Spectroscopic analysis of molecular quantum mechanics: The reactive and vibrational dynamics of hydroyylamine

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Let me first express my gratitude towards the Latsis Foundation and the ETH Research Committee for the award and for the opportunity to present my work to this distinguished audience. The honour is as great as it was unexpected. Given the increasing political bias economically exploitable projects I draw particular satisfaction from the fact that this prize has been awarded to truly fundamental research. This does not say anything against applied research, but as someone famous once noted: There is nothing as practical as a good theory.

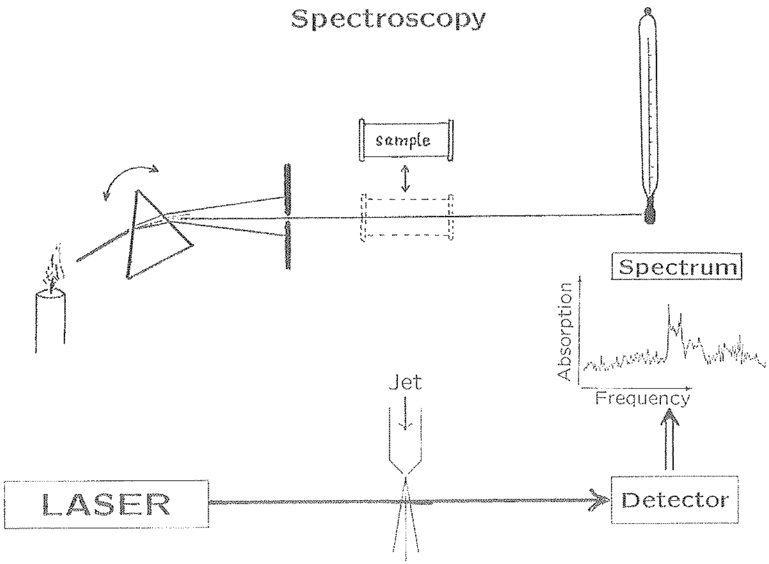
Introduction

A good theory, however, has to build on experiments. Combing the two makes for a powerful tool to unravel the microscopic foundations of chemical reactions. You may wonder whether we do not already know the foundations of chemistry? On a very fundamental level we do – or at least we have good reason to believe that quantum mechanics provides a large part of them – in principle. Solving the equations, however, that describe, e.g., your genetic code or the processes in a chemical plant still belongs to the realm of science fiction. Even if we could calculate every little detail of a DNA molecule with some phantastically fast computer, we still should like to understand. And the understanding lies in intuitive models that qualitatively describe rules and regularities – in scientific jargon approximate separability and symmetries.

Experimental Spectroscopy

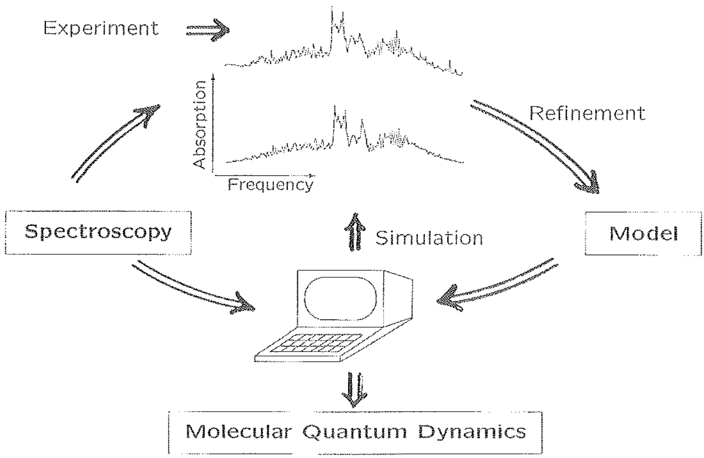
How can we observe the molecular motion? We certainly cannot simply buy a microscope and watch atoms move. In an indirect way, however, spectroscopy provides us with a very special microscope to study the intramolecular motion in the greatest possible detail. How does it work? Essentially spectroscopy is a way of measuring the colour of a molecule by determining how much light of a particular colour is absorbed by a sample.

