

An experimental investigation of molecular dications
and processes relevant to technological plasmas

A thesis presented for the degree of
Doctor of Philosophy
in the
Faculty of Science and Agriculture

Andrew Edward Slattery

MPhys

Department of Pure and Applied Physics
Queen's University Belfast

January 2004

Abstract

An investigation into the formation and dissociation of ionised molecules is reported in this thesis. The metastability of energy selected molecular ions with two positive charges, molecular dications has been investigated using the threshold photoelectrons coincidence (TPEsCO) ion coincidence technique and VUV synchrotron radiation in the energy range 20 – 50 eV. Lifetimes of energy selected metastable states have been determined from the experimental data obtained with an observation time window of ~ 0.01 to $2 - 4 \mu\text{s}$.

Metastable states of the dications of carbon dioxide (CO_2^{2+}), benzene ($\text{C}_6\text{H}_6^{2+}$), deuterio-benzene ($\text{C}_6\text{D}_6^{2+}$), hexafluorobenzene ($\text{C}_6\text{F}_6^{2+}$) and 2,4-hexadiyne ($\text{C}_6\text{H}_6^{2+}$) have been observed. Comparison of experimental data and theoretical potential energy surfaces suggests that the metastability of CO_2^{2+} is due to slow spin forbidden transitions from excited singlet states to the ground triplet state of the dication, followed by rapid dissociation of the ground state. The lifetimes of the larger molecular dications, $\text{C}_6\text{X}_6^{2+}$, were found to decrease as the internal energy increased. This trend is consistent with both statistical and tunnelling decay mechanisms. Rice, Ramsperger and Kassel (RRK) theory fits to the lifetime data gave approximate dissociation barrier heights of 0.8 to 1.7 eV for $\text{C}_6\text{H}_6^{2+}$ and $\text{C}_6\text{D}_6^{2+}$ and 1.1 to 2.2 eV for $\text{C}_6\text{F}_6^{2+}$. The barriers are expected to be $\sim 1\text{eV}$ higher if the decay mechanism is a tunnelling.

The spectroscopy of these dications was also studied with the TPEsCO technique. The ground and first two excited states of CO_2^{2+} were observed in TPEsCO spectra with vibrational resolution and are compared with time-of-flight-photoelectron-photoelectron coincidence, TOF-PEPECO, data.

The development of a new experiment to investigate the attachment of low energy electrons to molecular radicals is also described here. The interactions of electrons and molecules are of particular interest for the modelling of technological plasmas.

Contents

1.	Introduction	1
1.1	Introduction	2
1.2	Plasmas	2
1.3	Molecules in the Interstellar Medium	3
1.4	Molecular dications	4
1.5	Molecular ion studies	6
1.5.1	Photoionisation	6
1.5.2	Molecular ion spectroscopy	8
1.5.2.1	Photoelectron Spectroscopy	8
1.5.2.2	Zero kinetic energy spectroscopy	9
1.5.2.3	Threshold photoelectrons coincidence	9
1.5.2.4	Time-of-flight photoelectron- photoelectron coincidence	10
1.5.2.5	Double charge transfer	11
1.6	Molecular ion dynamics	11
1.6.1	Photoelectron photoion coincidence	11
1.6.2	TPEsCO ion coincidences	12
1.6.3	True and false coincidences.	13
1.7	Electron - Molecule interactions	15
1.7.1	Electron scattering	15
1.7.2	Electron impact ionisation.	16
1.7.3	Dissociative electron attachment	16
1.8	Molecular dissociation	18
1.9	Unimolecular reaction theory	19
1.9.1	Lindemann theory	20
1.9.2	RRK theory	21
1.9.3	Further developments	25
1.9.4	Kinetic shift	25
1.10	Tunnelling through a potential barrier	26
1.11	Dissociation rates of molecules from single and multiple potential well systems	29

