

Contents

1 Introduction into the Spectroscopy and Interactions of Metal Complexes.....	1
1.1 Introduction into interactions within metal complexes	1
1.2 Au-RG complexes.....	3
1.2.1 Interest in Au-RG complexes	3
1.2.2 Electronic states of interest in the Au-RG complexes	5
1.2.3 Previous investigations of the CM-RG complexes	7
1.2.4 Present study on Au-RG complexes	10
1.3 Metal and metal cation complexes important in the chemistry of the MLT region of the atmosphere.....	11
1.3.1 Introduction to metals in the MLT region of the atmosphere	11
1.3.2 Previous work on chemistry of the metals in the MLT region of the atmosphere	16
1.3.3 Present work on the chemistry of metal cations in the MLT region of the atmosphere	18
References	19
2 Experimental Procedure and Lava Source Design.....	24
2.1 Apparatus	24
2.2 Design of laser vaporization (LaVa) source	30
2.3 Formation of complexes within a supersonic jet expansion ..	35
2.4 Resonance enhanced multiphoton ionization (REMPI).....	37
References	44

3	Electronic Spectroscopy of the Au-Ar Complex.....	46
3.1	Introduction.....	46
3.2	Experimental.....	48
3.3	Results.....	48
3.3.1	$D^2\Pi_{1/2} \leftarrow X^2\Sigma_{1/2}^+$ and $D^2\Pi_{1/2} \leftarrow X^2\Sigma_{1/2}^+$ spectra.....	48
3.3.2	Extrapolation procedures for determining spectroscopic constants.....	52
3.4	Calculations.....	58
3.4.1	Calculations on the $X^2\Sigma_{1/2}^+$ ground state.....	58
3.4.2	Calculations on the excited states.....	60
3.4.3	Accuracy of calculations.....	64
3.4.4	Franck – Condon simulations of the $D^2\Pi_{3/2} \leftarrow X^2\Sigma_{1/2}^+$ Spectrum.....	65
3.5	Discussion.....	67
3.5.1	Au-Ar $X^2\Sigma_{1/2}^+$ state.....	67
3.5.2	Au-Ar $D^2\Pi_{1/2}$ state.....	67
3.5.3	Au-Ar $D^2\Pi_{3/2}$ state.....	73
3.5.4	Au-Ar $E^2\Sigma_{1/2}^+$ state.....	74
3.6	Conclusions.....	75
	References.....	77
4	Electronic Spectroscopy of the Au-Kr Complex.....	79
4.1	Introduction.....	79
4.2	Experimental procedure.....	80
4.3	Results.....	82
4.3.1	Overview of Au-Kr spectra.....	82

4.3.2	Isotopic analysis: Determination of absolute vibrational numbering.....	86
4.4	Calculation on Au-Kr complexes	89
4.4.1	Au-Kr $X^2\Sigma_{1/2}^+$ state.....	90
4.4.2	Au-Kr excited states.....	91
4.5	Analysis of results and discussion	94
4.5.1	Determination of experimental spectroscopic constants for Au-Kr.....	94
4.5.2	Franck-Condon Simulations	100
4.6	Conclusions	103
	References	104
5	Electronic Spectroscopy of the Au-Xe complex.....	106
5.1	Introduction.....	106
5.2	Experimental	107
5.3	Calculations on Au-Xe complex.....	108
5.3.1	Au-Xe $X^2\Sigma_{1/2}^+$ state	109
5.3.2	Au-Xe excited states	110
5.4	Experimental results and discussion.....	113
5.4.1	Spectrum in the vicinity of the Au ($6^2P_{1/2}$) atomic transition	113
5.4.2	Spectrum in the vicinity of the Au ($6^2P_{3/2}$).....	119
5.4.3	Possible involvement of Au-Xe ⁺ charge transfer states.....	126
5.4.4	Possible Involvement of Rydberg states.....	128
5.4.5	Possible involvement of states arising from the Au ($5d^96s^16p^1$) 4P asymptote	128

5.4.6	Mechanism for predissociation of the $D^2\Pi_{3/2}$ and $D^2\Pi_{1/2}$ states.....	132
5.4.7	Comparison to the cation.....	133
5.5	Conclusions	135
	References	136
6	Electronic Spectroscopy of the Au-Ne Complex	139
6.1	Introduction	139
6.2	Experimental	140
6.3	Experimental Results and Discussion	141
6.3.1	Au-Ne $D^2\Pi_{3/2}$ excited state	141
6.3.2	Au-Ne $D^2\Pi_{1/2}$ excited state	143
6.4	Computational methodology.....	145
6.4.1	Au-Ne $X^2\Sigma_{1/2}^+$ state	146
6.4.2	Au-Ne excited state calculations	146
6.5	Discussion	150
6.5.1	Non-observance of the $D^2\Pi_{1/2}$ state	150
6.5.2	FCF Simulation of the $D^2\Pi_{3/2} \leftarrow X^2\Sigma_{1/2}^+$ spectrum	151
6.6	Conclusions	154
	References	155
7	Summary of the Electronic Spectroscopy of the Au-RG Complexes.....	156
7.1	Introduction.....	156
7.2	Trends down Au-RG series.....	156
7.2.1	The $X^2\Sigma^+$ state.....	156
7.2.2	The Au ($6p$) states.....	159

