



ÉCOLE POLYTECHNIQUE  
FÉDÉRALE DE LAUSANNE

## Institut de Chimie Physique (ICP)

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# Laboratoire de Chimie Physique Moléculaire

Prof. Dr. Thomas R. Rizzo\*

The Laboratoire de chimie physique moléculaire is concerned with the development of new laser-based spectroscopic techniques and their application both in fundamental and applied research. Fundamental applications focus on investigating the chemical dynamics of molecules with large amounts of vibrational energy with a view toward modelling and perhaps controlling those dynamics. Practical applications are directed toward exploiting the selectivity of multiple laser spectroscopic techniques for analytical purposes and for isotope separation.

### Fundamental Research

A major thrust of our research effort is the development of new laser-based spectroscopic techniques to probe molecules at high energies in their ground electronic state. The frequency-resolved spectra of molecules at high energy provides important information on energy transfer within

a molecule. We measure high vibrational overtone spectra of molecules to learn about their intramolecular dynamics.

Unambiguous interpretation of vibrational overtone spectra requires the elimination of all sources of inhomogeneous congestion. Simplification of congested vibrational spectra can be achieved by cooling the molecules of interest in a supersonic free jet expansion or by the use of double resonance techniques. While both approaches significantly reduce the number of overlapping spectral transitions, for molecules of more than *ca.* five atoms, the simultaneous use of both methods is needed to prepare excited molecules in single rovibrational states on the ground potential-energy surface. Over the last few years, we have developed several double resonance versions of vibrational overtone spectroscopy which, when applied in either static gas cells or in supersonic free jets, allows us to promote molecules to single rovibrational levels at high energy. This degree of simplification has allowed us to examine the spectral splittings as a function of rotational and vibrational state and from these splittings infer the dynamics.

One specific project in our laboratory uses an IR-optical double resonance technique to prepare small molecules in single rovibrational states at energies above that



*Thomas Rizzo.* Born 1956 in Queens, New York. He received a B.S. in chemistry in 1978 at Rensselaer Polytechnic Troy, NY, and a Ph.D. in chemistry 1983 at the University of Wisconsin – Madison, where he worked with Prof. *F.F. Crim*. In 1984, he moved to the University of Chicago, where he did postdoctoral work with Prof. *D.H. Levy*. In 1986, he accepted the position of Assistant Professor of Chemistry at the University of Rochester, and in the same year received a *Camille and Henry Dreyfus Distinguished New Faculty Award*. At Rochester, Prof. *Rizzo* and his group developed a new generation of spectroscopic techniques for investigating highly vibrationally excited molecules. On the basis of this research, he received an *Alfred P. Sloan Fellowship* in 1991, the *Coblentz Society Spectroscopy Award* in 1992, and a *Fellowship* from the Japan Society for the Promotion of Science in 1993. He was promoted to the rank of Associate Professor with tenure in 1992 and Full Professor in 1994. In 1992, he was awarded the *Teacher of the Year Award* from the University of Rochester Student Association. In 1994, Prof. *Rizzo* accepted a position of *Professeur Ordinaire* at the EPFL, where he directs the Laboratoire de chimie physique moléculaire. He teaches courses in quantum chemistry, molecular spectroscopy, and laser applications in chemistry.

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needed to dissociate the molecule on the ground potential surface. An IR laser pulse first picks out molecules in a single or small subset of rotational states *via* a fundamental band of a light atom stretch vibration. An intense pulse from a visible dye laser then promotes the molecule to a state above the dissociation threshold *via* vibrational overtone excitation. The molecule then dissociates to form a fragment which we can probe using a variety of spectroscopic techniques including laser, induced fluorescence (LIF), two-photon ionization, or single-photon VUV ionization.

When applied in different configurations, this type of experiment can provide information on:

- 1) the rates of both intramolecular energy transfer and unimolecular dissociation,
- 2) the partitioning of energy among the dissociation fragments,
- 3) the precise energy of the bond that breaks.

Information of the types 1 and 2 will provide critical tests of statistical and dynamical calculations of unimolecular dissociation dynamics, *ab initio* potential-energy surfaces as well as models of intramolecular energy transfer.

We have recently demonstrated how the IR-optical double resonance photofragmentation can, among other things, provide extremely precise determinations of chemical bond energies by observing which quasibound states lie above and which lie below the dissociation threshold. Obtaining this kind of information is particularly important in the case of small free radicals. Despite the central role these species play in kinetic models of the atmosphere, combustion processes, and chemical vapor deposition, their chemical bond energies are often poorly known. We therefore plan to extend these type of studies to a number of small free radicals.

