nm/mole}^{-1}$ is associated with this rotatory motion.

Linear Motion: a Nanovalve.⁵ In [2]pseudorotaxanes, the dethreading and rethreading movements of the rod from the ring component are reminiscent of the motions of a linear motor. In this talk, we discuss (i) the tethering of pseudorotaxanes as gates at the entrances of $\sim 2 \text{ nm}$ diameter, cylindrical pores in nanostructured silica (ii) to create nanovalves (Figure 2) capable of trapping luminescent molecules and able (iii) to release them on demand by an appropriate external stimulus.

The [2]pseudorotaxane shown in the figure is employed as a gatekeeper in the form of a tethered 1,5-dioxynaphthalene containing derivative (DNPd) and acts as the gatepost. Cyclobis(paraquat-*p*-phenylene) which recognizes DNP units on account of a cooperative array of noncovalent interactions, serves as the gate that controls access in and out of the nanopores. Trapped and released tris(2,2'-phenylpyridyl)iridium (III), $\text{Ir}(\text{ppy})_3$ – which has a diameter of ca. 1 nm and exhibits fluorescent emission at 506 nm – is monitored by fluorescence spectroscopy. The operation of the nanovalve involves four stages – (i) preparing the container, (ii) filling it, (iii) closing the valve, and (iv) opening the valve to release its contents. Future applications could involve the trapping and release of other molecules such as drugs and enzymes. This operational supramolecular nanovalve is a true molecular machine consisting of a solid framework with movable parts capable of doing work.



REFERENCES

1. J.I. Zink and K.-S. Kim Shin, "Molecular Distortions in Excited Electronic States Determined from Electronic and Resonance Raman Spectroscopy", *Advances in Photochemistry*, vol. 16 (New York: Wiley), 1991.
2. S.E. Bailey, R.A. Eiekey, M.M. Abu-Omar and J.I. Zink, "Excited-State Distortions Determined from Structured Luminescence of Nitidorhenium(V) Complexes," *Inorg. Chem.*, 41, 1755, (2002).
3. J.V. Lockard, J.I. Zink, A. E. Konradsson, M.N. Weaver and S.F. Nelsen, "Spectroscopic Consequences of a Mixed Valance Excite State: Quantitative Treatment of Dihydrazine Diradical Dictation," *J. Am. Chem. Soc.*, 125, 13471 (2003).
4. M. F. Hawthorne, J. I. Zink, J. M. Skelton, M. J. Bayer, C. Liu, E. Livshits, R. Baer, D. Neuhauser, "Electrical of Photocontrol of the Rotary Motion of a Metallacarborane", *Science*, 303, 1849 (2004)
5. R. Hernandez, H.-R. Tseng, J. W. Wong, J. F. Stoddart and J. I. Zink, "An Operational Supramolecular Nanovalve", *J. Am. Chem. Soc.* **126**, 3370 (2004).