7.2.3	Hunds case (a)/(c) discussion	165
7.3	Velocity map imaging work	168
7.3.1	Au-Xe	169
7.3.2	Au-Ar and Au-Kr.....	172
7.4	Trends down the Coinage metal – RG series	173
7.5	Conclusions	177
	References	179

8 Ca⁺-X and Y-Ca⁺-X Complexes Important in the Chemistry of Ionospheric Calcium (X = H₂O, CO₂, N₂, O₂ and O)..... 182

8.1	Introduction.....	182
8.2	Calculational details	183
8.3	<i>Ab initio</i> calculations on Ca ⁺ -X complexes	185
8.3.1	CaO ₂ ⁺	185
8.3.2	Ca ⁺ -H ₂ O.....	186
8.3.3	Ca ⁺ N ₂	186
8.3.4	Ca ⁺ -CO ₂	187
8.3.5	Ca ⁺ O	187
8.4	Geometries of intermediate complexes	189
8.4.1	Intermediate complexes involving closed shell species .	189
8.4.2	Geometries of O-Ca ⁺ -X (where X is CO ₂ , N ₂ or H ₂ O) intermediate complex ions.....	191
8.4.3	Geometries of O ₂ Ca ⁺ -X (where X = CO ₂ , N ₂ or H ₂ O) intermediate complex ions.....	194
8.4.4	Geometries of O ₂ -Ca ⁺ -O Intermediate cluster ion.....	196
8.4.5	Ca ⁺ (X) ₂ Complexes	199
8.4.6	RCCSD(T) Calculations	201

8.5	Conclusions.....	203
	References.....	205
9	Mg⁺-X and Y-Mg⁺-X Complexes Important in the Chemistry of Ionospheric Magnesium (X = H₂O, CO₂, N₂, O₂ and O).....	208
9.1	Introduction.....	208
9.2	Computational details.....	210
9.3	<i>Ab initio</i> calculations on Mg ⁺ -X complexes.....	212
9.3.1	Mg ⁺ -H ₂ O.....	212
9.3.2	Mg ⁺ -N ₂	213
9.3.3	Mg ⁺ -CO ₂	214
9.3.4	MgO ⁺	216
9.3.5	MgO ₂ ⁺	218
9.3.6	MgO ₃ ⁺	219
9.4	Intermediate Y-Mg ⁺ -X complexes.....	220
9.4.1	Intermediate Complexes involving only closed-shell ligands.....	220
9.4.2	Geometries of [O-Mg-X] ⁺ intermediate complexes where (X= H ₂ O, CO ₂ and N ₂).....	224
9.4.3	Geometries of [O ₂ -Mg-X] ⁺ intermediate complexes (X = H ₂ O, CO ₂ and N ₂).....	227
9.4.4	Geometry of O-Mg ⁺ -O ₂ intermediate complex.....	229
9.4.5	Geometries of Mg ⁺ (X) ₂ complexes (X = H ₂ O, CO ₂ , N ₂ and O ₂).....	232
9.4.6	RCCSD(T) calculations.....	235
9.5	Conclusions.....	237
	References.....	239

List of Figures

Figure 1.1. The general form of a potential energy curve.....2

Figure 1.2. Schematic diagram showing the relationship between the atomic states, on the right-hand side of the figure with the molecular ones, on the left-hand side. Note that for the *A*, *B*, and *C* states the large doubly occupied (Au) 6*s* orbital surrounding the much smaller, singly occupied (Au) 5*d* orbitals has been omitted for the sake of clarity.6

Figure 1.3. Schematic diagram summarizing the important reactions of metals in the MLT region of the atmosphere in which $M = \text{Mg}^+$ and Ca^+ — see text. 15

Figure 1.4. The density profile of an observed (a) descending E_s that leads to the formation of Na_s layer (c). The descent of the E_s was simulated (b) so that the Na density predicted to arise from this event by the atmospheric model (d) could be compared to that observed in the actual sporadic event..... 17

Figure 2.1. Schematic diagram of experimental setup. Diagram adapted from reference 1. The grey triangles represent turning prisms while the dashed line is the gate valve that separates the two vacuum chambers: The nozzle chamber to the left and ionization chamber to the right..... 25