The wavelength or the frequency of the radiation just are more quantitative measure for the colour of light. Nowadays we may be technically more sophisticated using lasers and electronic detectors to study unusual samples like gaseous jets, but the principle is the same. The Atoms in a molecule typically vibrate at frequencies that correspond to longer wavelengths than our eyes could detect. Therefore we perform most of our experiments with infrared radiation. The absorption as a function of its frequency is what we call the spectrum.



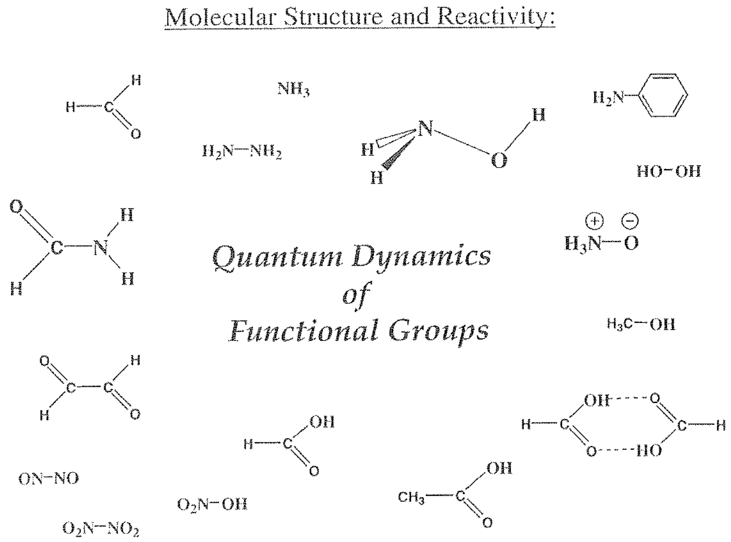
Spectroscopy and Quantum Dynamics

What does the spectrum tell us about the movement of molecules? This is where theory enters. Once we have come up with a model of the molecular motion quantum mechanics tells us how to calculate the spectrum we should observe. These are rather difficult calculations even for the fastest of modern computers, but you will see that the effort we have put into the development of efficient procedures has paid off. The comparison of the computer simulation with the spectrum actually measured tells us how good our model was. Then we can refine it until it agrees with experiment. Thus confirmed we can take the model and use quantum mechanics to compute whatever we want – well almost.



Quantum Dynamics of Functional Groups

In chemistry it is one of the fundamental assumptions that chemical properties are determined by molecular structure. The principle is of enormous practical importance, e.g. in the pharmaceutical industry where phenomenological structure – reactivity relationships are exploited to develop new drugs. As a heuristic principle this idea has been extremely successful, but where lie its microscopic foundations? This eventually leads to the question how atoms move in molecules. Are there types of motion characteristic of certain structural features that give rise to a particular chemical behaviour? If these dynamical properties are transferable between different compounds, how are they influenced by the molecular environment? The most natural way to pursue these fundamental questions is to isolate the subunit of interest in a small model system because there the laws of motion – the «dynamics» – can be investigated in the greatest possible detail. This is exactly what we do in our studies of the quantum dynamics of functional groups. Functional groups are particular subunits which are empirically associated with specific chemical properties. Here you see a small selection of systems we are interested in, built from just four elements: carbon, nitrogen, oxygen, and hydrogen. Combining the so – called aldehyde group with the amino group, e.g., leads to the smallest model for the primary processes of protein folding. Another combination, that of the amino group with the hydroxyl group, plays an important role in atmospheric chemistry.

