

Generation of strong electric fields in an ice film capacitor

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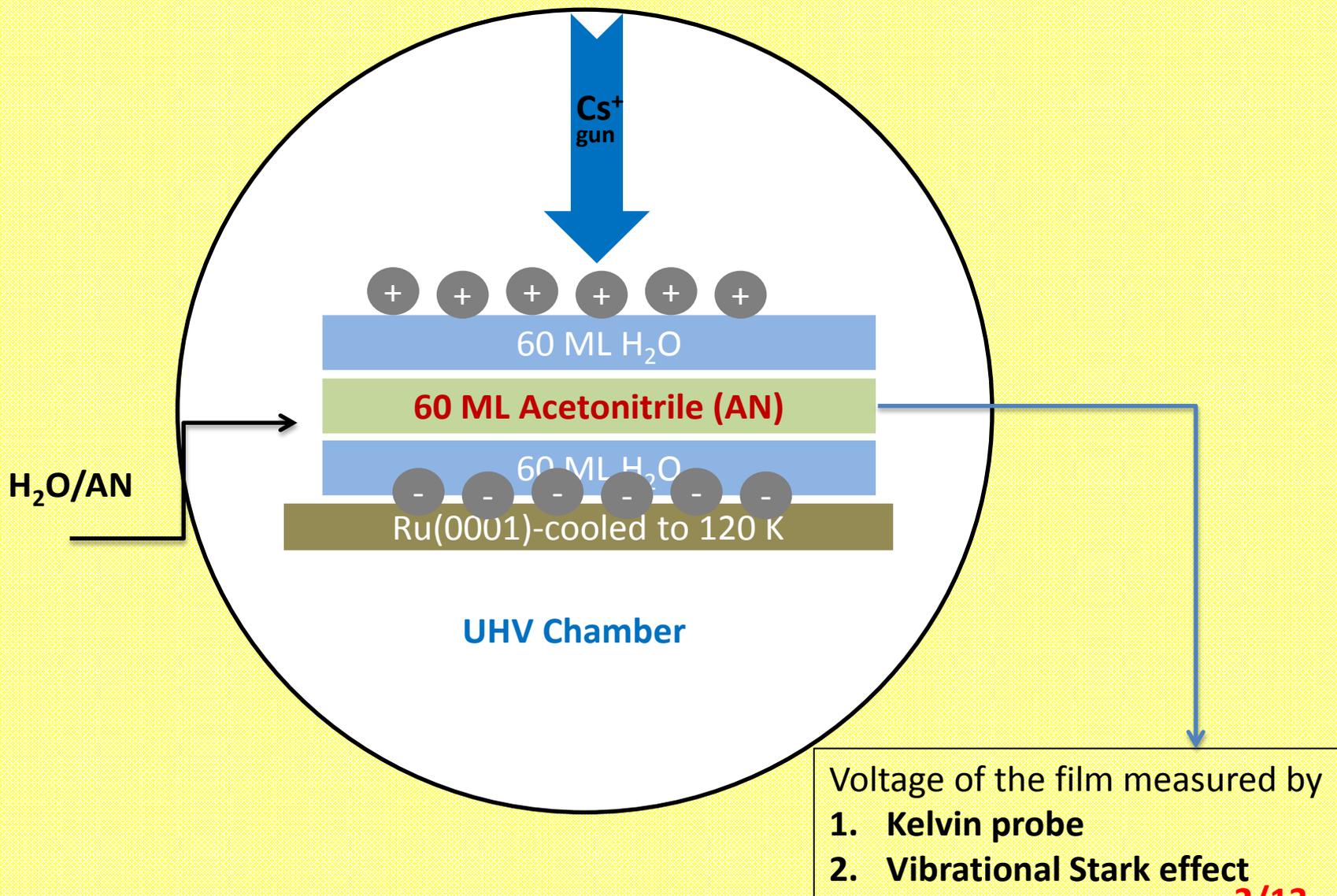
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Introduction

- **Electric fields** play an important role in chemical reactions and influence various physical and chemical phenomena in nature.
- **Rate of reactions** are influenced by the electric fields that are generated from local charge, dipole moment, polarizability of the reactant molecule and also by the fields from surrounding solvents in condensed phase.
- In this paper....**a new capacitor type device** was developed in an ice film grown on a cold metal substrate in UHV, and the film was charged by trapping Cs^+ ions on the ice surface with thermodynamic surface energy.
- The electric field within the charged film device was monitored through measuring the film voltage using a **Kelvin work function probe** and the **vibrational Stark effect** of acetonitrile using IR spectroscopy.