<u>Figure 2.2.</u> Assembly of stepper motor, Au rod, Lava source and Pulsed valve.....	26
<u>Figure 2.3.</u> Schematic of the general timing scheme used. The internal triggering of the Minilite Q-switch, which was relative to the Minilight flashlamps, is not shown on this timing scheme.....	29
<u>Figure 2.4.</u> Schematic of Liquid nitrogen cooling system.....	33
<u>Figure 2.5.</u> Technical diagram of laser vaporization source. Measurements are given in mm.	34
<u>Figure 2.6.</u> Comparison of the range of velocities in the gas reservoir and in the supersonic jet. The supersonic jet can be seen to have a considerably narrower distribution and therefore a considerably lower translational temperature.....	36
<u>Figure 2.7.</u> Diagram showing the two stages of resonance enhanced multiphoton ionization (REMPI). The 1+1' (left) and 1+1 (right) REMPI processes are shown.....	39
<u>Figure 2.8.</u> Diagram showing how FCF affects the intensity of vibrational bands observed on excitation to an excited electronic state..	43
<u>Figure 3.1.</u> Spectrum of Au-Ar corresponding to the $D^2\Pi_{1/2} \leftarrow X^2\Sigma_{1/2}^+$ transition. The dissociation limit is obtained from $T_{1/2} + D_0''$, where	

the ground state dissociation energy was determined from *ab initio* calculations (discussed in section 3.4.1). 50

Figure 3.2. Spectrum of Au-Ar corresponding to the $D^2\Pi_{3/2} \leftarrow X^2\Sigma_{1/2}^+$ transition. The dissociation limit is obtained from $T_{3/2} + D_0''$, where the ground state dissociation energy was determined from *ab initio* calculations (discussed in section 3.4.1). 51

Figure 3.3. A summary of the spectroscopic constants used, or determined, in Section 3.3.2 and in the analysis of Au-RG spectra. From equation 3.3 it can be seen that $\Delta G_{1/2}$ will be equal to $\omega_e - 2\omega_e x_e$ 55

Figure 3.4. LeRoy-Bernstein plot (a) and plot of vibrational spacings against wavenumber for vibrational features observed for the $D^2\Pi_{1/2}$ state. The solid circles represent the analysis of the first set of features ($n - n+6$), whilst open circles represent the analysis of the last set of features ($n+7 - n+11$). 57

Figure 3.5. LeRoy-Bernstein (a) and Birge-Sponer (b) analysis of vibrational features observed in $D^2\Pi_{3/2}$ spectrum. In which ν is that determined in Section 3.4.3. 58

Figure 3.6. RCCSD(T)/aug-cc-pVDZ calculated curves for Au-Ar electronic states arising from the lowest three atomic asymptotes. Note that the $A^2\Delta$ state lies slightly lower in energy than the $B^2\Pi$ state (but this is indiscernible on this scale), and that the $C^2\Sigma^+$ state was omitted from the calculations, but is expected to lie slightly above the

$B^2\Pi$ state. The $E^2\Sigma^+$ state was also omitted, but lies above the $D^2\Pi$ state. 61

Figure 3.7. CASSCF + MRCI + Q calculations for Au-Ar employing the d -aVQZ basis set. 63

Figure 3.8. Franck-Condon simulation of the $D^2\Pi_{3/2} \leftarrow X^2\Sigma_{1/2}^+$ transition for Au-Ar, using spectroscopic parameters calculated for the $D^2\Pi$ state (see text) and calculated spectroscopic parameters for the $X^2\Sigma_{1/2}^+$ state given in Table 3.6. Bottom trace: experimental spectrum. Middle trace: simulation. Top trace: overlay of the experimental and simulated spectra. 66

Figure 3.9. Schematic potential energy curves depicting the evolution of the shelf state. a) The pure Π and Σ curves b) The effects of spin-orbit splitting is shown c) Inclusion of spin-orbit interactions showing the mixing between states of the same Ω value. 73

Figure 4.1. Spectra recorded for the $D^2\Pi_{1/2} \leftarrow X^2\Sigma_{1/2}^+$ Au-Kr transition. The top four isotopically resolved traces were recorded at Bern,¹ whilst the bottom trace showing all the isotopomers was recorded in Nottingham. The absolute vibrational numbering is given; the determination of which is described in the section 4.2.2. The dashed line represents the Au $^2P_{1/2} \leftarrow ^2S_{1/2}$ transition. 83

Figure 4.2. Au-Kr $D^2\Pi_{3/2} \leftarrow X^2\Sigma_{1/2}^+$ spectra. The top trace is spectrum recorded using a (1+1) REMPI scheme in Bern,¹ whilst bottom trace is

recorded using (1+1') REMPI scheme in Nottingham. Absolute vibrational numbering is determined using isotopic analysis of features reported in Table 4.3. 85

Figure 4.3. Re-analysis of Isotopic shifts reported by Wallimann¹ for the $D^2\Pi_{1/2}$ spectra [(a) – (c)] and $D^2\Pi_{3/2}$ spectra [(d) – (f)]. The isotopomers compared for each of the plots are as follows (a) Au⁸⁰Kr and Au⁸⁴Kr, (b) Au⁸⁰Kr and Au⁸⁶Kr, (c) Au⁸³Kr and Au⁸⁶Kr, (d) Au⁸²Kr and Au⁸⁶Kr, (e) Au⁸³Kr and Au⁸⁶Kr, (f) Au⁸⁴Kr and Au⁸⁶Kr. 88