While this type of photofragment spectroscopy is extremely sensitive, it is limited to molecules with relatively low dissociation energies (< 270 kJ/mol). We have recently developed a variant of overtone induced photofragment spectroscopy that eliminates the restriction to molecules with low dissociation thresholds. In this new approach, a pulse from a CO<sub>2</sub> TEA laser selectively dissociates molecules that have been first excited to a high vibrational overtone level without dissociating the large excess of ground-state molecules. The overtone transition is then monitored by detecting the dissociation fragments as in usual implementations of photofragment spectroscopy. We call this approach IR-laser-assisted photofragment spectroscopy

(IRLAPS), and we have employed it to investigate the vibrational overtone transitions and intramolecular dynamics of a number of small molecules such as methanol, CF<sub>3</sub>H, and CF<sub>2</sub>HCl.

A complete understanding of molecular dynamics of highly excited vibrational states of molecules requires an unambiguous determination of energy transfer rates (IVR) between different vibrational modes as well as unimolecular dissociation rates. In addition to recently introduced techniques in the frequency domain (spectroscopy of highly excited molecules and unimolecular dissociation dynamics), we are undertaking a complementary approach in the time domain using femtosecond laser spectroscopy. By combining the single and double resonance excitation technique with the high time resolution of a femtosecond pulse, we have a highly selective and sensitive measurement tool for determining the dynamics.

In one case, a nanosecond IR laser pulse excites selectively a vibrational fundamental transition, preparing molecules in a specific rovibrational state. From this excited vibrational state, a broadband femtosecond laser pulse excites a vibrational state close to the dissociation threshold. We then probe the reaction products by a second femtosecond pulse to obtain the time scale for dissociation. In another experiment, we use a femtosecond laser pulse to prepare a coherent superposition of vibrational eigenstates by overtone excitation which evolves in time. We then probe the coherent motion of this 'zero-order' state by a second femtosecond laser pulse in either the IR or UV region of the spectrum. The absorption of this second photon is detected by monitoring the dissociation products using a nanosecond laser pulse.

By performing the same experiments in both the frequency domain and time domain, we can better understand the relationship of both approaches and use the one that is most appropriate for a given situation.

### Applied Research

One of the applied projects that have resulted from our fundamental research seeks to use the IRLAPS technique described above to separate the isotopes of silicon with the goal of producing thin films of the isotopically pure substance. Recent studies of isotopically pure diamond have revealed that the small (1%) <sup>13</sup>C impurity in the naturally occurring substance causes substantial changes in

certain properties. For example, reducing the <sup>13</sup>C impurity to 0.1% results in an increase in the room temperature thermal conductivity of 50% and an order of magnitude change in the laser damage threshold at 193 nm. One might expect other materials to exhibit equally dramatic changes in properties upon isotopic purification, including elemental silicon, which naturally occurs in the ratio 92.2:4.7:3.1 for the isotopes <sup>28</sup>Si, <sup>29</sup>Si, <sup>30</sup>Si. This project seeks to prepare pure thin films of <sup>28</sup>Si and <sup>30</sup>Si. Such films will then be examined for their special physical and optical properties.

We plan to separate silicon isotopes using a two-laser scheme in which the first excites the first overtone of the SiH stretch in silane, while a CO<sub>2</sub> laser selectively dissociates only the initially excited isotope. IRLAPS has demonstrated selectivity of more than a million to one for dissociation pre-excited molecules over ground-state molecules. Its successful application for isotope separation of silicon depends upon two factors: 1) our ability to resolve the isotope splittings in the first step of the two-laser scheme, and 2) our ability to generate the proper dissociating wavelengths.

We have recently constructed a time-of-flight mass spectrometer to use in these experiments for direct determination of the degree of isotope selectivity. Upon dissociation of a particular isotope of SiH<sub>4</sub> by IRLAPS, we will photoionize of the resulting SiH<sub>2</sub> radicals and directly detect their mass.

A second applied project uses single-photon vacuum ultraviolet (VUV) ionization of molecules in a time-of-flight mass spectrometer for analysis of complex mixtures. Ionization with a VUV photon tuned just above the ionization threshold results in formation of the molecular ion without fragmentation. This carries great advantages for mass-spectrometric analysis of mixtures insofar as it avoids the complications of overlapping fragmentation patterns that occur from electron impact ionization of such mixtures.

### Research Facilities

We currently operate four laser laboratories with state-of-the-art laser and data collection equipment. This includes Nd:YAG pumped high power dye laser systems with medium (0.04 cm<sup>-1</sup>) and high (0.02 cm<sup>-1</sup>) resolution. With these laser systems we have the capability to do IR difference frequency mixing, frequency doubling and tripling, Raman shifting,

and generation of VUV radiation *via* 4-wave mixing in rare-gases. We also have a Nd:YAG laser pumped lithium niobate OPO that produces tunable IR radiation from 1.2 to 3.5  $\mu$ . For characterization of these laser sources we employ pulsed wavemeters and a pulsed spectrum analyzer. We also have two pulsed TEA CO<sub>2</sub> lasers which produce 1.5 J per pulse at 20 Hz.

