Photodissociation dynamics of SCl_2: resonance enhanced multi-photon ionization/time-of -flight mass spectroscopy study

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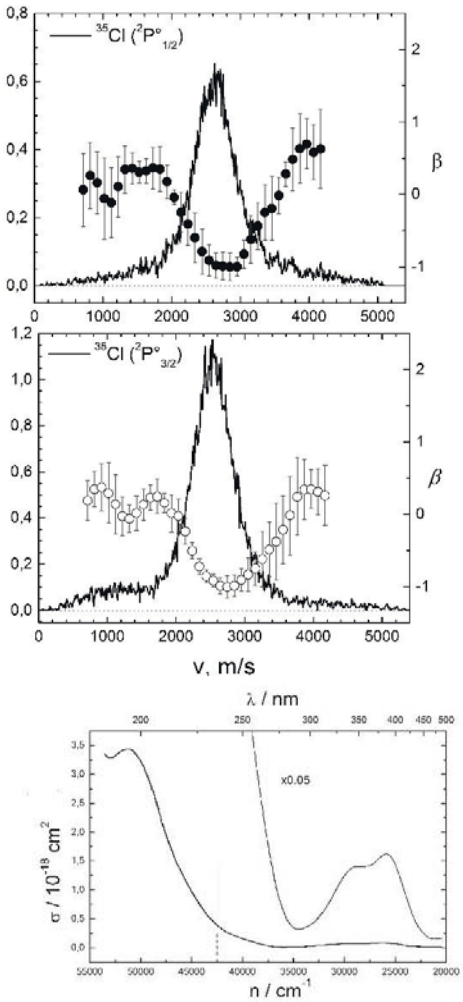
The dynamics of photodissociation of SCl_2 at 235 nm has been studied by monitoring of ground state $Cl(^2P_{3/2})$ and spin-orbitally excited $Cl^*(^2P_{1/2})$ atoms. Time-of-flight mass-spectroscopy and resonance enhanced multi-photon ionization (REMPI) combined with a position sensitive detector (delay-line anode) were employed. The three-dimensional (3D) momentum vector of a single reaction product was directly determined by this ion imaging technique. Also, the S^+ photoions have been produced and monitored by non-resonant multiphoton ionisation.



The speed distributions and speed-dependent anisotropy parameters β for all these three particles have been determined. The speed distributions of $Cl(^2P_{3/2})$ and $Cl^*(^2P_{1/2})$ atoms both have a single main peak, see first figure. This strong peak comes from direct abstraction of Cl atom from the parent molecule, the weak peaks are assigned to secondary processes, mainly to photodissociation of SCl and S_2Cl_2.

The anisotropy parameters β for chlorine atoms are close to -1, indicating that the one-photon photodissociation of SCl_2 at 235 nm is due to the perpendicular transition $^1A_1 \rightarrow {}^1B_2$ in the point symmetry group C_{2v}. The dipole transition moment of this transition is perpendicular to the plane of molecule. In the absorption spectrum of SCl_2 (see second figure) there is another transition $^1A_1 \rightarrow {}^1A_1$, which is much stronger, it has maximum near 190 nm, which is not far from 235 nm. Our β parameter indicates, that this strong transition have very small contribution to the photodissociation of SCl_2 at 235 nm.

The relative yields of excited $Cl^*(^2P_{1/2})$ atoms is found to be 0.38±0.04.