Construction of ice film capacitor

Instrumentation



Construction of ice film capacitor

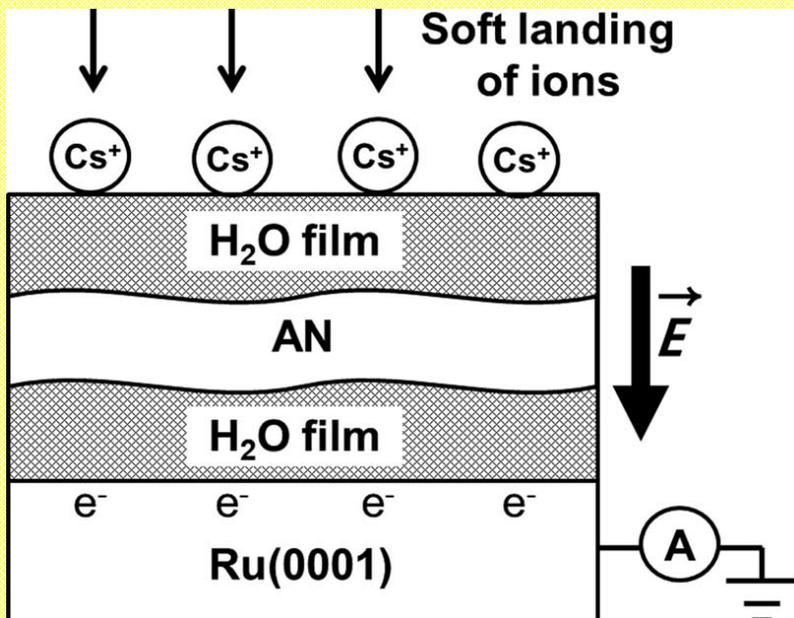
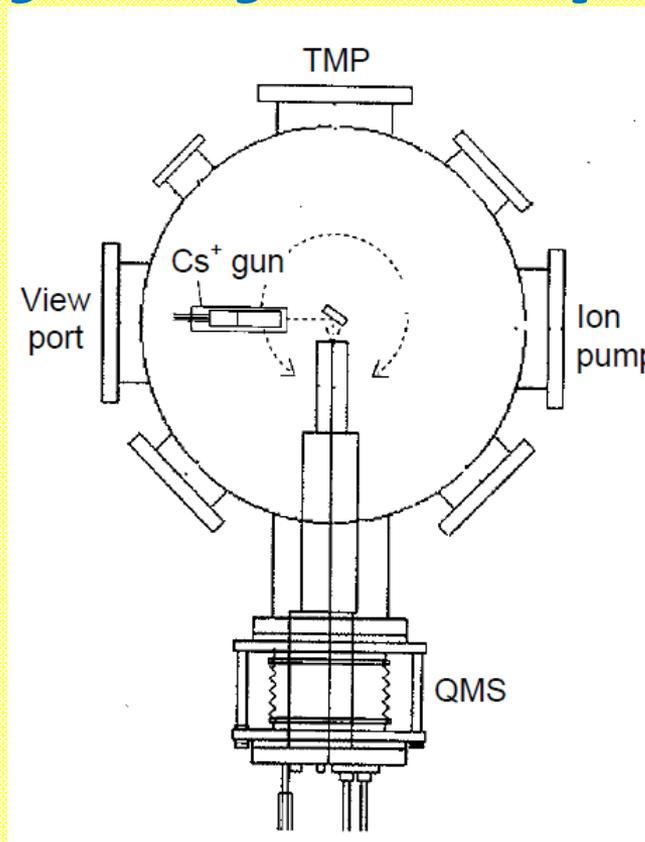
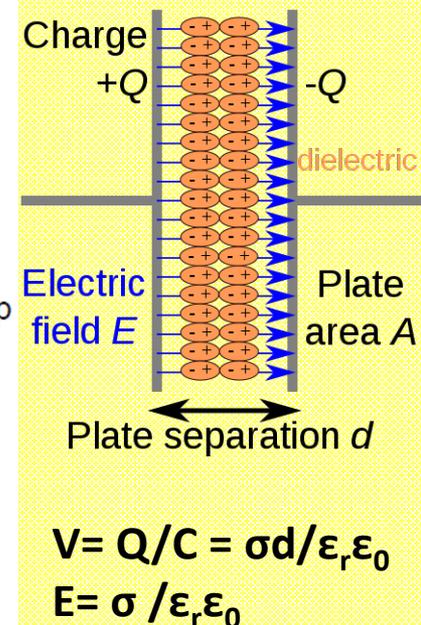


FIG. 1. Schematic of ice film capacitor. Ice film grown on a Ru(0001) metal surface is charged by depositing Cs⁺ ions onto the ice surface. The sample comprises H₂O and AN layers, where AN layer is introduced as a spectroscopic probe of electric field. Ion current is read by a current meter (A) connected to the Ru substrate.

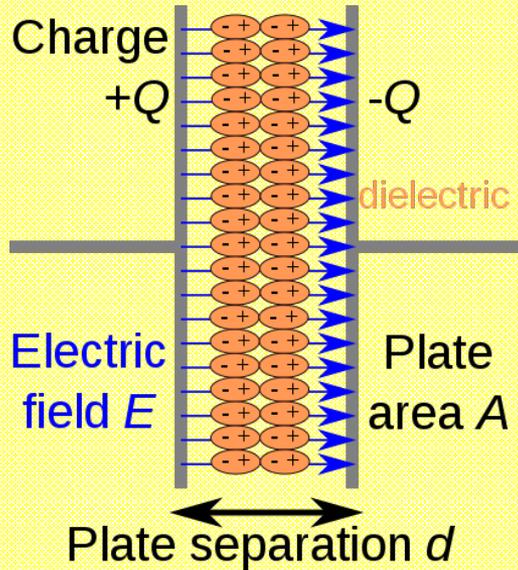


H. Kang, Bull. Korean Chem. Soc. 2011, 32, 389–398.

Cs⁺-beam current in the range (0.5–3) × 10⁻⁹ A, measured using a picoammeter connected to the Ru substrate



