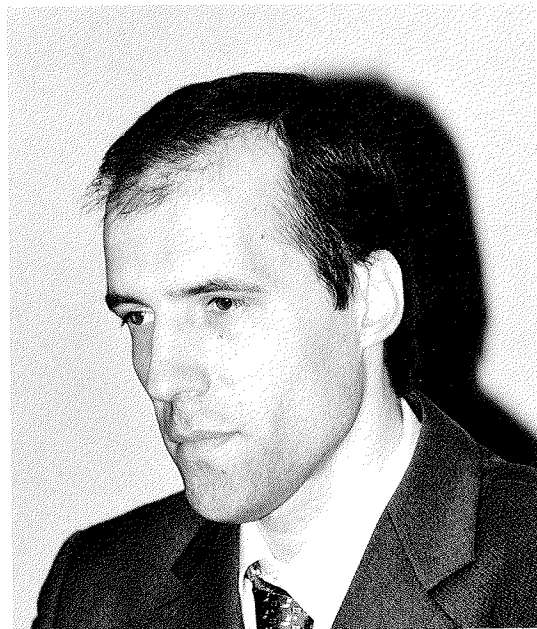


# HOW EXCITING ARE EXCITED MOLECULES ?



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The world around us is a constant state of restless motion : everything keeps changing appearance, shape and structure, sometimes very fast, other times imperceptibly slowly. If we could look down at the molecular level, we would see an intricate dance of atoms and molecules vibrating, interacting and exchanging energy with one another.

Whether our interest is motivated by practical purposes or pure curiosity, we find ourselves challenged with questions like : how do we interrogate matter at this microscopic level ? How do we describe a world that is not just a scaled-down version of the one we are familiar with ? What are the properties of its individual components, atoms and molecules ? How do these interact with one another ? How, finally, do we make sense of it all ?

Answers to such questions come from the increasingly sophisticated instruments that scientists have devised to interrogate matter and from the increasingly powerful models and calculations that they use to make sense of their findings. Figuring out these answers involves fields as diverse as physics, chemistry, biology, mathematics, just to mention a few.

In spite of an enormous body of work, there are many questions still to answer and we have to devise ever more ingenious and sophisticated ways of interrogating nature and convincing her to reveal her secrets. One area of science that has seen, in the last decades, a spectacular development in this sense, is optical spectroscopy : the branch of science concerned with the interaction between light and matter. In every day's life, we routinely perform some simple spectroscopy, perhaps without thinking of it. We do it every time we look at the color and the reflexes of an object to determine something about its nature or its properties and try to answer questions like : is this apple ripe or raw, is there wine or water in this glass, is this object made of metal or plastics ?

While conceptually and technically more involved, the experiments that I have been working on while at EPFL share one important trait with the above simple example. In both cases we observe the light transmitted, reflected and emitted by the object of our interest and from that we deduce some of its properties. We use lasers as a light source, typically three or four of them, each performing a different task. The short and intense bursts of light that they provide are used to select a

specific class of molecules to be investigated, excite them to a well-defined state, break them apart and finally detect the resulting fragments. Thus, we rely on the detection of the fragments as a proof that a whole series of intermediate events has occurred. This elaborate scheme allows us to perform measurements that would be otherwise very difficult or impossible to make. In particular, the ability to reach highly excited states with great sensitivity and selectivity allows singling out one voice from a crowd of different molecules that would all want to talk to us at the same time.

I'd like to focus our attention on a specific example : the measurement of the electric dipole moment of highly vibrationally excited molecules and, in particular, of water. The electric dipole moment is an important property that describes how the electric charge is distributed around in the molecule and how this charge shakes around—like in a microscopic antenna—when the molecule vibrates. This property determines, among other things, how the molecules interact with light and how much they absorb it.

One place where absorption of light by molecules is of enormous relevance is the Earth's atmosphere, as this absorption and the subsequent energy transfer processes have a profound influence on climate. Water is by far the dominant absorber in the atmosphere. It is then of paramount importance for our understanding of climate and of the atmosphere that the role of water is properly understood and modeled but this is, at present, far from being the case. A large fraction of the solar radiation absorbed in the atmosphere is unaccounted for, and many scientists believe that improper modeling of water absorption is the cause of the problem. Substantial controversy exists on the subject, as a direct experimental assessment of water absorption in the region of the solar spectrum turns out to be extremely difficult to achieve with the required precision. Sophisticated computer simulations are nowadays able to calculate molecular properties starting from fundamental physical principles and could potentially solve the controversy, but their accuracy needs to be validated against independent experimental measurements. For this purpose, a very stringent test of the accuracy of these calculations is their ability to reproduce accurate experimental dipole moment measurements of excited vibrational states. These measurements, routinely performed in molecules that are vibrationally at

rest, have so far been very difficult to perform in vibrationally excited molecules.

We have exploited the selectivity and sensitivity of our multiple-laser schemes to develop a technique that allows accurate dipole moment measurements up to very high excitation energies. Briefly, a laser pulse is used to excite selected molecules to a specific, and known, state of vibration and rotation. In the presence of an external electric field the molecules spin around in a complicated motion (precession) similar to that of a gyroscope or of a spinning top. After a prescribed amount of time, a second laser dissociates the excited molecules and a third one probes the resulting products. Since the dissociation probability depends on the relative orientation of the molecule and the dissociating laser, the amount of products detected reflects the precession of the molecule in the electric field. This in turn, depends on the electric dipole moment of the molecule, which can then be determined with high accuracy.

We have measured, with this technique, the dipole moment of water excited with 4, 5 and 8 quanta of OH stretching vibration. The absorption of light by water associated with these states falls exactly in the region where modeling of the absorption spectrum is most controversial. Comparison of our experimental results with *ab-initio* calculations shows important discrepancies and points to a serious possibility that significant problems exist with current models of atmospheric water absorption.

In conclusion, we have developed a general method for measuring the dipole moment of highly vibrationally excited molecules with good accuracy and used it to shed light on the controversial issue of modeling atmospheric water absorption. More generally, our work on highly vibrationally excited molecules shows that with the appropriate tools, small, highly energized molecules are an extremely rich and fascinating ground to explore. It is the combination of sophisticated multiple laser techniques, phenomenological models and accurate *ab-initio* calculations, that provides an unprecedented level of clarity in our understanding of these fundamental systems.