

Electrophilic Addition Reaction of Ethene with Hydrogen Chloride on Cold Molecular Films: Evidence of Ethyl Cationic Intermediate

Poong-Ryul Lee, Chang-Woo Lee, Joon-Ki Kim, Eui-Seong Moon and Heon Kang

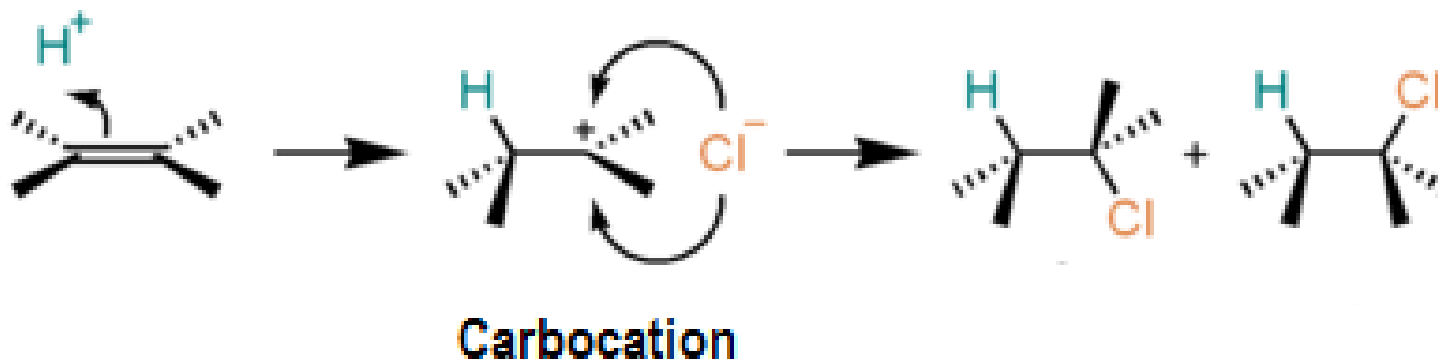
CHEMISTRY
AN ASIAN JOURNAL

Volume 6 Issue 3, March 1, 2011

Rabin Rajan J Methikkalam
(CY11D075)
19-01-2012

Introduction

- Trivalent carbocations are the intermediates in acid catalyzed electrophilic addition reaction of alkenes.



- 1° carbocations have neither been isolated nor identified with spectroscopy because of its lower thermodynamic stability and it was an experimental challenge of detecting 1° carbocations.
- Several studies demonstrated that a cold molecular surface can halt a reaction at an intermediate stage and the trapped intermediate can be identified with spectroscopic methods.

- In the present work electrophilic addition reaction of ethene with HCl on frozen molecular films were carried out.
- The study examines how the reaction proceeds on cold molecular surfaces and inspects the formation of ethyl cation intermediate ($C_2H_5^+$), the effect of water solvation and acid ionization on the reaction rate of the above reaction.
- Temperature-programmed desorption (TPD), reactive ion scattering (RIS) and low-energy sputtering (LES) techniques were used for the study.

Experimental Section

- UHV chamber equipped with instrumentation for Cs⁺ RIS, LES and TPD-MS.
- D₂O ice film was grown on a Ru(0001) substrate at 100 K and annealed at 140 K for 3 min to produce a polycrystalline ice film and the thickness was estimated by a TPD experiment as 2 bilayers (1BL = 1.1×10^{15} water molecules cm⁻²).
- Ethene film was prepared by condensing C₂H₄ or C₂D₄ at 73 K (1-2 molecular layers).
- Cs⁺ beam from a low energy ion gun collided with the sample surface and the scattered ions were detected by a QMS with its ionizer filament switched off.