Figure 4.4. Calculated RCCSD(T) potential energy curves for Au–Kr in the absence of spin-orbit interaction. Note that the $A^2\Delta$ state lies slightly lower in energy than the $B^2\Pi$ state (but this is indiscernible on this scale), and that the $C^2\Sigma^+$ state was omitted from the calculations, but is expected to lie slightly above the $B^2\Pi$ state. The $E^2\Sigma^+$ state was also omitted, but lies above the $D^2\Pi$ state. 92

Figure 4.5. CASSCF + MRCI + Q calculations on the $D^2\Pi_{\Omega}$ and $E^2\Sigma_{1/2}^+$ states including spin-orbit coupling. The slight kink in the E state potential is due to the mixing with the $D^2\Pi_{1/2}$ state. INSET: expanded view of the R region of the $D^2\Pi_{1/2}$ state showing the very shallow minimum caused by mixing with the $E^2\Sigma_{1/2}^+$ state. 93

Figure 4.6. Analysis of vibrational features observed for the Au-Kr $D^2\Pi_{1/2} \leftarrow X^2\Sigma_{1/2}^+$ transition. The top plot is that of a LeRoy-Bernstein extrapolation extrapolated to show D_L . The Birge-Sponer plot (middle) is extrapolated to show ν' at the dissociation limit. The fitting of the

vibrational levels to the Morse approximation is shown in the bottom plot. Results are reported in Table 4.5. 94

Figure 4.7. Analysis of vibrational features observed for the Au-Kr $D^2\Pi_{3/2} \leftarrow X^2\Sigma_{1/2}^+$ transition. Top plot: LeRoy-Bernstein plot extrapolated to show D_L . Middle: Birge-Sponer plot extrapolated to show ν' at D_L . Bottom: Vibrational levels are fitted to Morse approximation. Results are reported in Table 4.6..... 96

Figure 4.8. Schematic diagram based on the RCCSD(T) and CASSCF + MRCI + Q calculations, showing the spin-orbit curves relevant to the observed spectral region. Right-hand side: Overview. Left-hand side: Expanded view..... 99

Figure 4.9. The Franck-Condon simulation of the $D^2\Pi_{1/2} \leftarrow X^2\Sigma_{1/2}^+$ transition – see text for details. The simulated spectrum has been scaled so that the most intense feature matches that of the corresponding experimental one (trace e)..... 101

Figure 4.10. Franck-Condon simulation of the $D^2\Pi_{3/2} \leftarrow X^2\Sigma_{1/2}^+$ transition; as can be seen intensity to blue in the experimental spectrum is missing owing to predissociation – see text for details. The simulated spectrum (bold trace) has been scaled so that the intensity of the $\nu' = 27$ feature (indicated by vertical arrow) matches that of the corresponding experimental one..... 103

Figure 5.1. Calculated RCCSD(T) potential energy curves for Au–Xe in the absence of spin-orbit interaction. Note that the minimum of the $A^2\Delta$ state lies slightly lower in energy than that of the $B^2\Pi$ state (but this is indiscernible on this scale), and that the $C^2\Sigma^+$ state was omitted from the calculations, but is expected to be essentially identical with the $B^2\Pi$ and $A^2\Delta$ states. The $E^2\Sigma^+$ state was also omitted, but lies above the $D^2\Pi$ state – see Figure 4.2. 111

Figure 5.2. CASSCF + MRCI + Q calculations on the excited states of Au–Xe including spin-orbit coupling. The D and E states arise from the Au – localized $6^2P_J \leftarrow 6^2S_{1/2}$ excitation, the other states correspond to excitation of the Au 6s electron to the 7s and 7p Rydberg orbitals. The position of the Au($4P_{5/2}$) + Xe($1S$) asymptote has been marked using the experimental value for the Au($4P_{5/2}$) \leftarrow Au($6^2S_{1/2}$) excitation energy..... 112

Figure 5.3. Top trace shows the (1+1) REMPI spectrum obtained for the $D^2\Pi_{1/2} \leftarrow X^2\Sigma_{1/2}^+$ Au-Xe transition. The spectrum was recorded using a gas mix of 1.5 bar Xe topped up to 3.5 bar with Ne. The absolute vibrational numbering was determined from an isotopic analysis of vibrational features above $\nu' = 28$ (see text). Hot bands features are marked by an asterisk. The strong feature marked with an arrow does not fit the vibrational progression, and its intensity changed with conditions relative to the other features in the spectrum; it has yet to be assigned. Bottom trace shows Franck-Condon simulation of spectrum..... 115

Figure 5.4. High resolution scan over $\nu' = 31$ displaying the energy separation of individual isotopomers..... 116

