Chemical Sciences Division

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RNDr. Mirko Rokyta, CSc, Dean
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Dear Dean Rokyta,

I am writing to offer my evaluation of the thesis of Jan Dvořák, entitled "Contribution to theory of low-energy electron-molecule collisions." This thesis is a remarkable work of theory and computation that describes a tour-de-force solution to the question of how the motion of electrons and nuclei are coupled when electrons collide with molecules and can form states in which the colliding electron is temporarily bound to the molecule.

Such collisions have been the subject of experimental and theoretical investigations since the 1970s when it was realized that they create an especially efficient path for the transfer of energy from electrons in electric discharges to molecules in gases. Some of the earliest infrared lasers were powered by such energy transfers from electrons to molecules, and this type of collision became an early and important focus of modern molecular physics. At the end of the 1970s the first theoretical framework that focused on the simplest of such collisions was published by Louis Dubé and Arvid Herzenberg. It was able to treat only the vibration of a single bond in a molecule excited by electronic collisions. For decades no higher dimensional theory was successfully proposed or implemented.

As time went on in the 1990s and the first decade of this century, it became clear that the barriers to understanding this important energy transfer process are more than just questions of the number of molecular vibrations that are involved. It was discovered that molecules typically have more than one metastable electronic state accessible at low energies, and that they interact with each other as the molecule vibrates. As a result of coupling with the energy continuum of states of the electron, simple potential energy functions are insufficient to describe the vibrations of the molecule.

That is the point at which the work in this remarkable thesis and the accompanying experimental studies by the group of Juraj Fedor enter the scene. Jan Dvořák chose in his thesis work to pursue the difficult case of low-energy collisions with the CO_2 molecule, in which not one but three metastable electronic states of the CO_2^- anion play equal roles in the dynamics. He treated not one or two but rather all *four* dimensions of vibrational motion.

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Dvořák develops in this thesis a computational theory that probes the behavior of coupled metastable states at a level of detail and clarity so far beyond what has been done so far to treat this problem that it is a qualitative departure from the previous literature. The key here is that the metastable states (temporary states of the CO_2 anion) are coupled in such a way that the idea of the nuclei moving on potential surfaces that are local functions of the coordinates of the nuclei is simply not applicable. The presence of the virtual state (formally problematic to treat even alone as a single state) in the coupled set of three metastable states precludes any such simpler treatment.

Chapter 1 of the thesis gives a clear description of the problem and the idea of nonlocal potentials for the metastable anion states that couple them to the nonresonant scattering continuum. Then chapter 2 provides the summary of Dvořák's acccomplishment of treating three metastable electronic states and four dimensions of vibration together with a comparison with the original experiments of the Fodor group. This is an article published this year in the prestigious journal, Physical Review Letters. The comparison of theory and experiment in Figure 1 of that article is simply stunning. More important is the result shown in Figure 2 of that paper which appears on page 27 of the thesis.

The puzzle posed by the experiment was why the experiment sees (1) simple peaks in the spectrum of energy loss of scattered electrons corresponding to excitation of vibrational states of CO2 for low energy losses, then (2) a "chaotic" and irregular spectrum at intermediate energies and finally, (3) well resolved multiplets of vibrational peaks at the highest energies. Those highest peaks correspond to vibrational states with 19, 20 or 21 quanta of excitation. Dvořák's theory and calculations reproduce that behavior. In more technical terms these highly excited states of CO_2 are called "polyads" because they involve the excitation of different vibrational motions with similar energies, and they are visible in both the theoretical calculations and the experimental spectrum. This paper, and the one that follows it in Chapter 2 of the thesis, describing the theory and numerical methods in detail break new ground in the study of electron-electron molecule collisions. It is unlikely that we will see the equivalent of this advance in the field applied to other systems for years to come. It is a stunning achievement.

A critical observation of the experiment makes as order returns at energies above the "chaos" is that not all the members of the polyad groups of states are visible in the experiment. The theory in this thesis explains why in the third paper in Chapter 2 that has been submitted to Physical Review A. That paper treats the physics of the polyads in detail in a beautifully clear theoretical development explaining the calculations and exhibiting the wave functions for the highly excited polyad states in Figure 3. This third paper in Chapter 2 identifies and explains the "propensity" rules that govern which states will actually be visible in the experiment. That is an outstanding achievement in this field.

Chapter 3 of the thesis turns to another problem in resonant electronic collisions with molecules. In these collisions the colliding electron forms metastable states, as it does in the case of CO_2. However in this problem the electron can be permanently bound as the metastable anion dissociates into fragments before the it decays back into an excited molecule and an electron. This process is known as dissociative attachment, and it adds the complexity of the dissociative energetic continuum of nuclear motion.

In chapter 3 Dvořák develops a general theory for treating this process in a case that involves two anion states and two nuclear degrees of vibrational freedom. The theory is intended to treat the common case in which both a π and σ resonance (called a virtual state) are involved in the process. The electron attaches to the π metastable state and the nuclear motion couples to the dissociative σ metastable state, which produces the products of the reaction, namely a bound anion and a neutral molecular fragment. Alternatively, the electron can attach directly at lower energies to the dissociative σ state. Both processes are treated in the computational theory in this thesis. This chapter describes, to my knowledge, the most complete treatment of this general case of dissociative attachment that has ever been proposed or implemented.

The case Dvořák studies is dissociative attachment to pyrrole to produce an anion and a hydrogen atom. Despite the complete theory given in the thesis, the computational results still underestimate the cross section for dissociative attachment of electrons to pyrrole that is observed experimentally. The next step in solving this puzzle is not clear. I would have bet that this theory would provided a complete description of the experiment.

Overall, it is my opinion that this thesis constitutes an extraordinary contribution of the highest caliber to the physics of electron-molecule collisions. Two papers based on it have appeared describing its ground-breaking results already, and a third is submitted and will no doubt be accepted by the Physical Review A.

In your letter requesting this evaluation you ask that I comment specifically on the form of the thesis. I think that the form presentation in this thesis is excellent. It combines the author's version of three manuscripts that are published or submitted with clear and complete expository chapters that provide both perspective for the contributions in this thesis and detail of the theoretical ideas.

You also request that I opine as to whether the thesis proves the author's ability for creative scientific work. To that question my answer is an unequivocal "yes." This thesis is a tour-de-force of new theoretical invention and synthesis of earlier ideas in ground-breaking applications. I believe Jan Dvořák has the potential to become a leading theorist in molecular physics, and this thesis is a giant step for him in that direction.

Sincerely,