Equations concerning parallel plate capacitor



$$V = Q/C = \sigma d / \epsilon_r \epsilon_0$$

Q - surface charge of Cs⁺ ions

C - capacitance of the film

σ - surface charge density

d - film thickness

ϵ_r - dielectric constant of the sample

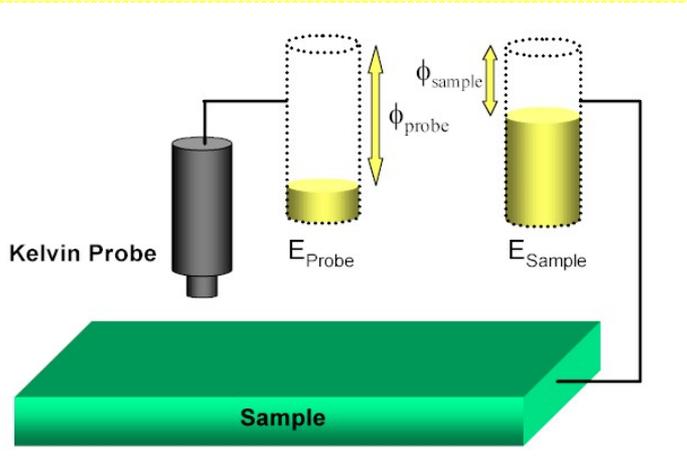
ϵ_0 - vacuum permittivity

Electric field strength within the sample will be

$$E = \sigma / \epsilon_r \epsilon_0$$

Electric field measurement

a. Film voltage measurement with a Kelvin probe

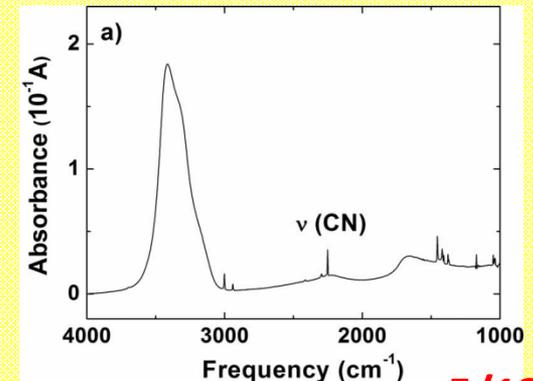
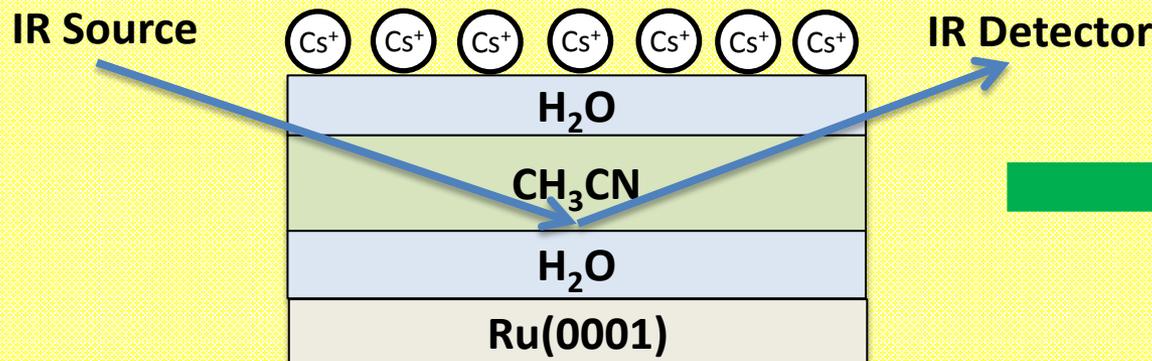


Kelvin Probe measures,

Contact Potential Difference (CPD) = $\phi_{\text{probe}} - \phi_{\text{sample}}$
 ΔCPD , the difference of film voltages measured before and after Cs^+ deposition is what is important for the experiment

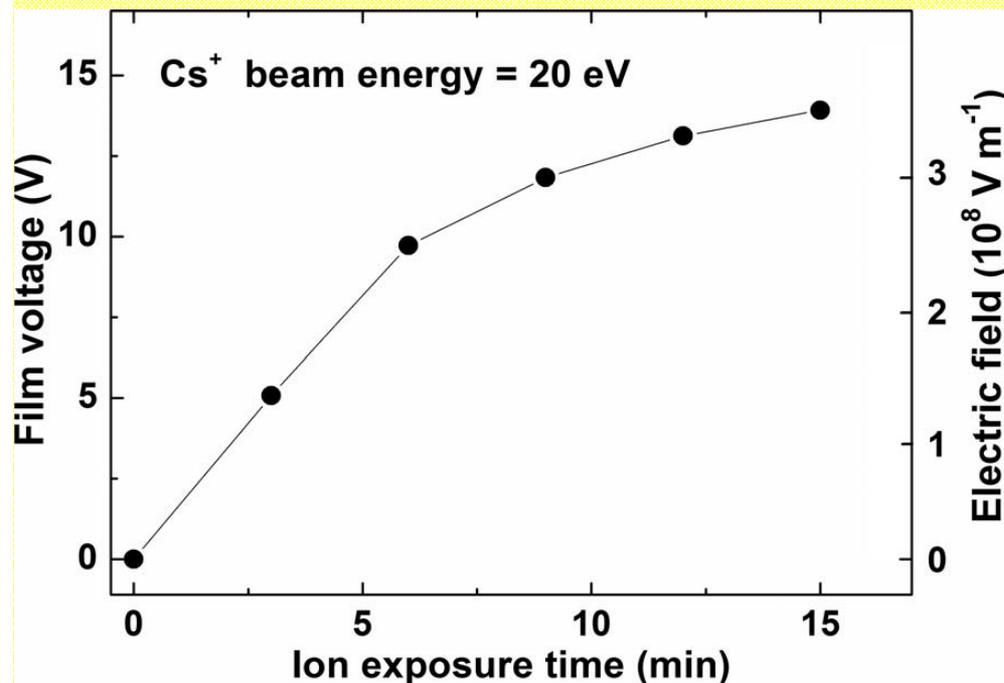
<http://research.shu.ac.uk/espnet/ESP.htm>