Results

3.1. HCl and Ethene on water-ice film

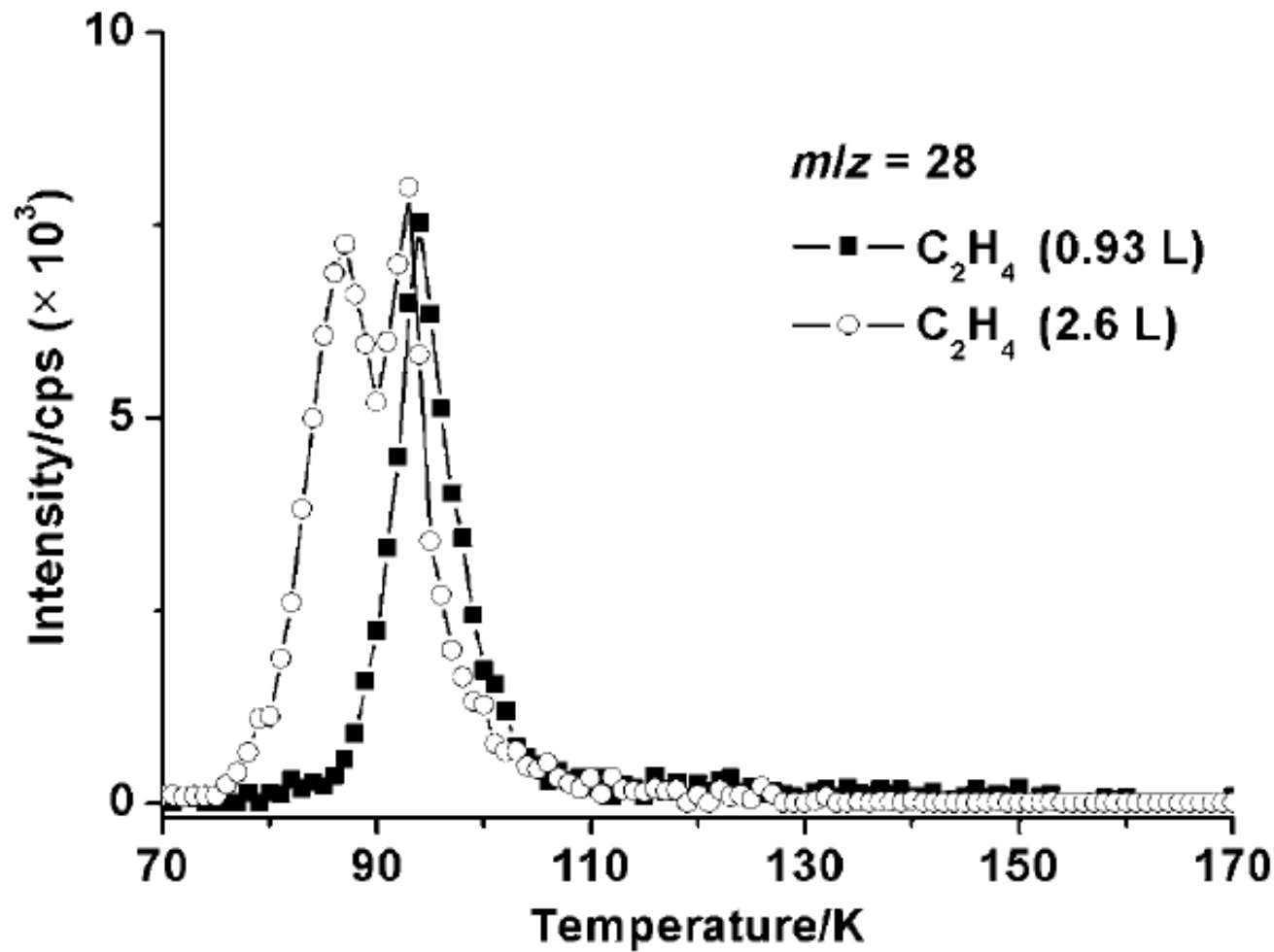


Figure 1. TPD spectra of C₂H₄ adsorbed on D₂O-ice film (2 BL thickness) grown on Ru(0001). C₂H₄ gas exposure was 0.93 L (■) and 2.6 L (○). The sample heating rate was 1 Ks⁻¹. The intensity scale is counts s⁻¹