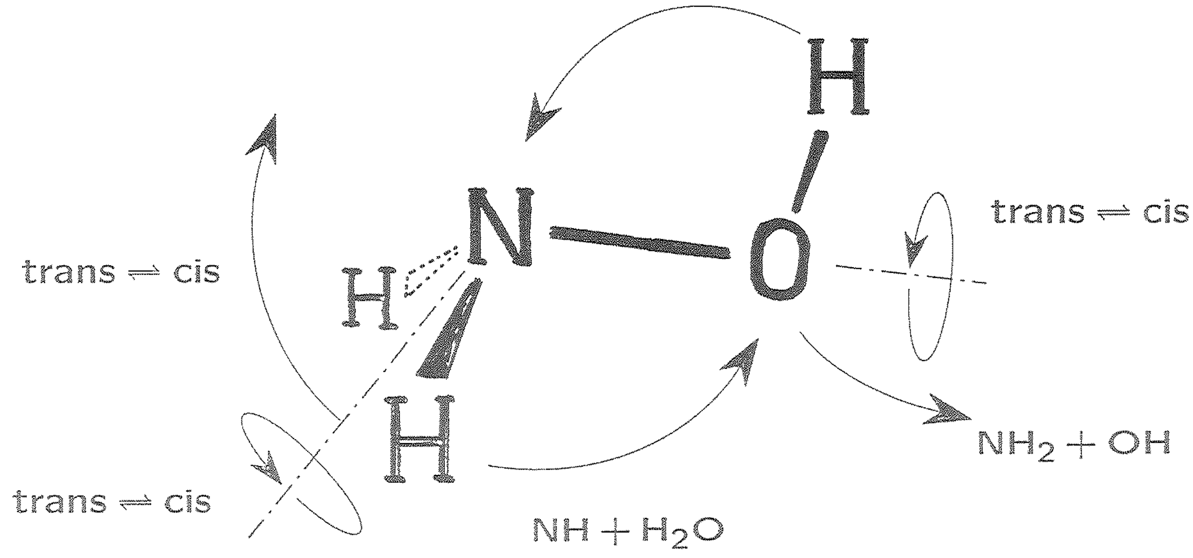


Reactive Vibrational Dynamics: Hydroxylamine

Our study of this particular system – most appropriately called hydroxylamine – beautifully illustrates the approach. The molecule may not strike you as particularly complicated, but the richness of its chemistry is astounding, with each process associated with a particular motion of the molecule. All of them leave their traces in the form of complicated signal patterns in the absorption spectra we measure.

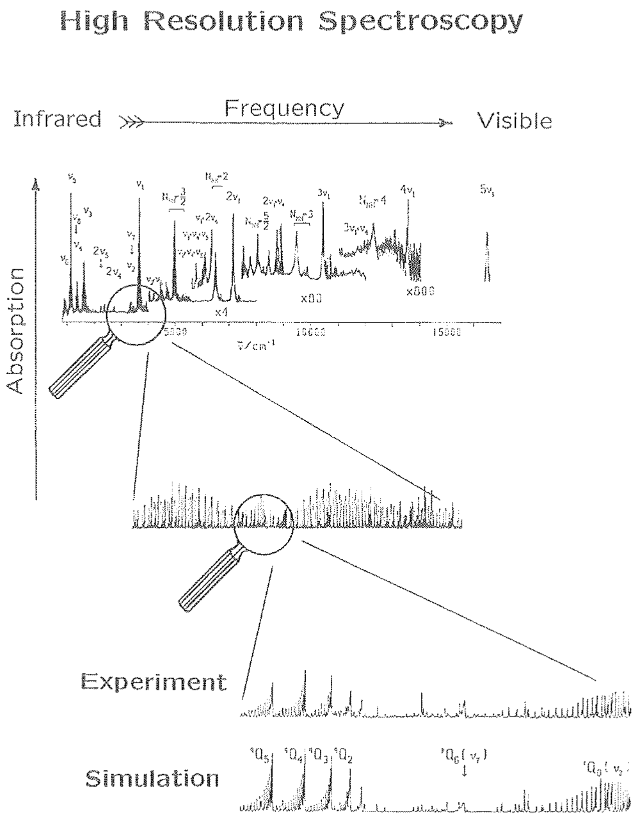
Reactive Vibrational Dynamics in Hydroxylamine