b. Vibrational Stark effect



Electric field measurement

a. Film voltage measurement with a Kelvin probe



Dividing ΔCPD with film thickness (d) gives the electric field strength (E) within the film, $E = \Delta\text{CPD}/d$.

The film thickness was estimated by measuring the water coverage in TPD experiments and from the water monolayer coverage ($1.1 \times 10^{19} \text{ molecules m}^{-2} \text{ ML}^{-1}$) and the density of amorphous ice, assuming that the amorphous ice structure was isotropic.

FIG. 2. Kelvin probe measurement of film voltage (ΔCPD) as a function of Cs^+ -beam exposure time. The left ordinate indicates the measured film voltage, and the right ordinate indicates the electric field strength. The sample was an AN-sandwiched H_2O -ice film, which comprised $\text{H}_2\text{O}(18.7 \text{ nm})/\text{AN}(20.5 \text{ nm})/\text{H}_2\text{O}(24.0 \text{ nm})/\text{Ru}(0001)$. The sample temperature was maintained at $\sim 70 \text{ K}$ during ion exposure and voltage measurement.

$$E(\text{AN}):E(\text{H}_2\text{O})=1/\epsilon_r(\text{AN}):1/\epsilon_r(\text{H}_2\text{O})$$

$$\begin{aligned}\Delta\text{CPD} &= V(\text{H}_2\text{O})_{\text{top}} + V(\text{AN}) + V(\text{H}_2\text{O})_{\text{bottom}} \\ &= V(\text{H}_2\text{O})_{\text{total}} + V(\text{AN}) \\ &= (\sigma/\epsilon_0) \times [d(\text{H}_2\text{O})/\epsilon_r(\text{H}_2\text{O}) + d(\text{AN})/\epsilon_r(\text{AN})],\end{aligned}$$

where $V(\text{H}_2\text{O})$ voltages across the top and bottom H_2O layers; $d(\text{H}_2\text{O})$ is the total thickness of two H_2O layers.

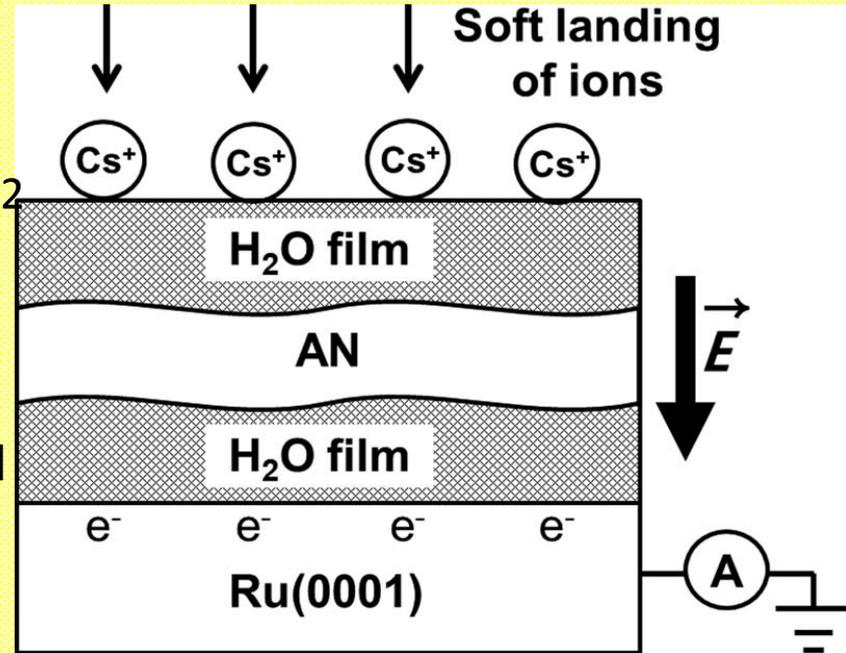
Also it can be shown from the above derivation that the field strength inside the AN layer is related to the film voltage:

$$E(\text{AN}) = \text{CPD}/[d(\text{AN}) + d(\text{H}_2\text{O}) \epsilon_r(\text{H}_2\text{O})/\epsilon_r(\text{AN})]$$

$$\epsilon_r(\text{H}_2\text{O})/\epsilon_r(\text{AN}) = \epsilon^\infty(\text{H}_2\text{O})/\epsilon^\infty(\text{AN}) = 4.57/2.26 = 2.02$$

high-frequency relative permittivity (ϵ^∞) of liquids

After 15 min of Cs^+ exposure the electric field inside the AN layer is $3.5 \times 10^8 \text{ Vm}^{-1}$ and that in H_2O layer is $1.7 \times 10^8 \text{ Vm}^{-1}$.



