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

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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 μs.

Metastable states of the dications of carbon dioxide (CO_2^{2+}), benzene ($C_6H_6^{2+}$), deutero-benzene ($C_6D_6^{2+}$), hexafluorobenzene ($C_6F_6^{2+}$) and 2,4-hexadiyne ($C_6H_6^{2+}$) 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, $C_6X_6^{2+}$, 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 $C_6H_6^{2+}$ and $C_6D_6^{2+}$ and 1.1 to 2.2 eV for $C_6F_6^{2+}$. The barriers are expected to be ~ 1eV 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.