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Modeling of Mutual Anion-Cation Neutralization Processes

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14. ABSTRACT This report results from a contract tasking Laser-Laboratorium Göttingen (LLG) as follows: The Grantee investigated the basic processes in the dynamics of electron-catalyzed mutual neutralization of plasmas. He has arrived at a better quantitative understanding of the rates of 'normal' neutralization processes (1) and the energy partitioning in them. Additionally he compared various options for a theoretical understanding of the electron-catalyzed process (2) and has furthered the most probable explanations.					
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1. Summary

This final report summarizes the progress made over the past year in a variety of projects conducted jointly with Dr. A. A. Viggiano's research group at the AFRL or done within my research group at Goettingen in support of these joint projects. These studies are all centered around a kinetic modeling of the encounter of charged species (ions and electrons), or polar neutrals, either with ions or neutral molecules. Basic theoretical studies included the attachment of electrons to polar/polarizable neutral molecules, the capture of ions by neutral molecules, and the mutual capture of dipolar molecules, all being relevant for a quantitative

understanding of mutual capture of anions and cations to be followed by a kinetic modeling of the dissociation dynamics of highly excited molecular species formed by the latter process. On the experimental side, a number of specific reaction systems were considered and quantitatively interpreted by theoretical methods developed within this grant/award and before. These systems were the attachment of electrons to C_{60} , $POCl_3$, and CF_3 as well as the clustering of NO^+ with water and the subsequent reaction mechanism involving dissociation processes of water-clustered NO^+ species. Studies of the described kind are of central importance for the understanding of a series of practical applications such as plasma-assisted propulsion, reentry of space crafts, and ionospheric chemistry.

2. Introduction

This project continues an extensive research program on the quantitative understanding of elementary processes in plasma chemistry, conducted jointly with the research group of Dr. A. A. Viggiano at the AFRL and supported by basic theoretical work done at Goettingen. During the period of the present report, on the theoretical side models for the capture of electrons by polarizable and polar neutral molecules were elaborated in such a form that they can easily be used by experimentalists to be incorporated in the kinetic modeling of practical systems. At the same time the capture of ions and the mutual capture of dipolar neutral molecules were considered, such that a complete “tool box” now is available for treating at least the initial stages of reactive encounters. For later stages of the excited reaction complexes until the end of the reactive process, a lot needs to be done. To identify these needs, a number of specific reaction systems were studied, each of which represented prototypes of elementary plasmachemical processes. The results of the present collaboration are well acknowledged within the very active community and a continuation appears most promising. Within the AFRL, Dr. Viggiano’s results were acknowledged by the award of the title of an AFRL Fellow and the described research to a small extent contributed to his nomination.

3. Methods, Assumptions, and Procedures

On the theoretical side, capture theory was elaborated by using quantum and classical scattering theory for electrostatic interaction potentials between charged and neutral species. Either these potentials were isotropic or anisotropic. In any case, absorbing boundary conditions were applied for short distances between the reaction partners. It remains to be seen to what extent the capture process can be separated from subsequent reactive processes

of the highly excited either charged or neutral intermediate collision complexes of the reaction. Likewise, in the case of electron attachment and detachment processes, the question of a separability of electronic and nuclear motions needs careful attention.

On the experimental side, the extensive AFRL studies of thermal plasmachemical processes by a variety of ion flow tubes (like SIFT or TIFT) provided data on the pressure and temperature dependences (as well as absolute values) of rate coefficients. The new development of the VENDAMS technique (variable electron and neutral density attachment mass spectrometry) provided an access to hitherto not accessible reactions. The combination of such experimental studies with a quantitative interpretation on the basis of the derived practically useful versions of the theory undoubtedly produced considerable added value.

4. Results and Discussion

4.1 Electron capture theory

In our effort to analyze electron attachment (and the reverse detachment) processes in a quantitative way, we have split the treatment into a first stage, the capture process, and a second stage, the electron-phonon coupling part which incorporates the electron into the electron cloud of the neutral target species. During the present period, we have finished the treatment of the capture processes by casting the results into approximate analytical formulae which are easy to use within kinetic modeling. In these articles we succeeded to include higher partial waves (beyond s-wave capture, see Ref. 1), to account for finite target sizes (important for attachment to clusters like C_{60} , see Ref. 2), and to treat the important influence of polar target molecules (see Ref. 3). Refs. 1 – 3 form the basis for the analysis of the experimental systems described in sections 4.3 – 4.5.

