Efficient Conversion of Nitrogen Dioxide into Nitrous Acid on Ice Surfaces

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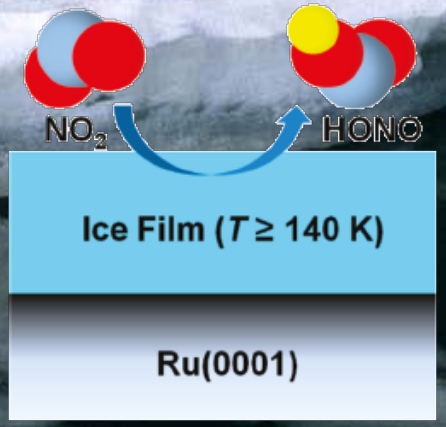

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Introduction:

❖ $2NO_2 + H_2O \rightarrow HONO + HNO_3$ is a well known reaction in chemistry.

❖ The reaction is important in a number of technologies and in atmospheric chemistry.

❖ The mechanism of the reaction is not so simple as it looks like.

❖ Several proposals have been made for the heterogeneous hydrolysis mechanism of NO_2,which include the formation of a NO_2-water complex at the air-water interface as well as intermediate involving N_2O_4.

❖ Ice surfaces offer an interesting model for the investigation of NO_2-water interactions in a two-dimensional water environment.

❖ Previous studies have been done with NO_2 interaction with ice surfaces using IRRAS, TPD and photoelectron spectroscopy.

❖ **In this paper, efficient conversion of NO_2 into nitrous acid on the ice surface at a temperature of 140 K, has been described.**

Experimental:

