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Research News

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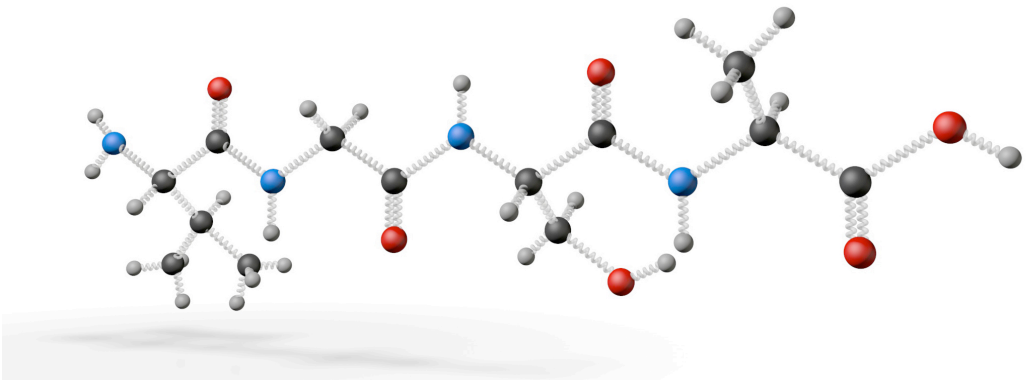
Removing aberrations from the world's greatest microscope

Nowadays, we take the "balls and springs" picture of molecular structure and motion for granted[1]. Indeed, it is hard to overstate the importance of this picture of molecular dynamics. It is in essence how chemists and physicists think about what makes molecules change their shape, move, dissociate, or rearrange. In short it is at the heart of what chemistry is. Furthermore, the "balls and springs" picture of molecular dynamics serves as the basis for real time computer simulations of all kinds of molecular phenomena, even protein folding or enzyme activity. If such computer simulations can be trusted, we may even think of this as the world's greatest microscope, one which yields a picture of the motion of every atom in the system.



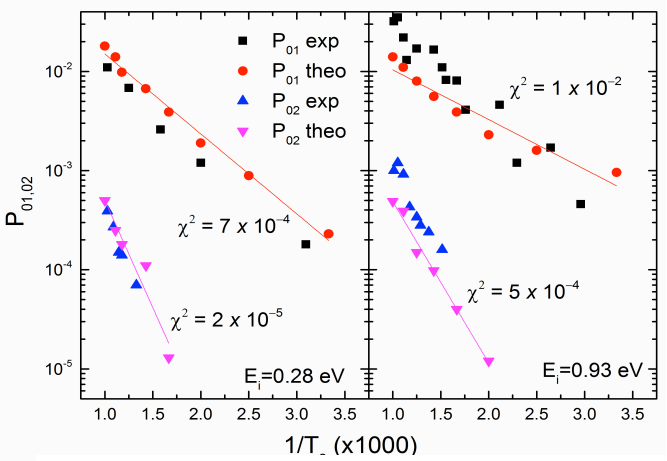
But of course, molecules are not made up of "balls and springs". They are made up of very light negatively charged electrons that move extremely rapidly and positively charged nucleons that move sluggishly by comparison, since their masses are thousands of times larger. We might think of a swarm of bees following an elephant holding a bouquet of flowers with his trunk as he moves. No matter how fast the elephant moves, the bees always find their favorite spot of the elephant (the flowers) to swarm around. Regardless of how the elephant moves, we always know where the bees are. They are near the bouquet. By analogy, because the bee-like electrons move so quickly relative to the elephantine nucleons, we assume that the electrons can adjust instantaneously to the motion of the nucleons. Hence, we always know everything we need to know about what the electrons are doing if we simply

[1] Methods have even been developed to allow the "springs to break" as real chemical bonds must be capable of doing.

know the positions of the nucleons. This assumption, known as the Born-Oppenheimer approximation, allows us to determine, in a relatively simple way, the energy of the molecule in the readjusted field produced by the electrons at every possible position of the nucleons. We call this the potential energy surface (PES) and it is the existence of this PES that allows us to conceptualize molecules like a bunch of balls connected together by springs.

But what if the Born-Oppenheimer approximation were to fail? What if the bees do not always move fast enough to find their favorite swarming spot on the elephant? In that case how the bees swarm depends on how the elephant moves. In molecules, it means that how the electrons swarm around the nucleons depends not only on where the nucleons are, but on how they are moving. In such a case, the theory of molecules and the theory of chemistry is much more difficult and the simple "balls and springs" picture is out the window.

Some years ago we discovered unambiguous experimental evidence that the Born-Oppenheimer approximation breaks down when highly energetic molecules exchange their energy with a solid metal. We could see this in several ways. One of the most convincing experiments showed electrons ejected from the solid metal when a molecule lost vibrational energy. You might imagine the elephant slapping one of the bees so hard with the bouquet of roses that the bee was stunned and knocked to the ground. Since that time it has been clear that new theories of chemistry which do not rely on the Born-Oppenheimer approximation were needed. We needed a way to know how the electrons respond to the motion of the nucleons. Until recently, this has been a frustrating limitation to our knowledge about chemistry.



An example of the comparison between experiment and theory. See Angew. Chemie Int. Ed. 124, 5038-5042 (2012) for details.

In the paper highlighted here[2], we have made the first successful quantitative comparison between a wide set of highly detailed experimental measurements and a theory not relying on the Born-Oppenheimer approximation. This represents a new approach to the theoretical description of chemical reactions that may turn out to be more widely valid than our present methods as it successfully circumvents one of the most fundamental assumptions previously required to describe chemistry.

One of the most interesting aspects of the new understanding we gain from this work is the recognition that energy can be converted from one form to another in ways that were previously not considered likely. That is the nuclear motion, which can be thought of like heat, can be converted to electronic motion. It remains to be seen if this new understanding will lead to new applications in the field of energy conversion. But it is clear that we are making progress in improving the world's greatest microscope, atomic scale simulations of molecular dynamics.

Original publication:

Russell Cooper, Christof Bartels, Aleksandr Kandratsenka, Igor Rahinov, Niel Shenvi, Zhisheng Li, Daniel J. Auerbach, John C. Tully, Alec M. Wodtke: Multiquantum vibrational excitation of NO scattered from Au(111): Quantitative comparison of benchmark data to ab initio theories of nonadiabatic molecule-surface interactions. *Angew. Chemie Int. Ed.*124, 5038-5042 (2012).

[2] *Multiquantum vibrational excitation of NO scattered from Au(111): Quantitative comparison of benchmark data to ab initio theories of nonadiabatic molecule-surface interactions.* Russell Cooper, Christof Bartels, Aleksandr Kandratsenka, Igor Rahinov, Niel Shenvi, Zhisheng Li, Daniel J. Auerbach, John C. Tully Alec M. Wodtke, *Angew. Chemie Int. Ed.* 124, 5038-5042 (2012).

Further Information:

The Department of Dynamics and Surfaces at the Max Planck Institute for Biophysical Chemistry:
www.mpibpc.mpg.de/wodtke

Science & Technology Review: “Using a virtual microscope”
https://www.llnl.gov/str/April01/Colvin.html

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