Figure 5.5. Isotopic shift analysis of the features observed for the $D^2\Pi_{1/2} \leftarrow X^2\Sigma_{1/2}^+$ Au-Xe transition (a) – (c) and in the region of the Au ($6^2P_{3/2}$) atomic transition (d) – (e). The larger dots represent the experimental shifts; smaller dots theoretical shifts. ξ represents a running integer variable, allowing theoretical shifts to be compared to experiment..... 117

Figure 5.6. The solid line represents the Morse approximation fit for the $\nu' = 28$ -32 levels of the ^{197}Au - ^{132}Xe . The open circles are the energies of these features and the crosses the energies of the $\nu' < 28$, indicating that all features are part of the same vibrational progression..... 118

Figure 5.7. (1+1') REMPI spectrum of Au-Xe $\Xi_{1/2}$ state..... 121

Figure 5.8. High resolution scan over a single vibrational transition ($\nu' = 8$) of the spectrum in Figure 5.7, showing the contribution of different isotopomers. 122

Figure 5.9. Comparison of Birge-Sponer plots when lower energy features ($\nu' = 4 - 7$) of $\Xi_{1/2}$ spectrum plotted as part of (a) ^{197}Au - ^{129}Xe and (b) ^{197}Au - ^{132}Xe vibrational progressions. The “kink” observed in (b) indicates that the features are not part of this vibrational progression..... 123

Figure 5.10. Schematic of potential energy curves in the energy region close to the Au 6^2P_J levels. The *A*, *B* and *C* states arise from the Au (2D_J) + Xe (1S) asymptotes. These curves are generated by using the RCCSD(T) curves, and shifting them according to the experimental atomic splitting, and assuming the curves are not interacting with any others. The *D* and *E* states are the CASSCF+MRCI+Q curves that have been shifted so that the atomic spin-orbit asymptotes are at the correct energy. The dashed curve represents the state from which the spectrum in Figure 5.7 arises. The left-hand diagram is in the absence of interaction between the dashed curve and the *E* state. The right-hand diagram is in the presence of this interaction. Note the production of a barrier consistent with observations..... 125

Figure 6.1. (1+1) REMPI spectrum of $D^2\Pi_{3/2} \leftarrow X^2\Sigma_{1/2}^+$ transition for $^{197}\text{Au}-^{20}\text{Ne}$. The vibrational numbering was determined from an analysis of isotopic shifts between isotopomers (see text)..... 142

Figure 6.2. Comparison of $^{197}\text{Au}-^{20}\text{Ne}$ and $^{197}\text{Au}-^{22}\text{Ne}$ spectra for the low-energy ($\nu' = 0-2$) region of $D^2\Pi_{3/2} \leftarrow X^2\Sigma_{1/2}^+$ transition. 143

Figure 6.3. Calculated (lines with small circles) and experimental (large circles, with error bars) isotopic shifts between vibrational energy levels in $^{197}\text{Au}-^{20}\text{Ne}$ and $^{197}\text{Au}-^{22}\text{Ne}$, for various absolute numberings, where the $\nu' - \xi$ value labels the observed features. Centres of the asymmetric bands have been estimated. 144

<u>Figure 6.4.</u> Morse analysis (a) and LeRoy-Bernstein analysis (b) of vibrational features observed for the $^{197}\text{Au}-^{20}\text{Ne}$ $D^2\Pi_{3/2}$ state.....	145
<u>Figure 6.5.</u> Calculated RCCSD(T)/aVQZ potential energy curves for the X , A , B and D states of Au-Ne. Note that the A and B states cannot be resolved from each other on this scale, and the C state (not calculated) would also be expected not to be resolvable. The E state, also not included, lies to higher energy (see Figure 6.6)	148
<u>Figure 6.6.</u> CASSCF+MRCI+Q/aVQZ calculations for the $D^2\Pi_{1/2}$, $D^2\Pi_{3/2}$ and $E^2\Sigma_{1/2}^+$ states of Au-Ne.	149
<u>Figure 6.7.</u> Franck-Condon simulation of the $D^2\Pi_{3/2} \leftarrow X^2\Sigma_{1/2}^+$ transition for $^{197}\text{Au}-^{20}\text{Ne}$, using parameters from the ab initio calculations reported (see text). The intensities of the simulated spectrum have been scaled so that the $v' = 0$ intensity matches the experimental one.	152
<u>Figure 6.8.</u> Simulated rotational profiles for the vibrational features of the $D^2\Pi_{3/2} \leftarrow X^2\Sigma_{1/2}^+$ transition for $^{197}\text{Au}-^{20}\text{Ne}$	153
<u>Figure 7.1.</u> CASSCF+MRCI+Q/aVQZ calculations for the $D^2\Pi_{1/2}$, $D^2\Pi_{3/2}$ and $E^2\Sigma_{1/2}^+$ states of Au-He.	160
<u>Figure 7.2.</u> Graph showing how Δ varies with respect to S ; each normalized to the spin-orbit splitting parameter, ζ	166

