SPECTROSCOPY AND INTERACTIONS OF METAL AND METAL CATION COMPLEXES

Richard John Plowright

Submitted to the University of Nottingham for the degree of Doctor of Philosophy

January 2010

Abstract

The work in this thesis looks at the spectroscopy and interactions of metals and metal cation complexes. There are two aspects of this vast subject that are considered: the electronic spectroscopy of Au-RG complexes and the ion-molecule chemistry of metals important in the mesosphere-lower thermosphere (MLT) region of the atmosphere.

The spectroscopy of the molecular states in the vicinity of the strong Au $^2P_{3/2,\,1/2} \leftarrow {}^2S_{1/2}$ atomic transition, have been studied for the Au-RG (RG = Ne, Ar, Kr, Xe) series using resonance enhanced multiphoton ionization (REMPI). The spectroscopy of these systems was more involved than expected and high level *ab initio* calculations were required to complement and aid interpretation of the REMPI spectra obtained.

Two main effects were seen to influence the spectroscopy in this energetic region — the mixing between $D^2\Pi_{1/2}$ and $E^2\Sigma_{1/2}{}^+$ states through spin-orbit interactions and the interaction of lower lying states arising from the Au(^2D) + RG ($1S_0$) asymptote, resulting in predissociation being observed.

The MLT is the only region of the Earth's atmosphere in which metals exist in a free atomic state. It is known that their presence in this region occurs *via* the ablation of meteors entering the upper atmosphere, but certain aspects of their chemistry are still unclear.

Using high level *ab initio* theory, spectroscopic constants were determined for metal cation complexes that can be formed in this region. These values are used by collaborators in conjunction with laboratory measurement to establish accurate rate coefficients that will allow the ion-molecule chemistry of calcium and magnesium in the MLT region to be modelled.

Publications covered in this thesis

Theoretical study of the $X^2\Sigma^+$ states of the neutral CM–RG complexes (CM = coinage metal, Cu, Ag and Au; RG = rare gas, He–Rn), A. M. Gardner, R. J. Plowright, M. J. Watkins, T. G. Wright, W. H. Breckenridge, *J. Chem. Phys.*, submitted.

A Velocity Map Imaging Study of the Gold – Rare Gas Complexes: Au-Ar, Au-Kr and Au-Xe, W. S. Hopkins, A. P. Woodham, S. R. Mackenzie, R. J. Plowright and T. G. Wright, *J. Chem. Phys.*, submitted.

Electronic Spectroscopy of the $6p \leftarrow 6s$ Transition in Au–Ne: Trends in the Au–RG Series, R. J. Plowright, A. M. Gardner, C. D. Withers, T. G. Wright, M. D. Morse and W. H. Breckenridge, *J. Phys. Chem. A*, 2010, **114**, 9, 3103.

Theoretical study of Mg^+-X and X-Mg-Y^+ complexes important in the chemistry of ionospheric magnesium, (X,Y = H_2O, CO_2, N_2, O_2 and O), R. J. Plowright, T. J. McDonnell, T. G. Wright and J. M. C. Plane, *J. Phys. Chem. A*, 2009, **113**, 33, 9354.

Theoretical study of Ba^{n+}-RG (RG = rare gas) complexes and transport of Ba^{n+} through RG (n = 1,2; RG = He-Rn), M. F. McGuirk, L. A. Viehland, E. P. F. Lee, W. H. Breckenridge, C. D. Withers, A. M. Gardner, R. J. Plowright and T. G. Wright, *J. Chem. Phys.*, 2009, **130**, 194305.

Electronic Spectroscopy of the Au-Xe Complex, R. J. Plowright, M. J. Watkins, A. M. Gardner, C. D. Withers, T. G. Wright and W. H. Breckenridge, *Phys. Chem. Chem. Phys.*, 2009, **11**, 1539.

Electronic spectroscopy of the Au(6p)-Kr complex, R. J. Plowright, M. J. Watkins, A. M. Gardner, T. G. Wright, W. H. Breckenridge, S. Wallimann and F. Leutwyler, *J. Chem. Phys.*, 2008, **129**, 15, 154315.

Theoretical study of Ca^+-X and Y-Ca^+-X complexes important in the chemistry of ionospheric calcium (X, Y = H_2O, CO_2, N_2, O_2, and O), R. J. Plowright, T. G. Wright and J. M. C. Plane, *J. Phys. Chem. A*, 2008, **112**, 29, 6550.