4.2 Theories of ion-quadrupole and dipole-dipole capture

The capture of ions by unpolar molecules can be treated by the well-known Langevin equation. However, this equation is only valid under classical conditions. In earlier work we have investigated at which (low) energies and temperatures quantum effects set in. We now have investigated the influence of molecular quadrupole moments on this onset of quantum phenomena (Ref. 4). At the same time, in Refs. 5 and 6 we have treated the mutual capture of two polar neutral molecules at low energies. Processes of this type in the upper ionosphere compete with ion-molecule processes and, therefore, deserve careful analysis.

4.3 Mechanism of formation of hydrated clusters of NO^+

The capture of water molecules by NO^+ ions and hydrated NO^+ ions, $\text{NO}^+(\text{H}_2\text{O})_n$, is of importance for ionospheric chemistry. In Ref. 7, we have combined new experiments for the reaction, particularly for $n = 2 - 5$, with a kinetic analysis. Recombination, dissociation, and bimolecular metathesis reactions were found to contribute and were modelled as far as this appears possible today.

4.4 Electron attachment to POCl_3

Continuing earlier experimental work on the nondissociative and partly dissociative electron attachment to POCl_3 , being an important electron scavenger, we now were able to provide a complete theoretical modeling of the system. This was our first system with a large dipole moment of the neutral target, to which the theory of Ref. 3 could be applied. We could show that the thermal electron attachment produces nonthermal internal energy distributions of the formed anion (see Ref. 8), a fact which has always been overlooked in the past. Competing dissociations of the formed excited anions explain the product spectrum at moderate temperatures. In Ref. 9, however, we could also show that thermal dissociation of collisionally stabilized anions takes over at high temperatures.

4.5 Electron attachment to clusters like C_{60}

In our attempt to understand electron attachment to medium size and large clusters and to characterize their electron emission lifetimes, we focussed attention on the electron attachment to fullerene C_{60} . Before we could analyze the electron emission from energy-selected C_{60}^- anions, we had to measure the thermal rate constant for electron attachment to C_{60} , see Ref. 10. We succeeded to do this experiment which is of central importance for an understanding of electron emission lifetimes as measured in anion storage rings. We expect more experiments of this type to come from the new generation of ion traps and ion storage rings such that our work has provided a prototype experiment to be repeated with other clusters.

4.6 Electron attachment to CF_3 radicals

Electron attachment to radicals has been studied successfully for the first time. As such reactions with fluorocarbon radicals like CF_3 play a central role in plasma etching of microchips, their detailed study deserved particular effort. For electron attachment to CF_3 , the experiments showed a number of intriguing properties, in particular the fact that the overall

rate as well as product branching fractions depended both on the pressure and the temperature, see Ref. 11. We were able by kinetic modeling to reproduce all experimental observables. The system was interpreted as showing the simultaneous influence of electron attachment, electron detachment, anion collisional stabilization and anion unimolecular dissociation. A particular aspect was the analysis of electron-phonon coupling factors which were assumed to be separable. This aspect will play a major role in our forthcoming analysis of the temperature dependence of electron attachment processes. This property so far has not found a satisfactory quantitative explanation. It is needless to say that further progress of plasmachemical kinetics requires a solution of this problem which will form a central part of our future work.

5. Conclusion

The work of the present grant/award has served a series of purposes. On the way to a complete understanding of electron attachment processes as well as anion-cation mutual neutralization processes, a number of “ingredients” had to be investigated by theory and by combination of experiments with theory. Primary capture processes for the two types of processes now appear reasonably well characterized by approximate analytical expressions which can be easily applied. The second part of the problem, characterized by the interaction of electronic and nuclear motions, requires a large amount of work left for the future. Nevertheless, we feel that large progress could be made and we are grateful to EOARD for the support of our collaboration.

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7. List of Symbols, Abbreviations, and Acronyms

AFRL	Air Force Research Laboratory at Hanscom AFB
EOARD	European Office for Aerospace Research and Development
VENDAMS	Variable electron and neutral density attachment mass spectrometry
SIFT	Selected ion flow tube
TIFT	Turbulent ion flow tube