For ultrafast time-resolved measurements, we employ a femtosecond laser system containing a cw Ar-ion-laser pumped Ti:Sapphire laser and a Nd:YAG pumped chirped pulse amplification (CPA) system in a temperature- and dust-controlled laboratory. At a repetition rate of 1 kHz the system produces 100 fs laser pulses at 1 mJ pulse energy at 800 nm. For diagnostics we use a scanning autocorrelator and

a Frequency-Resolved Optical Gating (FROG) detector. Tunable visible and IR radiation is created by an optical parametric amplifier which delivers *ca.* 0.1 mJ at 1.6  $\mu$  and 1 kHz repetition rate of the pump laser. For the combination with the nanosecond laser pulses, a 20 Hz Nd:YAG pumped amplifier is set up to boost the energy of the Ti:Sapphire pulses to a level of *ca.* 5 mJ per pulse. We also use a Nd:YAG pumped dye amplifier chain seeded by white light from a continuum generation unit.

#### Some Recent Publications

- 'Laser Techniques in Chemistry', Eds. A.B. Myers and T.R. Rizzo, Wiley, New York, 1995.
- 'Vibrational Overtone Spectra of Jet-Cooled

CF<sub>3</sub>H by Infrared Laser Assisted Photofragment Spectroscopy', O.V. Boyarkin, R.D.F. Settle, T.R. Rizzo, *Ber. Bunsenges. Phys. Chem.* **1995**, *99*, 504.

- 'Rotational State Selected Vibrational Overtone Spectroscopy of Jet-Cooled Molecules' O.V. Boyarkin, T.R. Rizzo, *J. Chem. Phys.* **1995**, *103*, 985.
- 'Double Resonance Vibrational Overtone Spectroscopy of CF<sub>3</sub>H in a Supersonic Free Jet', O.V. Boyarkin, T.R. Rizzo, *Proceedings of the SPIE* **1995**, *2548*, 241.
- 'Multiple Time Scales in the Intramolecular Vibrational Energy Redistribution of Highly Excited Methanol', L. Lubich, O.V. Boyarkin, R.D.F. Settle, D.S. Perry, T.R. Rizzo, *Faraday Discuss. Chem. Soc.* **1996**, *102*, in press.
- 'Secondary Timescales of Intramolecular Vibrational Energy Redistribution in CF<sub>3</sub>H Studied by Vibrational Overtone Spectroscopy', O.V. Boyarkin, T.R. Rizzo, *J. Chem. Phys.* **1996**, *105*, 6285.

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## Research at the Laboratory for Photonics and Interfaces

(Institute of Physical Chemistry II)

Prof. Dr. Michael Grätzel\*

### 1. Introduction

Laboratory for Photonics and Interfaces (LPI), the second chair of the Physical Chemistry Institute will soon be completing 20 years of its existence under the direction of Prof. Michael Grätzel. Set up initially as a chair devoted to study of fundamental aspects of photochemical processes in solution, the research interests of the group have expanded significantly over the years. Today a wide spectrum of research projects are studied cov-

ering areas of photochemistry, photoelectrochemistry, colloids, catalysis (thermal, photo-, and electro-), and surface science. The knowledge and the expertise gained in the first decade working on colloids, membranes and thin films have led to current efforts devoted to photo-, electro-, and photoelectrochemical systems based on nanocrystalline materials. Significant advances in the fields of colloid and sol-gel chemistry in the last two decades now allow fabrication of micro- and nano-sized structures using finely divided monodispersed colloidal particles [1–4]. Nanocrystalline semiconductor films are constituted by a network of mesoscopic oxide or chalcogenide particles such as TiO<sub>2</sub>, ZnO, Nb<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub>, Ta<sub>2</sub>O<sub>5</sub>, CdS, or CdSe, which are interconnected to allow electronic conduction to take place. The pores between the particles are filled with



Michael Grätzel was born in 1944 in Germany. Studied Chemistry at the Free University of Berlin, from where he obtained 'Habilitation' in 1975. Doctoral thesis research (on fast kinetic studies of radiation-induced formation of radicals in solution, Tech. Univ. of Berlin) was carried out at the *Hahn-Meitner* Institute, Berlin, and this was followed by a two-year stay at the Radiation Laboratory of the Univ. of Notre Dame, Indiana, USA. Has been a professor at EPFL since 1977. Served as Head of the Dept. of Chemistry from 1983–1985 and from 1991–1993. Author of over 500 journal publications, two books, two edited monographs, and 10 patents. Has been a visiting Professor at the Univ. of California, Berkeley, and National Renewable Energy Research Labs (NREL), Colorado, USA; Visiting lecturer at Univ. of Texas at Austin, Fellowship of the Japanese Society for the Promotion of Science. Member of editorial board of several journals and acts as consultant to international industrial corporations. Was awarded recently a honorary Doctor of Science (D.Sc. honoris causa) by Uppsala Univ. in Sweden.

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