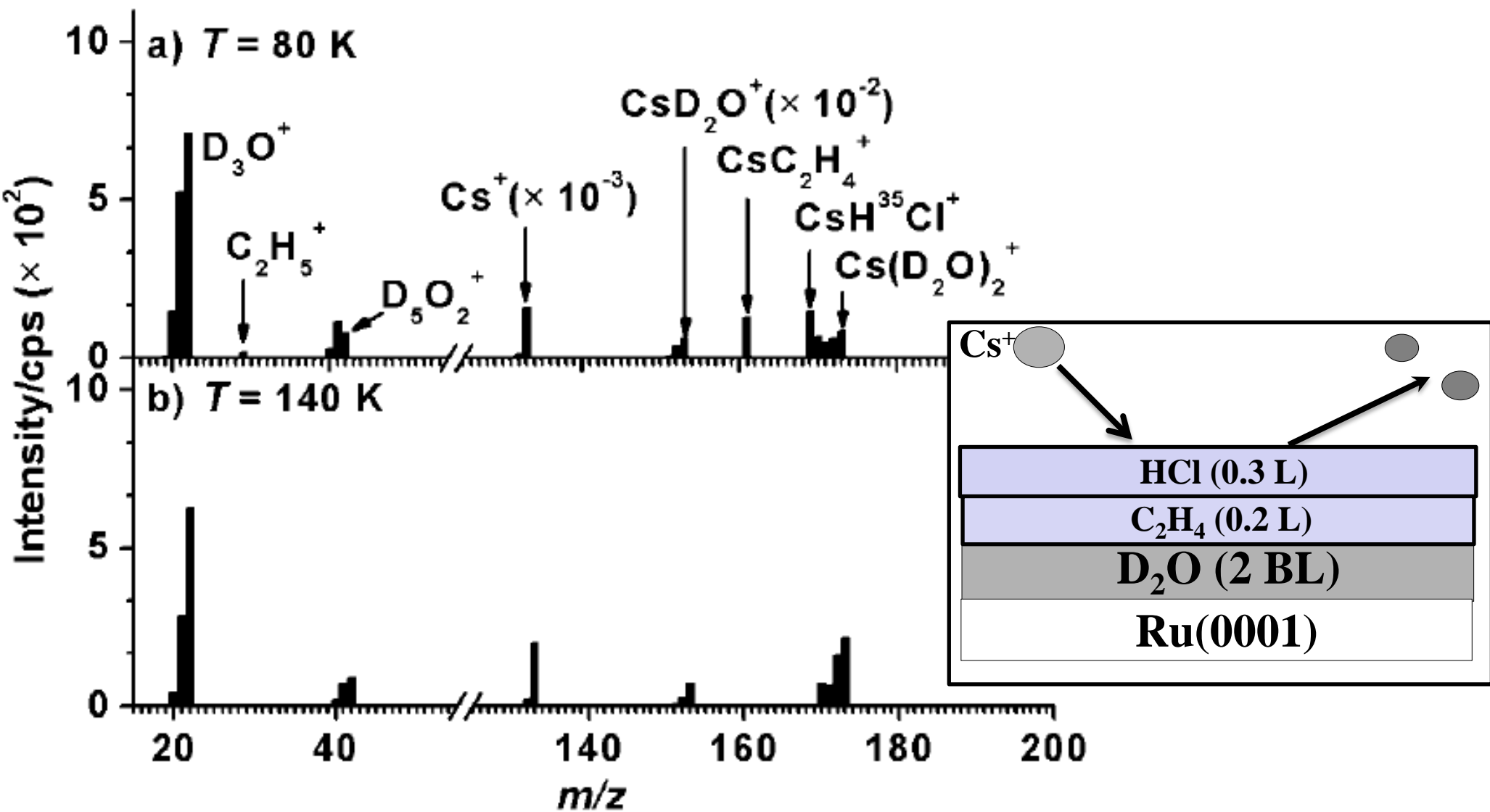


Figure 2. LES and RIS signals measured from D_2O -ice film (2 BL thickness) with adsorbed C_2H_4 and HCl (Sample A). C_2H_4 and HCl gas exposures were 0.2 and 0.3 L, respectively. The spectrum was obtained at sample temperatures of 80 K (a) and 140 K (b). The signal intensities shown are reduced by the factors indicated.