Figure 7.3. (inset) The Au fragment image observed following excitation of the Au-Xe $\Xi_{1/2}$ ($v'=13$) level. The left hand side shows the raw image, the right hand side the result of the image reconstruction. The smaller less-well resolved rings at the centre of the image are Au atoms produced in direct dissociation of Au-Ar which is produced simultaneously with Au-Xe. The main figure shows the extracted TKER spectra observed by imaging the Au fragment following excitation of each Au-Xe $\Xi_{1/2}$ (v') level. Extrapolation to zero TKER confirms that predissociation occurs into the Au ($^2P_{1/2}$) + Xe (1S) channel. This diagram was produced by Dr. W. Scott Hopkins and used with the permission of Dr. S. R. Mackenzie. 171

Figure 7.4. MOLDEN contour diagrams of the HOMO for each CM-RG complex calculated at the RCCSD(T) R_e values. The spacings of the contours are constant and were selected to show the details clearly for all complexes. The different colours indicate opposite signs of the wavefunction. Diagram produced by A. M. Gardner. 176

Figure 8.1. B3LYP/6-311++G(2d,p) geometry optimized structures of Y-Ca⁺-X complexes. Note that the lines joining atoms do not necessarily indicate a chemical bond. 198

Figure 8.2. Alternative B3LYP/6-311++G(2d,p) and MP2/6-311++G(2d,p) geometry optimized structures of O-Ca⁺-O₂ complexes. Note that the lines joining atoms do not necessarily indicate a chemical bond. 199

Figure 8.3. B3LYP/6-311++G(2d,p) geometry optimized structures of $\text{Ca}^+(\text{X})_2$ complexes. Note that the lines joining atoms do not necessarily indicate a chemical bond.201

Figure 9.1. Schematic diagram of reactions important to the ion-molecule chemistry of Mg and Mg^+ in the MLT region of the atmosphere. The red arrows represent ligand switching reactions..210

Figure 9.2. B3LYP/ 6-311G(2d,p) Optimized geometries of Mg^+-X complexes. Note that the lines joining atoms do not necessarily indicate a chemical bond.217

Figure 9.3. B3LYP/6-311+G(2d,p) optimized geometries of $[\text{X}-\text{Mg}-\text{Y}]^+$ complexes. Note that the lines joining atoms do not necessarily indicate a chemical bond.223

Figure 9.4. B3LYP/6-311+G(2d,p) optimized geometries of $[\text{MgX}_2]^+$ complexes. Note that the lines joining atoms do not necessarily indicate a chemical bond.233

List of Tables

<u>Table 3.1.</u> Summary of spectroscopic constants derived in reference 1.	47
<u>Table 3.2.</u> Line positions for $D^2\Pi_{1/2} \leftarrow X^2\Sigma_{1/2}^+$ spectrum shown in Figure 3.1. The first observed peak is denoted as n	49
<u>Table 3.3.</u> Line positions for $D^2\Pi_{3/2} \leftarrow X^2\Sigma_{1/2}^+$ spectrum shown in Figure 3.2. The first observed peak is denoted as n	51
<u>Table 3.4.</u> Results of LeRoy-Bernstein and vibrational spacing analysis for the $D^2\Pi_{1/2}$ state. Details in text.	56
<u>Table 3.5.</u> Results of LeRoy-Bernstein and Birge-Sponer analysis for $D^2\Pi_{3/2}$ state.	57
<u>Table 3.6.</u> Au-Ar $X^2\Sigma_{1/2}^+$ state calculated spectroscopic constants at RCCSD(T) level using specified basis set.	59
<u>Table 3.7.</u> Rotational constants required to obtain a theoretical peak shape and width similar to that observed experimentally for the $D^2\Pi_{1/2}$ state. B_0'' was determined theoretically as 0.036 cm^{-1} . The dashed line indicates the change in regime within the progression.	68

Table 3.8. Rotational constants required to obtain a theoretical peak shape and width similar to that observed experimentally for the $D^2\Pi_{3/2}$ state. B_0'' was determined theoretically as 0.036 cm^{-1}74

Table 4.1. Spectroscopic constants for Au-Kr reported by Wallimann.¹ Details in text.80

Table 4.2. Assignment of features observed for the $D^2\Pi_{1/2} \leftarrow X^2\Sigma_{1/2}^+$ transition. The positions for “all isotopomers” was determined at Nottingham, whilst the isotopically resolved complexes were recorded at Bern.¹.....84

Table 4.3. Assignment of features observed for the $D^2\Pi_{3/2} \leftarrow X^2\Sigma_{1/2}^+$ transition. The positions for “all isotopomers” was determined at Nottingham, whilst the isotopically resolved complexes were recorded at Bern.¹.....86

Table 4.4. Calculated spectroscopic constants for $^{197}\text{Au}-^{84}\text{Kr } X^2\Sigma_{1/2}^+$ 91