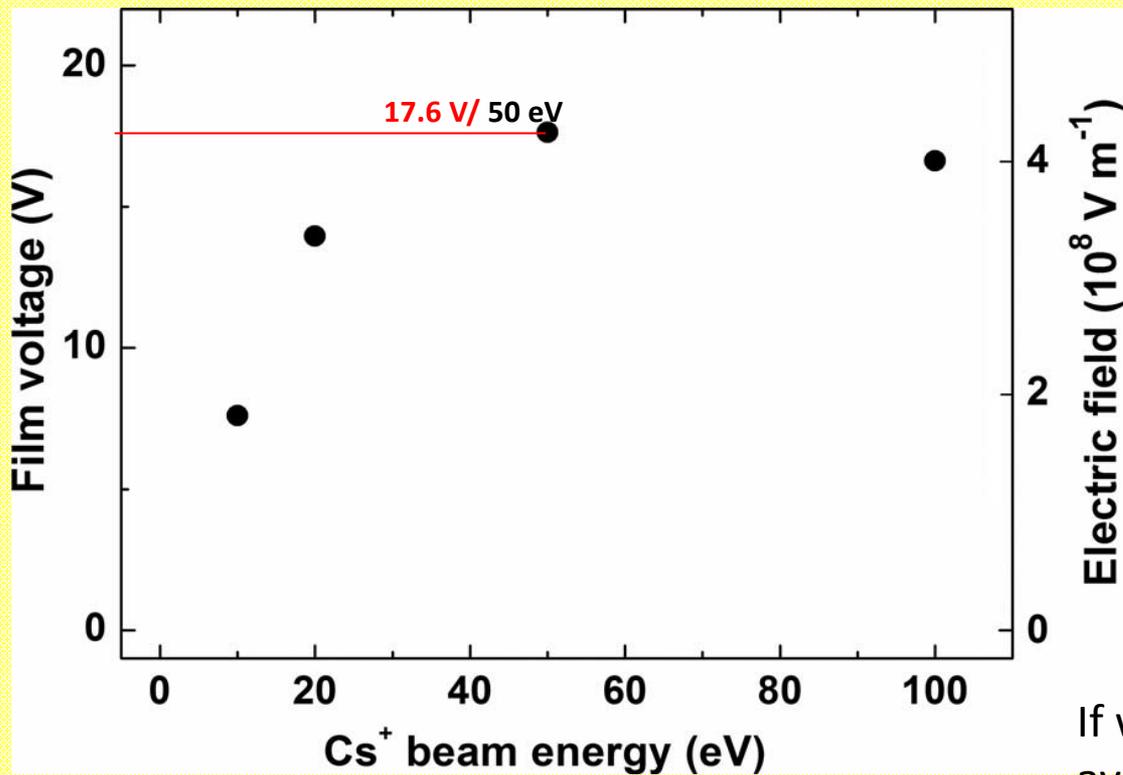


FIG. 3. Maximum film voltages attained after ion-exposure saturation at different beam energies. The estimated field strength inside the AN layer is shown along the right axis. The sample structure was H₂O(20.1 nm)/ AN(19.0 nm)/H₂O(25.8 nm)/Ru(0001).

The maximum charge density on the ice film surface can be limited either by the instrumental factors or by the intrinsic nature of the sample.

At a film voltage of **17.6 V**, the estimated internal field is $4.2 \times 10^8 \text{ Vm}^{-1}$ in the AN layer and $2.1 \times 10^8 \text{ V m}^{-1}$ in the H₂O layer.

If we use $d = 6.5 \times 10^{-8} \text{ m}$ and $\epsilon_r \approx 2$ as an average value for the samples shown in here, the surface charge density will be $\sigma = V\epsilon_r\epsilon_0/d \approx 5 \times 10^{-3} \text{ C m}^{-2}$ at film voltage **17.6 V**. This value corresponds to the Cs⁺ surface coverage of $\sim 3 \times 10^{16} \text{ ions m}^{-2}$, which is an enormously dense population of ions floating on the ice surface.