Qualitative theoretical investigation of Au(6p)-Ar, T. G. Wright, M. J. Watkins, R. J. Plowright and W. H. Breckenridge, *Chem. Phys. Letts.*, 2008, **459** (1-6), 70.

Reinvestigation of the Electronic Spectroscopy of the Au-Ar Complex, R. J.Plowright, V. L. Ayles, M. J. Watkins, A. M. Gardner, R. R. Wright, T. G. Wright and W. H. Breckenridge, *J. Chem. Phys*, 2007, **127**, 20, 204308 .

Other publications not covered in this thesis

The A $^2\Sigma^+$ State of NO-Ne, V. L. Ayles, R. J. Plowright, M. J. Watkins, T. G. Wright, J. Klos, M. H. Alexander, P. Pajón-Suarez, J. Rubayo-Soneira and R. Hernández-Lamoneda, *Chem. Phys. Letts.*, 2007, **441**, 181.

A Theoretical Study of the Ion-Molecule Chemistry of K^+.X Complexes (X = O, O_2, N_2, CO_2 and H_2O): Implications for the Upper Atmosphere, J. M. C. Plane, R. J. Plowright and T. G. Wright. *J. Phys. Chem. A*, 2006, **110**, 3093. [Msci research project]

Acknowledgements

First and foremost I would like to thank my supervisor Tim Wright who first of all planted the seed of interest in this area during my Msci research project. He asked me to come back to his group as a PhD student and I hope I have repaid his faith in my ability. He has been a pleasure to work for and has been understanding of the need for both a summer and winter holiday.

My post-doctorial assistant Mark Watkins was fantastic in teaching me about the experiment. The knowledge he passed on has been invaluable. The super sub challenge is a fond memory. Thanks to Adrian Boatwright who was always on hand if needed when Mark left, and with whom I have enjoyed many a chat.

I have been very lucky in people who I have worked with during my time in Nottingham, all of A40 past and present deserve a mention: Victoria Ayles who aided Mark in my laboratory training, Jay Jeffs and Hisham Al-zubaidi who I originally shared a lab, Carolyn Withers who politely nodded at my many scribblings, Victor Tame-Reyes who greeted me with a bottle of Cuban rum on arrival and project students Tom McDonnell and Jack Graneek who fitted easily in to the group. A special mention to Adrian Gardner who after two summer projects and a Masters project finally joined as a PhD student in August 2009, and with whom I have enjoyed many a night both in and out of the Lab. Also I am thankful to Neil Barnes for salvaging many of my DIY attempts and only mentioning them once or twice a week.

A thank you to the many people who have collaborated on the work in this thesis in particular Scott Hopkins, Stuart Mackenzie, John Plane and Bill Breckenridge and to the EPSRC for the research studentship.

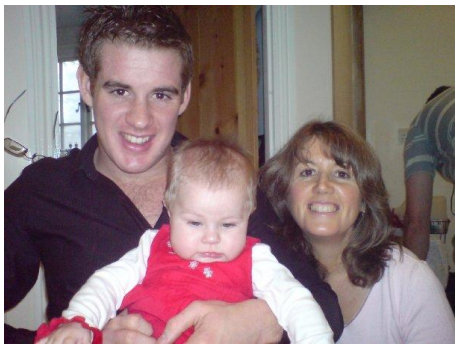
Finally I would like to thank my family and friends for the support they have given me.

The SOCAR group and collaborators (From left to right) Adrian Gardner, Me, Carolyn Withers, Tim Wright, (Mike George and James Calladine) and Mark Watkins

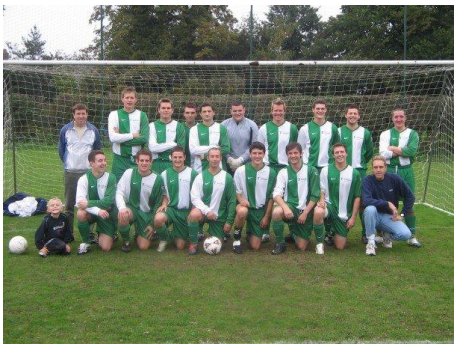
Physical chemistry Christmas meal 2009 (From left to right) Mick Staniforth, Victor Tame-Reyes, Jonny Midgley, Me and Adrian Gardner

A physical chemistry paintballing day — July 2007

Family trip to Sweden — January 2009



Me with my niece and mum — Christmas 2007



SBAFC — September 2007