Table 4.5. Spectroscopic constants (cm^{-1}) obtained using vibrational features of $D^2\Pi_{1/2} \leftarrow X^2\Sigma_{1/2}^+$ spectrum of $^{197}\text{Au}-^{84}\text{Kr}$95

Table 4.6. Spectroscopic constants (cm^{-1}) obtained using vibrational features of $D^2\Pi_{3/2} \leftarrow X^2\Sigma_{1/2}^+$ spectrum of $^{197}\text{Au}-^{84}\text{Kr}$96

<u>Table 5.1.</u> Calculated spectroscopic constants for $^{197}\text{Au}-^{132}\text{Xe } X^2\Sigma^+$	110
<u>Table 5.2.</u> Transition wavenumbers for the $D^2\Pi_{1/2} \leftarrow X^2\Sigma_{1/2}^+$ transition. For $\nu' = 28-32$ these are isotopomer specific, as noted; for $\nu' = 16-27$, these are the peak maxima, which are expected to correspond to the $^{197}\text{Au}-^{132}\text{Xe}$ isotopomer.	114
<u>Table 5.3.</u> Table of spectroscopic constants derived for the $D^2\Pi_{1/2}$ state (cm^{-1}).....	119
<u>Table 5.4.</u> Table showing $^{197}\text{Au}-\text{Xe}$ isotopomer line positions (cm^{-1}) for the $\Xi_{1/2}$ spectrum. For $\nu' = 8-13$ these are isotopomer specific as noted in text; for $\nu' = 4-7$ the reported position corresponds to the peak maxima suspected to be $^{197}\text{Au}-^{129}\text{Xe}$. ¹⁸	121
<u>Table 5.5.</u> Table of spectroscopic constants derived for the $\Xi_{1/2}$ state (cm^{-1}).	124
<u>Table 5.6.</u> D_0 values for the $D^2\Pi_{3/2}$ excited state and $X^1\Sigma^+$ cation states and their ratios.....	134
<u>Table 6.1.</u> Line position (cm^{-1}) for features observed for the $D^2\Pi_{3/2} \leftarrow$ $X^2\Sigma_{1/2}^+$ transition.	143
<u>Table 6.2.</u> Derived spectroscopic constants (cm^{-1}) for the $^{197}\text{Au}-^{20}\text{Ne}$ $D^2\Pi_{3/2}$ state.	145

<u>Table 6.3.</u> Calculated spectroscopic constants, and 0-1 and 1-2 vibrational intervals for the $X^2\Sigma_{1/2}^+$ state of $^{197}\text{Au}-^{20}\text{Ne}$ at the RCCSD(T) level of theory.	146
<u>Table 7.1.</u> Calculated spectroscopic constants, and 0-1 and 1-2 vibrational intervals for the $X^2\Sigma^+$ of Au-RG at the RCCSD(T) level of theory.	158
<u>Table 7.2.</u> CASSCF+MRCI+Q+SO values of Δ/ζ for Au-RG at the minima of the $D^2\Pi_{3/2}$ curves. Also included are the RCCSD(T)/daVQZ R_e and D_e values for the $D^2\Pi$ excited state neutral and $X^1\Sigma^+$ ground cationic states.....	165
<u>Table 7.3.</u> Variation in separation of $D^2\Pi_{1/2}$ and $D^2\Pi_{3/2}$ states of $^{197}\text{Au}-^{84}\text{Kr}$ as a function of ν' . Ratio is that of the separation to the atomic value of 3815.4 cm^{-1}	167
<u>Table 7.4.</u> Summary of theoretically derived spectroscopic constants for the $X^2\Sigma_{1/2}^+$ state of the CM-RG complexes. Constants presented for Cu-RG and Ag-RG complexes are “best” results from reference 9, whilst those for Au-RG are from this work.	174
<u>Table 8.1.</u> Dissociation energies (kJ mol^{-1}) for Ca^+-X complexes ($\text{X} = \text{H}_2\text{O}, \text{CO}_2, \text{N}_2, \text{O}$ and O_2).....	186

Table 8.2. Total energies, electronic states and harmonic vibrational frequencies for X-Ca⁺-Y complexes (where X and Y = CO₂, N₂ and H₂O) calculated at MP2/6-311++G (2d,p) level of theory. Note that N₂(s) indicates N₂ approaching in a side-on manner, whilst *i* indicates an imaginary frequency. The global minima are highlighted. 190

Table 8.3. Total energies, electronic states and harmonic vibrational frequencies for X-Ca⁺-Y complexes (where X and Y = CO₂, N₂ and H₂O) calculated at B3LYP/6-311++G (2d,p) level of theory. Note that N₂(s) indicates N₂ approaching in a side-on manner, whilst *i* indicates an imaginary frequency. The global minima are highlighted. 191