Electric field measurement

b. Vibrational Stark effect

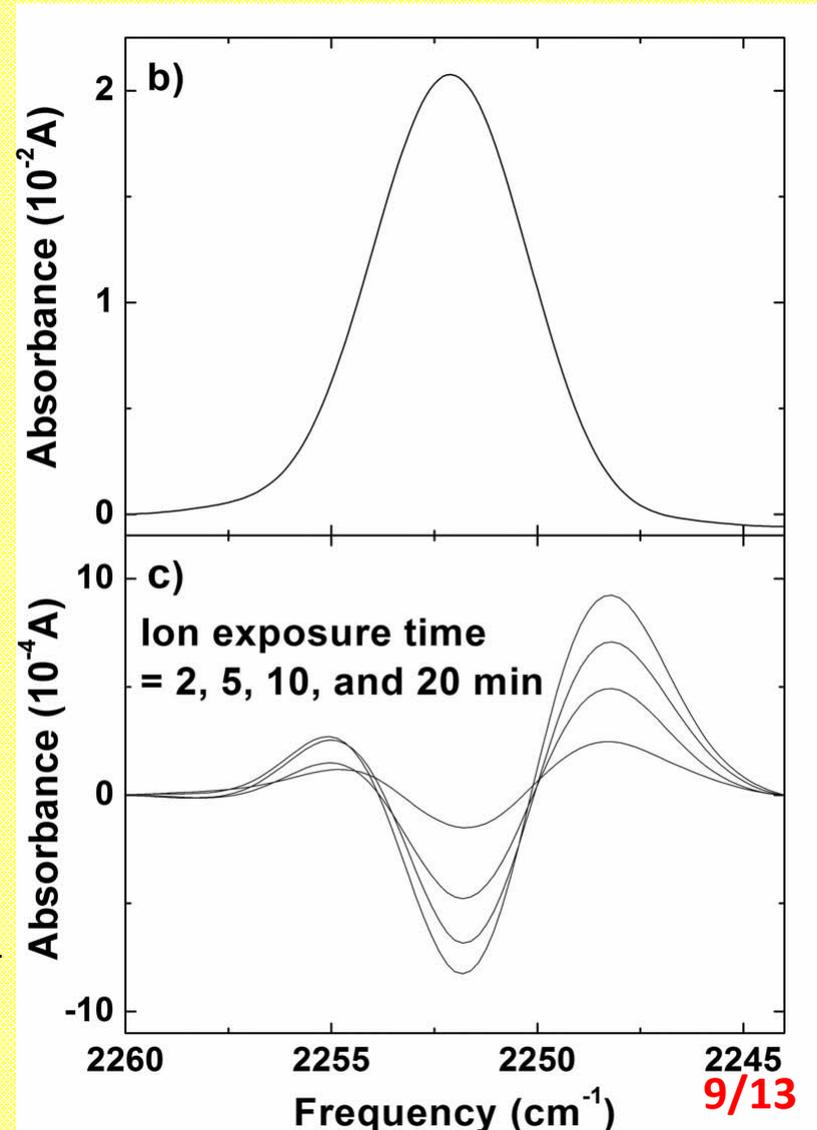
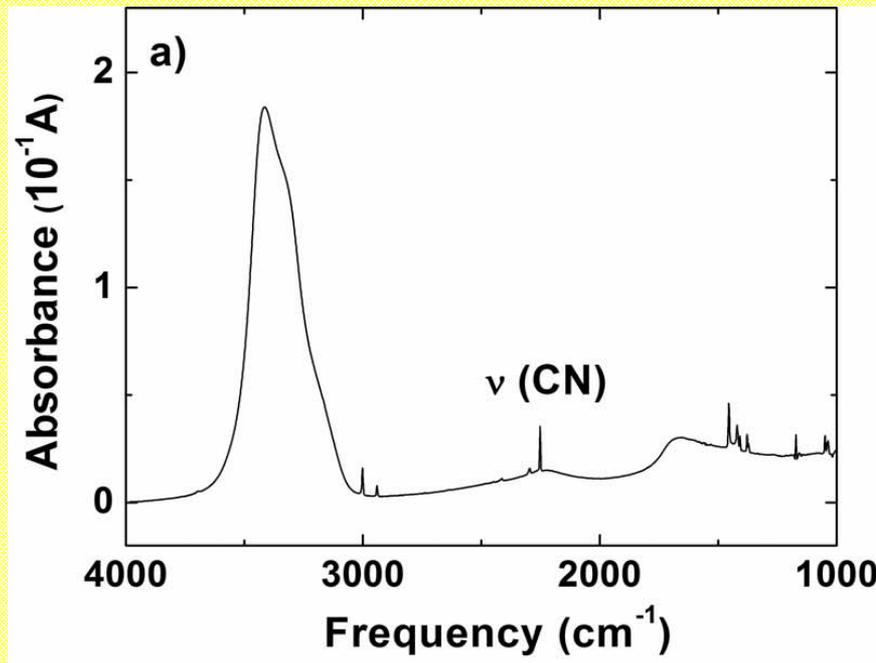


FIG. 4. (a) RAIR spectrum of an AN-sandwiched H₂O film. (b) The absorption of $\nu(\text{C}\equiv\text{N})$ stretch mode (2252 cm^{-1}) shown on a magnified scale. (c) The Stark difference spectra, which show that $\nu(\text{C}\equiv\text{N})$ peak became broader when the length of Cs⁺ exposure, or the applied electric field, was increased. The four lines in the order of increasing shoulder intensity correspond to the ion exposures for 2, 5, 10, and 20 min, respectively. The ion beam energy was 20 eV. The sample temperature was maintained at $\sim 70 \text{ K}$ during ion exposure and spectral acquisition.

The VSE method measures the electric field strength at the position of the chromophore, which is called the “local electric field (**F**).” The local field can be somewhat different from the externally applied field (**E**), and the difference is expressed by $\mathbf{F} = f\mathbf{E}$, where f is the local field correction factor. Exact value of f is not known generally believed to be close to unity for frozen molecular solids.

