

# Quantum Chemistry in Basel

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*Abstract.* As an example of our work, a recent study of the *Rydberg* states and dissociation pathways of the  $\text{H}_3\text{O}$  *Rydberg* radical is reviewed.



Martin Jungen was born in and has studied in Basel. He completed his Ph.D. in 1967 with H. Labhart at the University of Zürich. After postdoctoral studies with W. Bingel and W. Kutzelnigg in Göttingen, he returned to Basel for his Habilitation (1973). Since 1987, he has been Professor in Basel.

Today, quantum-chemical programs are accessible to anyone equipped with sufficient computer power; these programs have been made popular recently by a *Nobel* prize. Although this relieves quantum chemists from routine calculations, the situation is somewhat dangerous; it seems to invalidate quantum-chemical research and it gives a powerful instrument to users who often are not sufficiently familiar with the theoretical background and may misuse it.

The focus of my research group is different from conventional quantum chemistry. Our computational work is mainly done with self-made programs. We are interested in the theoretical treat-

ment of molecular electronically excited states, and we collaborate with many experimentalists in the field of molecular spectroscopy. Although our predictions cannot be as precise as the resolution of modern laser spectroscopy, the theoretical attributions of optical transitions (wavelengths and intensities) are often an important aid to the interpretation of spectra. Our research could be called 'Computational Electronic Spectroscopy'.

As an example, I shall review our most recent article 'The  $\text{H}_3\text{O}$  *Rydberg* Radical' [1]. The  $\text{H}_3\text{O}$  molecule does not exist in a chemical sense; in its ground state it dissociates to  $\text{H}_2\text{O} + \text{H}$  or  $\text{H}_2 + \text{OH}$ . Indeed, the ground-state potential surface has been the subject of various quantum-chemical investigations in order to study the elementary reaction:



However, the parent ion  $[\text{H}_3\text{O}]^+$  is a stable species with an equilibrium pyramidal structure similar to that of  $\text{NH}_3$ ; in addition, an infinite number of *Rydberg* states have a potential minimum.

We have been asked to make predictions about the emission wavelengths of highly excited  $\text{H}_3\text{O}$  molecules which would be produced by neutralizing a beam of  $[\text{H}_3\text{O}]^+$  ions. Spectroscopy of this emission is hoped to give insight into the nature of the 'metastable' state states of  $\text{H}_3\text{O}$ ; an analogous case was the famous detection of metastable  $\text{H}_3$  by Herzberg and coworkers 20 years ago. Our task was to find the energies of a number of *Rydberg* levels of  $\text{H}_3\text{O}$  and the intensities of the expected electronic transitions. (*Rydberg* states are electronically excited states often neglected by chemists; they arise when one electron is moving in a spatially extended atomic-like orbital corresponding to a higher principal quantum number). Using our

special methods and programs, this is not complicated. We believe that the precision of the predicted wavelengths is 10 nm. The immediate result of this study was that spectroscopists learned that, in contrast to  $\text{H}_3$ , the most intense emission lines for  $\text{H}_3\text{O}$  should appear not in the visible, but in the infrared spectral region.

Good spectroscopic resolution requires a sufficiently long lifetime of the observed species. By simple comparisons of the calculated energies with possible dissociation limits, it turned out that the final states of some of the most important emission processes of *Rydberg* excited  $\text{H}_3\text{O}$  (namely the two lowest excited semi-valence states) might be dissociative and therefore badly resolved; even continuous spectra should be expected. A detailed quantum-chemical study of the involved potential surfaces, however, resulted in the prediction that a fast dissociation of  $\text{H}_3\text{O}$  is expected only on the ground-state surface. The next two higher electronic states are metastable. After the emission process, the molecule is surrounded by potential walls which it would have to penetrate or transgress after redistribution of vibrational energy before it eventually arrived at a lower-lying dissociation limit. The higher *Rydberg* states of  $\text{H}_3\text{O}$  are stable excited states, *i.e.*, their potential minima are below the respective adiabatic dissociation limits. Although we cannot make precise statements for the lifetimes of the metastable species (the multidimensional problem of nuclear motion requires much more effort than we can afford), we are reasonably hopeful that all the interesting states will be sufficiently long-lived that spectroscopic investigations will be successful.

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