1.11.1	Single potential well	29
1.11.2	Multiple potential well systems	30
1.12	Dication lifetime studies	33
1.13	References	36
2.	Experimental procedure for TPEsCO ion coincidences	39
2.1	Introduction	40
2.2	Light source	41
2.3	Beamline	42
2.4	Apparatus	45
2.5	Threshold electron detection and TPEsCO spectrometry	46
2.6	Time of flight mass spectrometer	47
2.7	Data collection methods	48
2.8	References	49
3.	Data analysis methods	50
3.1	Introduction	51
3.2	Interpretation of coincidence spectra	51
3.3	Removal of false coincidences	57
3.3.1	Random pulse triggered spectra	61
3.3.2	One electron triggered spectra	63
3.3.3	Two electron triggered spectra	69
3.3.4	Experimental considerations for the removal of false coincidences	77
3.4	Monte-Carlo simulations and lifetime calculations	83
3.4.1	The simulation of an ion time-of-flight mass peak	84
3.4.2	The simulation of molecular dication fragmentation	90
3.4.3	Optimisation of Monte Carlo simulation	93
3.4.4	Lifetime determination	96
3.4.4.1	Metastable fraction	98
3.4.4.2	Dissociated fraction	98
3.4.4.3	Undissociated fraction	99

3.4.5	Examples of simulated spectra and lifetime determination	102
3.4.5.1	Iteration process	102
3.4.5.2	Lifetime calculation tests	104
3.5	General considerations	111
3.6	References	115
4.	Results and discussion – CO ₂	116
4.1	Introduction	117
4.2	Spectroscopy of CO ₂ ²⁺	117
4.2.1	The X ³ Σ _g ⁻ ground state	120
4.2.2	The a ¹ Δ _g and b ¹ Σ _g ⁺ excited states	123
4.2.3	Electronic states at higher energies	125
4.3	The Metastability of CO ₂ ²⁺	126
4.3.1	Mass spectra and branching ratios	127
4.3.2	Indirect double photoionisation	132
4.3.3	Lifetime determination	135
4.4	References	139
5.	Results and discussion – C ₆ X ₆	141
5.1	Introduction	142
5.2	Spectroscopy of C ₆ X ₆ ²⁺ dications	142
5.2.1	Benzene, C ₆ H ₆	142
5.2.2	Deutero-benzene, C ₆ D ₆	144
5.2.3	2,4-Hexadiyne, C ₆ H ₆	146
5.2.4	Hexafluorobenzene, C ₆ F ₆	148
5.3	Metastability of C ₆ X ₆ ²⁺	151
5.3.1	Benzene dication, C ₆ H ₆ ²⁺	151
5.3.2	Deutero-benzene dication, C ₆ D ₆ ²⁺	158
5.3.3	Hexafluorobenzene dication, C ₆ F ₆ ²⁺	164
5.3.4	2,4-Hexadiyne dication, C ₆ H ₆ ²⁺	170
5.4	General discussion of dissociation and metastability	176
5.4.1	Dication Lifetimes	176

5.4.2	The fragmentation of $C_6H_6^{2+}$ and $C_6D_6^{2+}$	177
5.4.3	Benzene and deuterio-benzene	178
5.4.3.1	Tunnelling	178
5.4.3.2	Isotope effect	182
5.4.4	Benzene and 2,4-hexadiyne	184
5.4.5	Benzene and hexafluorobenzene	187
5.4.6	Fitting the RRK model to the lifetime data	188
5.4.6.1	Benzene and deuterio-benzene	190
5.4.6.2	2,4-hexadiyne	192
5.4.6.3	Hexafluorobenzene	195
5.5	Investigation of other aromatic molecules	196
5.6	References	197
6.	Low-energy electron radical interactions - a new experiment	199
6.1	Introduction	200
6.2	Apparatus design	200
6.3	Theory and development	201
6.3.1	Electron energy selection and magnetic guidance	201
6.3.1.1	Magnetic field	202
6.3.1.2	Trochoidal electron monochromator	203
6.3.2	Ion detection	205
6.3.2.1	Time-of-flight mass spectrometer	205
6.3.2.2	Preliminary tests of TOFMS	206
6.3.3	Radical production	208
6.4	Preliminary tests for electron-molecule interactions	208
6.5	Conclusions and future development	210
6.6	References	211
	Conclusion	212
	Acknowledgements	215