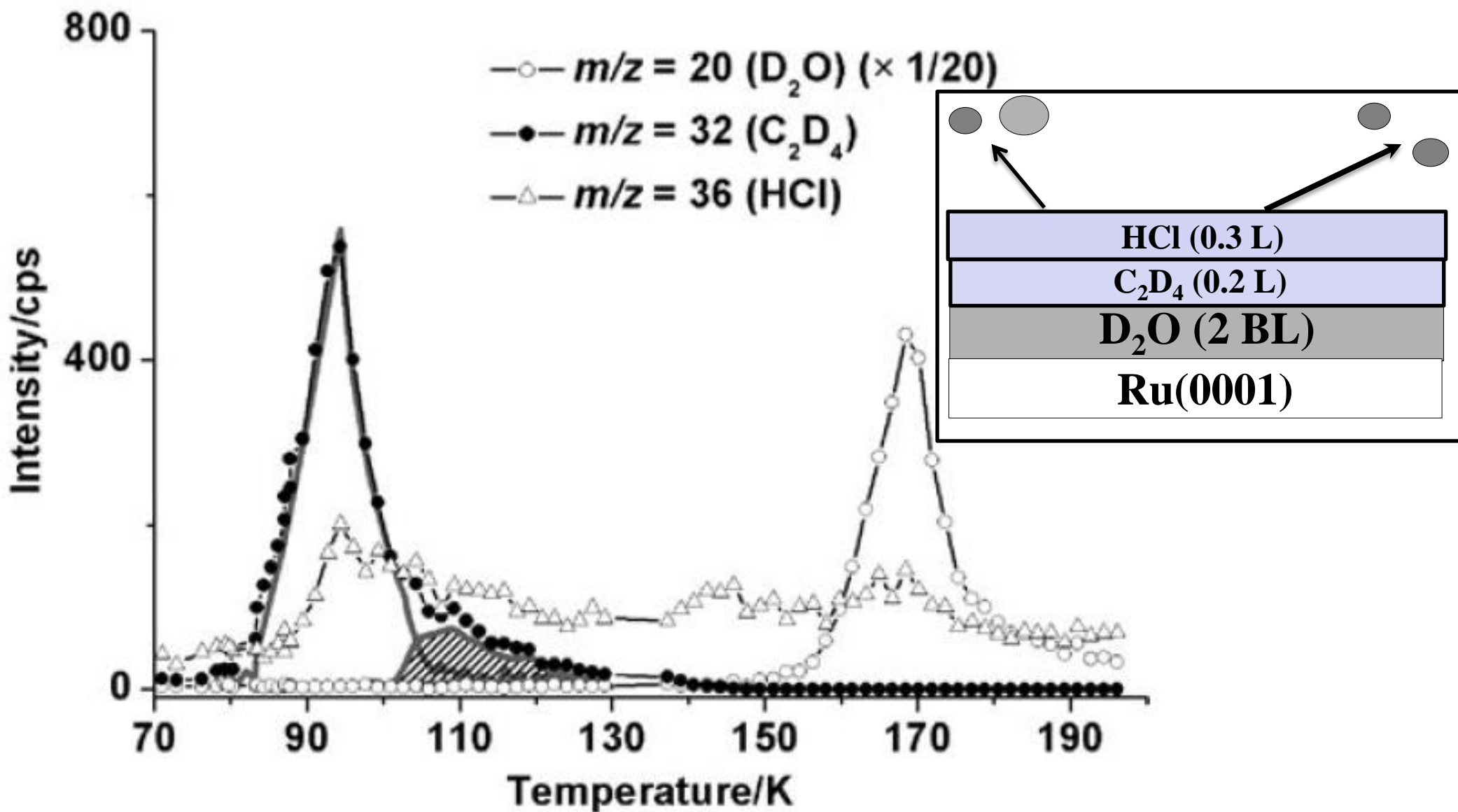


Figure 3. TPD Spectra of C_2D_4 and HCl adsorbed on D_2O . Heating rate 1 K s^{-1}

