

Photodissociation dynamics of CF₂Cl₂ molecule in aerosol particles

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The chlorofluorocarbons (CFCs) are extremely inert compounds which decay only in the upper stratosphere after absorption of high energy solar radiation. The decomposition pathway can lead to formation of reactive Cl radicals which triggers the ozone depletion cycle. One of the crucial questions for stratospheric chemistry is how is the photodissociation dynamics of these species influenced by the aerosol particles in the stratosphere? The polar stratospheric cloud (PSC) particles can adsorb CFCs and change their photochemistry.

To investigate this effect, we have studied the UV photodissociation of CF₂Cl₂ (CFC-12) molecule in molecular beam experiment: first we study the photodissociation of an isolated molecule, then simulate the influence of the solvent by the simplest archetype solvent species, i.e. rare gas atoms in Ar and Xe clusters, and finally we will investigate the CFC photodissociation on ice nanoparticles.

We have overlapped the molecular beam with two laser beams. The photodissociation was studied at 193 nm, and Cl(²P_{3/2}) and Cl*(²P_{1/2}) fragments were ionized using (2+1) REMPI schemes around 235 nm. The ionic products were guided onto position sensitive 2D detector by velocity mapping electrode configuration. From the images recorded by a CCD camera complete 3D information about the fragment velocities can be obtained.

The Cl-fragments images of are shown in Fig. 1: (a) corresponds to the photodissociation of isolated molecule, and (b) originates from CF₂Cl₂ in clusters. The circular edges in both images correspond to the fast Cl fragment, while the central bright spot in (b) corresponds to Cl atoms with near zero kinetic energy due to the cluster caging effect.

The graph below the images shows the corresponding Cl-fragment kinetic energy distributions (KEDs). These results resolve a discrepancy from the previous CF₂Cl₂ molecule photodissociation studies (Baum 1993, and Yen 1993). The presence of the slow Cl fragments in the spectra points to the secondary dissociation of CF₂Cl fragment radical. Our measurements show that more than one Cl atom can be released per one UV-photon from a CF₂Cl₂ molecule, and also that a Cl₂ molecule can be released instead. In addition all these fragments can be trapped by cage effect if the photodissociation happens on PSC particles. All these conclusions can have significant consequences for stratospheric ozone modelling.

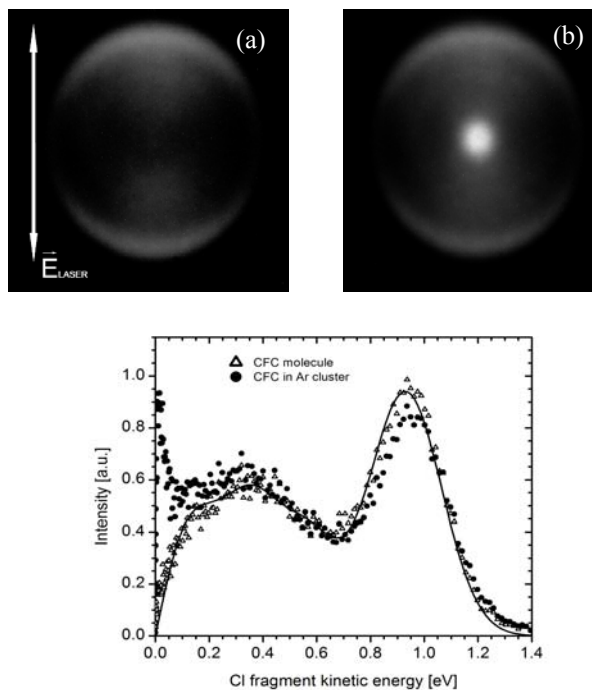


Figure 1. Images of Cl atoms from photolysis of (a) CFC-12 molecules and (b) CFC in Ar clusters, together with corresponding velocity distributions (bottom).

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Baum, G., Huber, J. R. (1993) *Chem. Phys. Lett.* **20**, 261.
Yen, M., Johnson, P. M., White, M. G. (1993) *J. Chem. Phys.* **99**, 126.