The Stark effect on the $\nu(\text{C}\equiv\text{N})$ stretch mode was analyzed following the method of Andrews and Boxer, which was developed for nitrile compounds with isotropic molecular orientation in glassy samples.

$$\Delta\bar{\nu} = -\frac{1}{hc} \left(\Delta\mu \cdot \mathbf{F} + \frac{1}{2} \mathbf{F} \cdot \Delta\alpha \cdot \mathbf{F} \right)$$

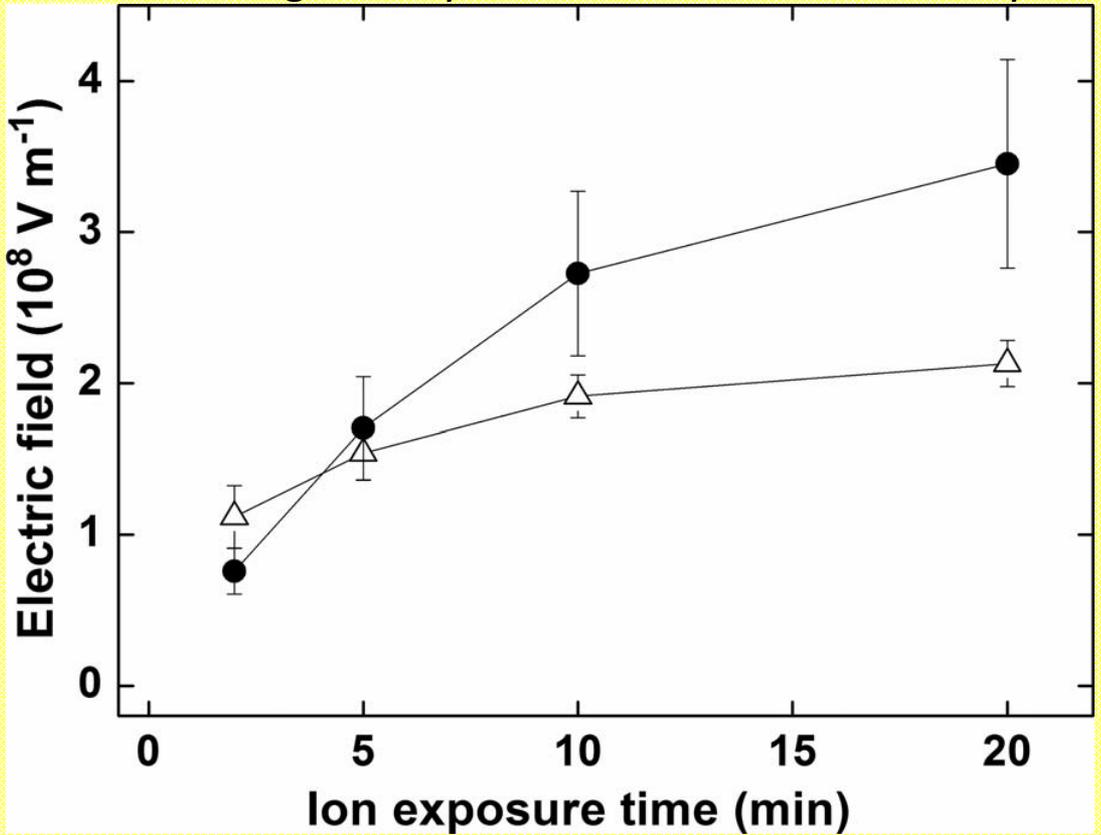


FIG. 5. Estimated electric fields from the results of Kelvin probe (●) and VSE (Δ) measurements. The sample was the same as the one used for Fig. 4, with the structure of H₂O(21.3 nm)/AN(17.9 nm)/H₂O(27.4 nm)/Ru(0001). The VSE data are from the Stark difference spectra shown in Fig. 4(c), and the field was estimated using $|\mu|/f = 0.0258$ D with $f = 1.0$. The error bar for VSE is estimated from the spectral noise level.

$$\Delta A(\bar{\nu}) = \alpha A(\bar{\nu}) + \beta \bar{\nu} \frac{\partial}{\partial \bar{\nu}} \frac{A(\bar{\nu})}{\bar{\nu}} + \gamma \bar{\nu} \frac{\partial^2}{\partial \bar{\nu}^2} \frac{A(\bar{\nu})}{\bar{\nu}}$$