Table 8.4. Total energies, electronic states and harmonic vibrational frequencies for OCa⁺-Y complexes (where X = CO₂, N₂ and H₂O) calculated at MP2/6-311++G (2d,p) level of theory. Note that N₂(s) indicates N₂ approaching in a side-on manner, whilst *i* indicates an imaginary frequency. The global minima are highlighted. 193

Table 8.5. Total energies, electronic states and harmonic vibrational frequencies for OCa⁺-X complexes (where X = CO₂, N₂ and H₂O) calculated at B3LYP/6-311++G (2d,p) level of theory. Note that N₂(s) indicates N₂ approaching in a side-on manner, whilst *i* indicates an imaginary frequency. The global minima are highlighted. 194

Table 8.6. Total energies, electronic states and harmonic vibrational frequencies for O₂Ca⁺-X complexes (where X = CO₂, N₂ and H₂O) calculated at MP2/6-311++G (2d,p) level of theory..... 195

Table 8.7. Total energies, electronic states, harmonic vibrational frequencies for O_2Ca^+-X complexes (where $X = CO_2, N_2$ and H_2O) calculated at B3LYP/6-311++G (2d,p) level of theory. 195

Table 8.8. Total energies, electronic states and harmonic vibrational frequencies for the O_2Ca^+-O complexes calculated at B3LYP/6-311++G (2d,p) level of theory. Note that $O_2(s)$ indicates O_2 approaching in a side-on manner, whilst i indicates an imaginary frequency. The global minima are highlighted. 197

Table 8.9. Total energies, electronic states and harmonic vibrational frequencies for $Ca^+(X)_2$ complexes calculated at the B3LYP/ 6-311++G(2d,p) level. Note that sN_2 or sO_2 indicates N_2 or O_2 approaching in a side-on manner. The global minima are highlighted. 200

Table 8.10. RCCSD(T)/aug-cc-pVQZ/B3LYP/6-311++G(2d,p) total energies and summary of lowest energy state and associated rotational constants. 202

Table 8.11. Binding Energies for $X-Ca^+-Y$ Complexes ($kJ mol^{-1}$).... 203

Table 9.1. Total energies, electronic states, harmonic vibrational frequencies and rotational constants of the Mg^+-X complexes obtained at the B3LYP/6-311+G(2d,p) level of theory.^a 214

Table 9.2. Dissociation energies (kJ mol^{-1}) of the $\text{Mg}^+\text{-X}$ complexes ($\text{X} = \text{H}_2\text{O}, \text{CO}_2, \text{N}_2, \text{O}, \text{O}_2$ and O_3). D_0 (D_e) values shown.215

Table 9.3. Total energies, electronic states and harmonic vibrational frequencies of the $\text{X-Mg}^+\text{-Y}$ ($\text{X}, \text{Y} = \text{CO}_2, \text{H}_2\text{O}$ and N_2) complexes optimized and calculated at B3LYP/6-311+G(2d,p) level of theory. Rotational constants are given for the highlighted global minima only. $s\text{N}_2$ denotes side-on binding, otherwise the binding is end-on, whilst i indicates an imaginary frequency.221

Table 9.4. Total energies, electronic states and harmonic vibrational frequencies of the $\text{O-Mg}^+\text{-X}$ ($\text{X} = \text{CO}_2, \text{H}_2\text{O}$ and N_2) complexes optimized and calculated at B3LYP/6-311+G(2d,p) level of theory. Rotational constants are given for the highlighted global minima only. $s\text{N}_2$ denotes side-on binding, otherwise the binding is end-on, whilst i indicates an imaginary frequency.226

Table 9.5. Total energies, electronic states and harmonic vibrational frequencies of the $\text{O}_2\text{-Mg}^+\text{-X}$ ($\text{X} = \text{CO}_2, \text{H}_2\text{O}$ and N_2) complexes optimized and calculated at B3LYP/6-311+G(2d,p) level of theory. Rotational constants are given for the highlighted global minima only. $s\text{O}_2$ denotes side-on binding, otherwise the binding is end-on, whilst i indicates an imaginary frequency.228

Table 9.6. Total energies, electronic states and harmonic vibrational frequencies of the $\text{O}_2\text{-Mg}^+\text{-O}$ complexes optimized and calculated at B3LYP/6-311+G(2d,p) level of theory. Rotational constants are given

for the highlighted global minima only. sO₂ denotes side-on binding, otherwise the binding is end-on, whilst *i* indicates an imaginary frequency.....231

Table 9.7. Total energies, electronic states and harmonic vibrational frequencies of the X-Mg⁺-X (X = O₂, CO₂, H₂O and N₂) complexes optimized and calculated at B3LYP/6-311+G(2d,p) level of theory. Rotational constants are given for the highlighted global minima only. sO₂ and sN₂ denotes side-on binding, otherwise the binding is end-on, whilst *i* indicates an imaginary frequency.234

Table 9.8. RCCSD(T) Total Energies236

Table 9.9. Binding Energies, *D*₀ (*D*_e) of the X-Mg⁺-Y complexes (kJmol⁻¹)238