3.2. Hydronium Ions and Ethene on water-ice film

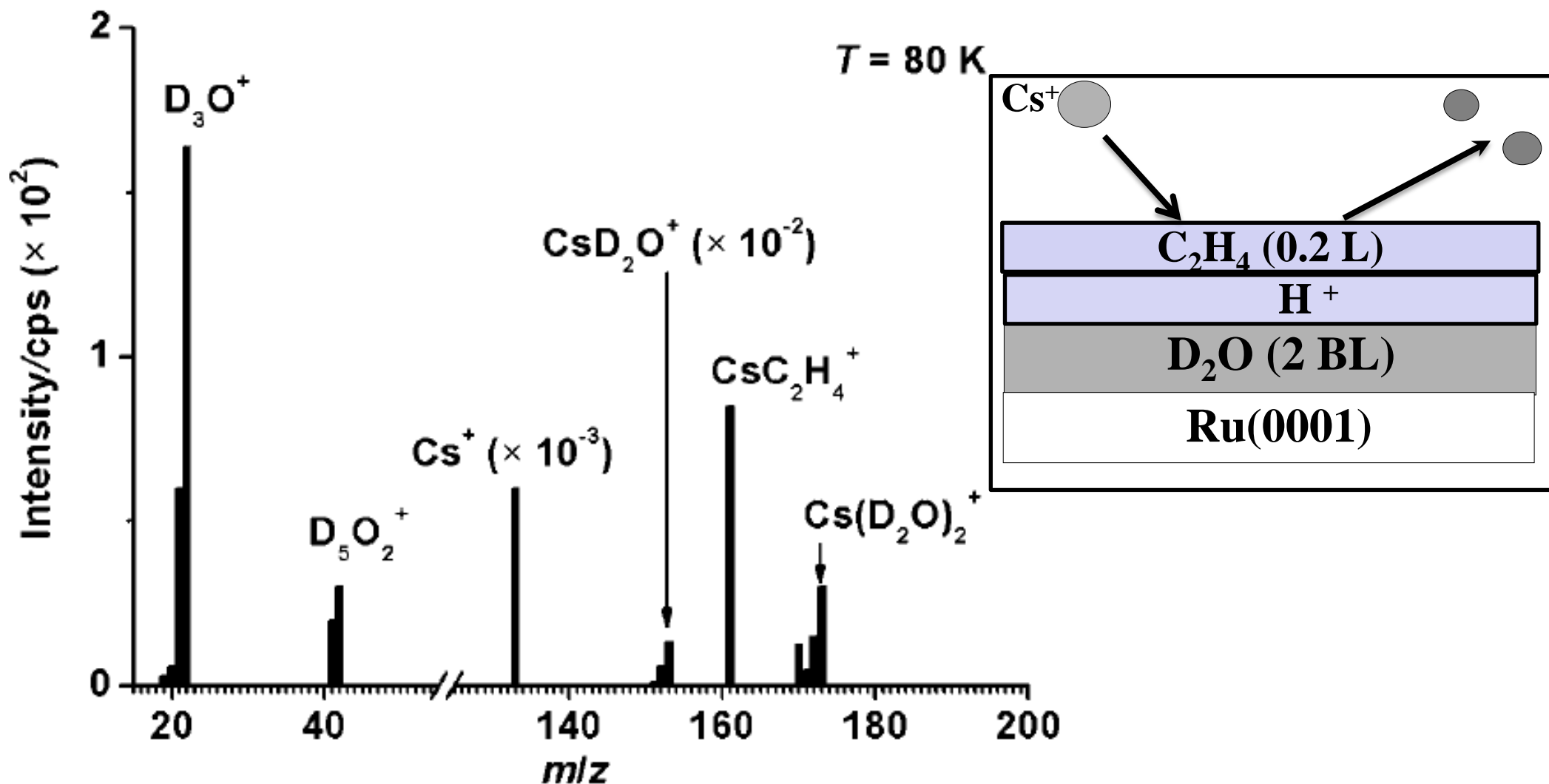


Figure 4. LES and RIS signals from D_2O -ice film with adsorbed C_2H_4 and hydronium ions. Hydronium ions were generated from the ionization of HCl (0.3 L) on the ice surface at 140 K. C_2H_4 was then adsorbed on the surfaces at 73 K for 0.2 L. The spectrum was obtained at a sample temperature of 80 K.