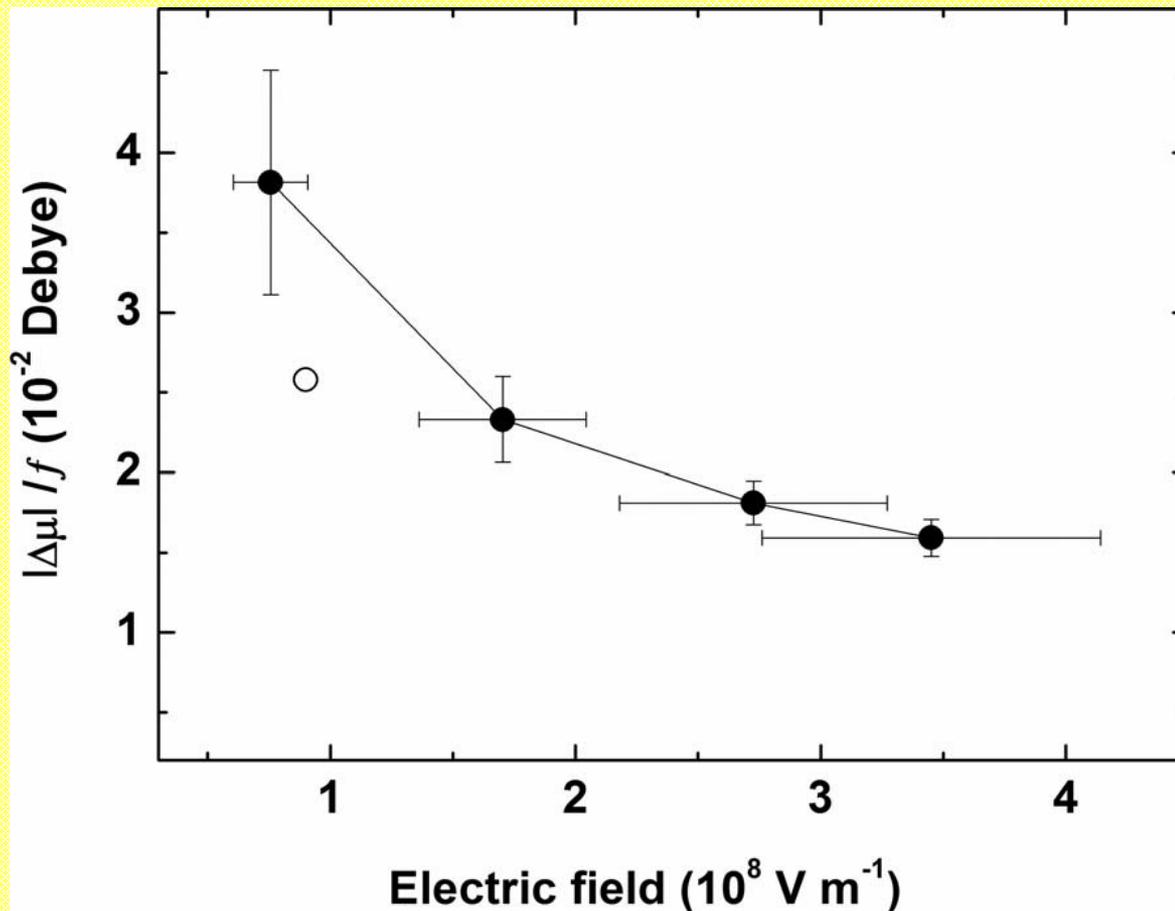


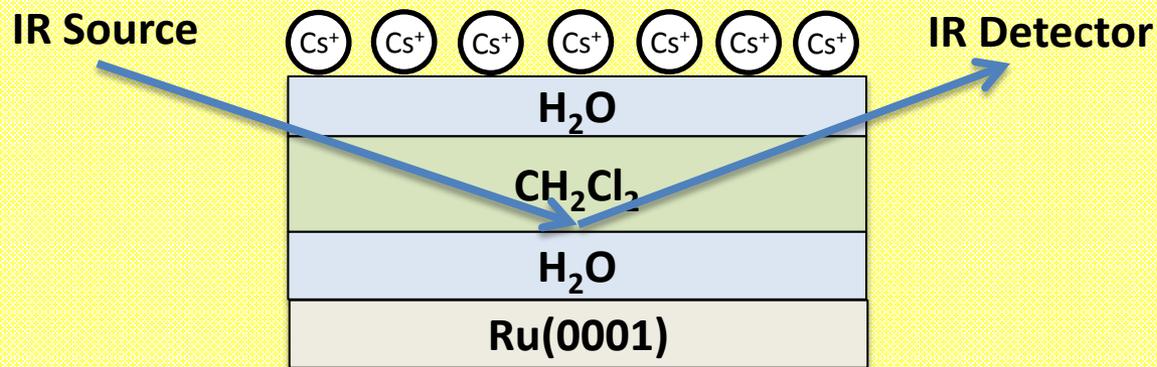
FIG. 6. Difference dipole moment ($|\mu|/f$) of AN used for the VSE analysis of $\nu(\text{C}\equiv\text{N})$ peak at various field strengths. Kelvin probe results were used as a field reference for calculating $|\mu|/f$ (see text). Open circle is the $|\mu|/f$ value reported in Ref. 5.

Summary

- This work demonstrates that strong electric field can be generated inside an ice film by depositing Cs⁺ ion beams onto the film.
- Unlike conventional devices that use electrically biased metal plates, the present device is charged by using thermodynamic energy that traps Cs⁺ ions on the ice film surface.
- The internal field of the charged film was estimated through the measurements of film voltage using a Kelvin probe and the vibrational Stark shift of AN trapped in the sample.
- The two methods gave agreeable results in the field region $(1-2) \times 10^8 \text{ V m}^{-1}$, where the current VSE analysis model is mostly applicable.
- It was shown that the field strength can be increased to $4.2 \times 10^8 \text{ V m}^{-1}$ (or $2.1 \times 10^8 \text{ V m}^{-1}$) inside the AN (or H₂O) layer after the Cs⁺ beam exposure to saturation, which is approximately one order higher than the field strength achievable by conventional capacitor methods.

Future perspective

- Investigation of the effects of electric field on phase transition in condensed-phase molecular systems.



Thank you all....