$NH_3 + O_3 \rightarrow\rightarrow NH_3O \rightleftharpoons NH_2OH$



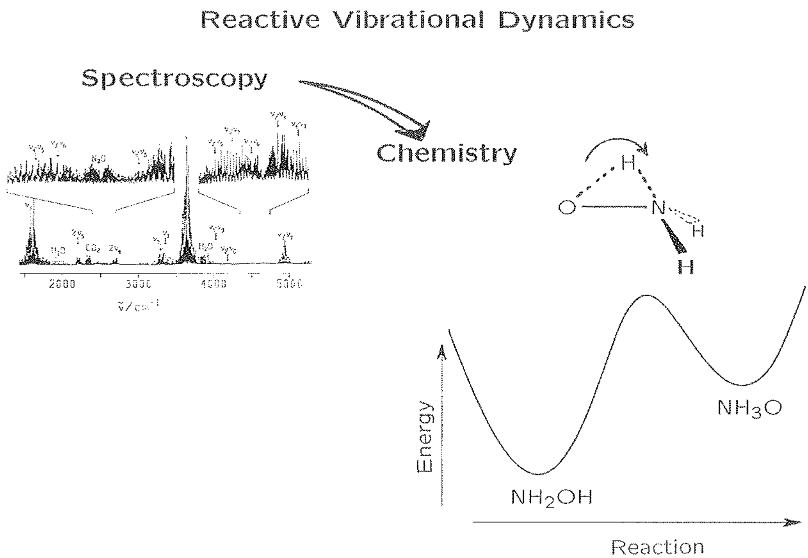
High Resolution Spectroscopy

Our experiments cover the whole range from the infrared to the visible part of the spectrum with characteristic absorption patterns everywhere. On closer inspection each of these patterns decomposes further and further into thousands of sharp signals, so – called absorption lines. This is what we call high resolution spectroscopy. We can put labels on these patterns – the quantum numbers – that already tell us something about the underlying motion. But as I have explained before we even can devise an explicit model to simulate the spectrum. As you can see the simulation agrees with our experiment up to the highest resolution.



Reactive Vibrational Dynamics: Spectroscopy Rightarrow Chemistry

Thus confirmed our model tells us every little detail about what happens on a molecular scale. To pick one example: The more energy we put into the molecule the more it vibrates – just as if the atoms were connected by springs. Nothing unusual so far but at a certain point some of these springs are stretched to such an extent that atoms chance places: a chemical reaction occurs – hence the term «reactive vibrational dynamics». In this case a hydrogen atom transfers from the oxygen to the nitrogen atom to form ammonia oxide – a molecule that should be extremely unstable according to conventional chemical wisdom. Its formation has not only wider implication for the stability of related compounds. It also explains important steps in the atmospheric chemistry and in industrial processes used for cleaning exhaust fumes of power plants. On a microscopic level the hydrogen transfer only takes a trillionth of a second. But we can still observe it without any particularly fast machinery. Such are the wonders of spectroscopy that we can still enjoy a cup of coffee at leisure while the molecules are working for us.



Outlook

Within this short presentation I have of course only been able to give you a glimpse of the treasures molecular spectroscopy holds in store for the chemist. It is the textbook example of an interdisciplinary science between physics and chemistry that allows us to raise those treasures. But I cannot often enough repeat how crucial the proper combination of experiment and theory is for this undertaking – or to put it more philosophically: theory without experiment is void, but experiment without theory is blind.

Acknowledgements

I am pleased to acknowledge on this occasion the support by Professor Quack and his group which my endeavors in the field have enjoyed over the years in Zurich. Our work has greatly profited from the favourable environment fundamental research still finds at the ETH and to which the Latsis foundation contributes in the most generous way. May this never change!