3.3. Hydrogen Chloride on Frozen Ethene Film

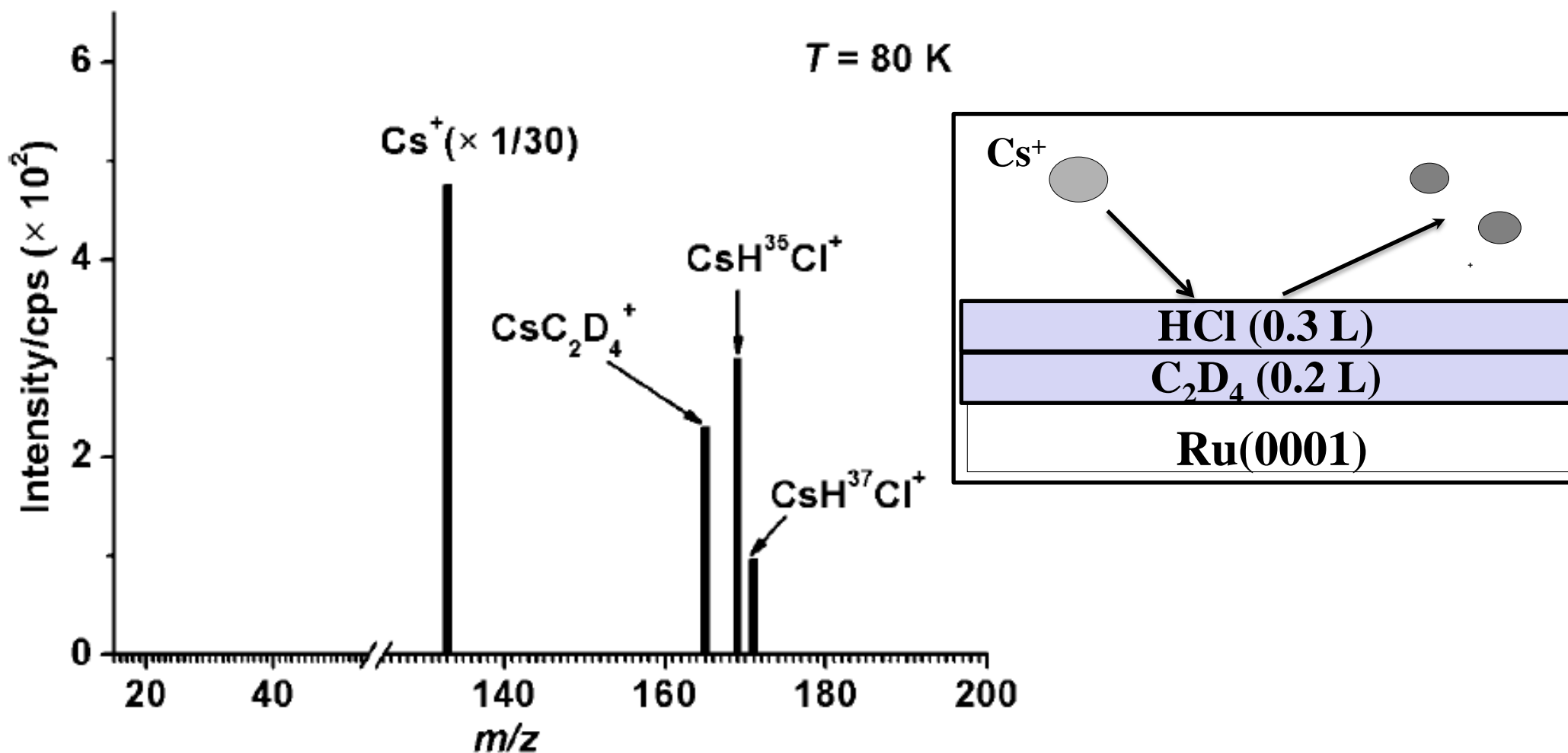


Figure 5. LES and RIS results of Sample C, which was prepared by adsorbing 0.3 L of HCl onto C₂D₄ film condensed on Ru-(0001) at 73 K. The sample temperature was 80 K during acquisition of the spectra.

Conclusion

- The adsorption of ethene and HCl on an ice surface leads to the formation of the π -complex of HCl and ethene which is stable below 93 K.
- A small amount of ethyl cationic species is also formed on the surfaces below 100 K via direct proton transfer from molecular HCl to ethene and water solvation play a crucial role in this transfer.
- At higher temperature the ethyl cation dissociates into ethene and hydronium and chloride ions.
- Ethyl chloride is not formed because the passage over the reaction transition state is kinetically blocked on the ice surface.

Future Plans

- Organic reaction mechanism and its intermediates are more correctly predicted using RAIRS.
- Similar experiment can be done by producing H⁺ ions directly to the surfaces at low energy.
- Changing solvent will lead us to better understanding of the solvation phenomena in such reaction.

Thank you all...