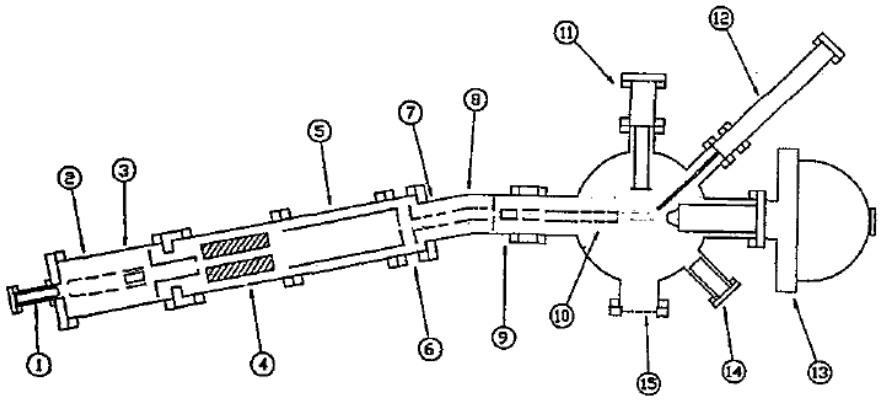
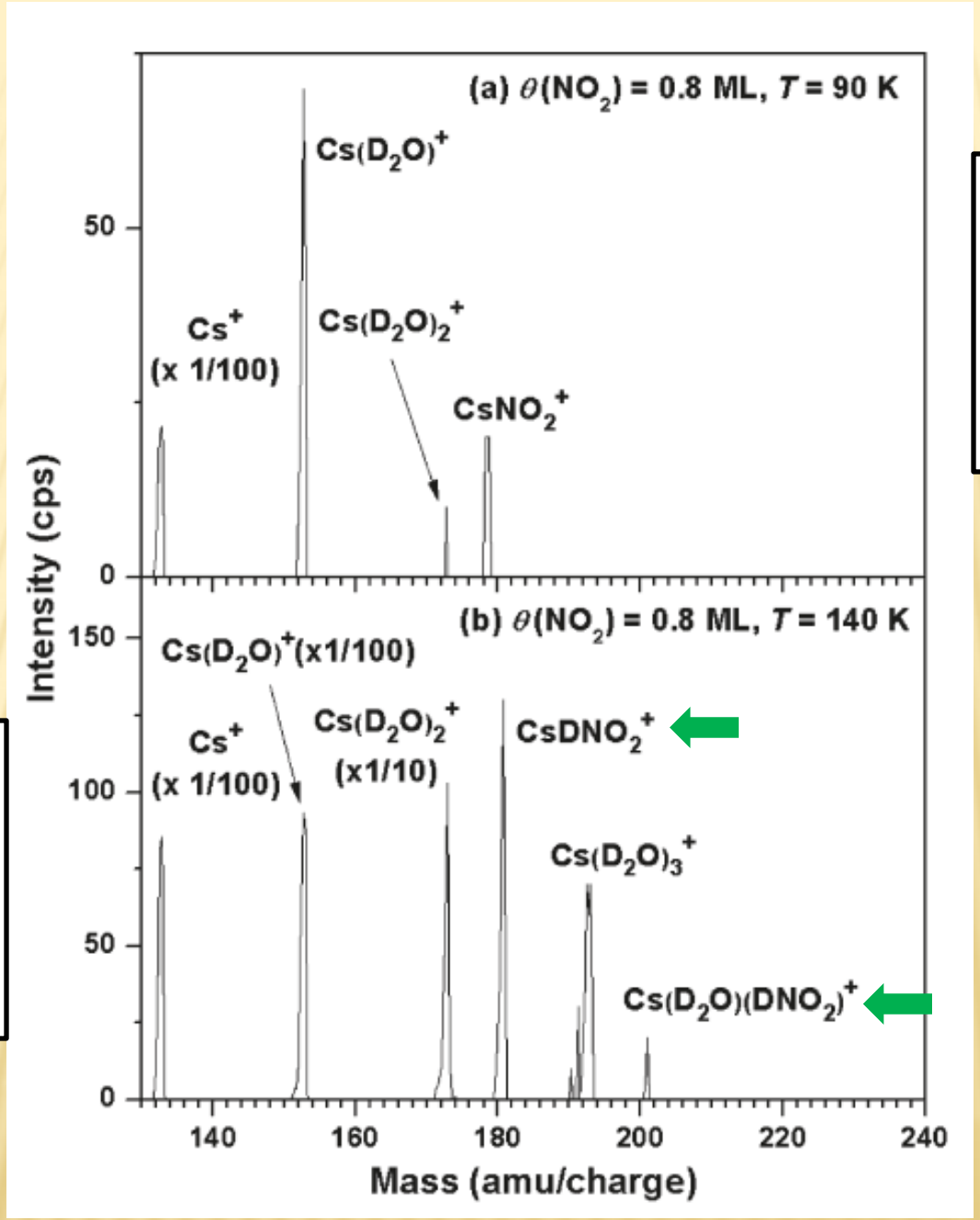
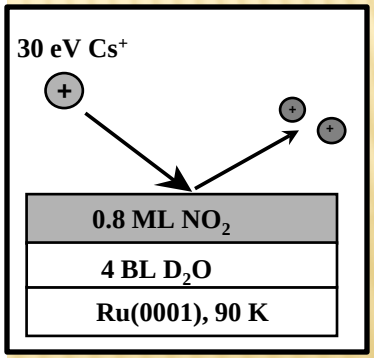


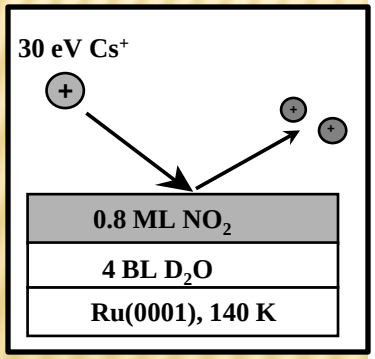
FIG. 1. Schematic diagram of ion beamline and UHV analysis chamber. The components labeled are (1) ion source; (2) extraction and acceleration lenses; (3) *x*,*y*-deflector; (4) Wien velocity filter; (5) flight tube; (6) gate valve; (7) Einzel lens; (8) 12° deflector for neutrals elimination; (9) *x*,*y*-deflector; (10) deceleration and focusing lenses; (11) quadrupole mass spectrometer; (12) UV source; (13) 180° hemispherical energy analyzer; (14) Auger electron gun; and (15) viewport.

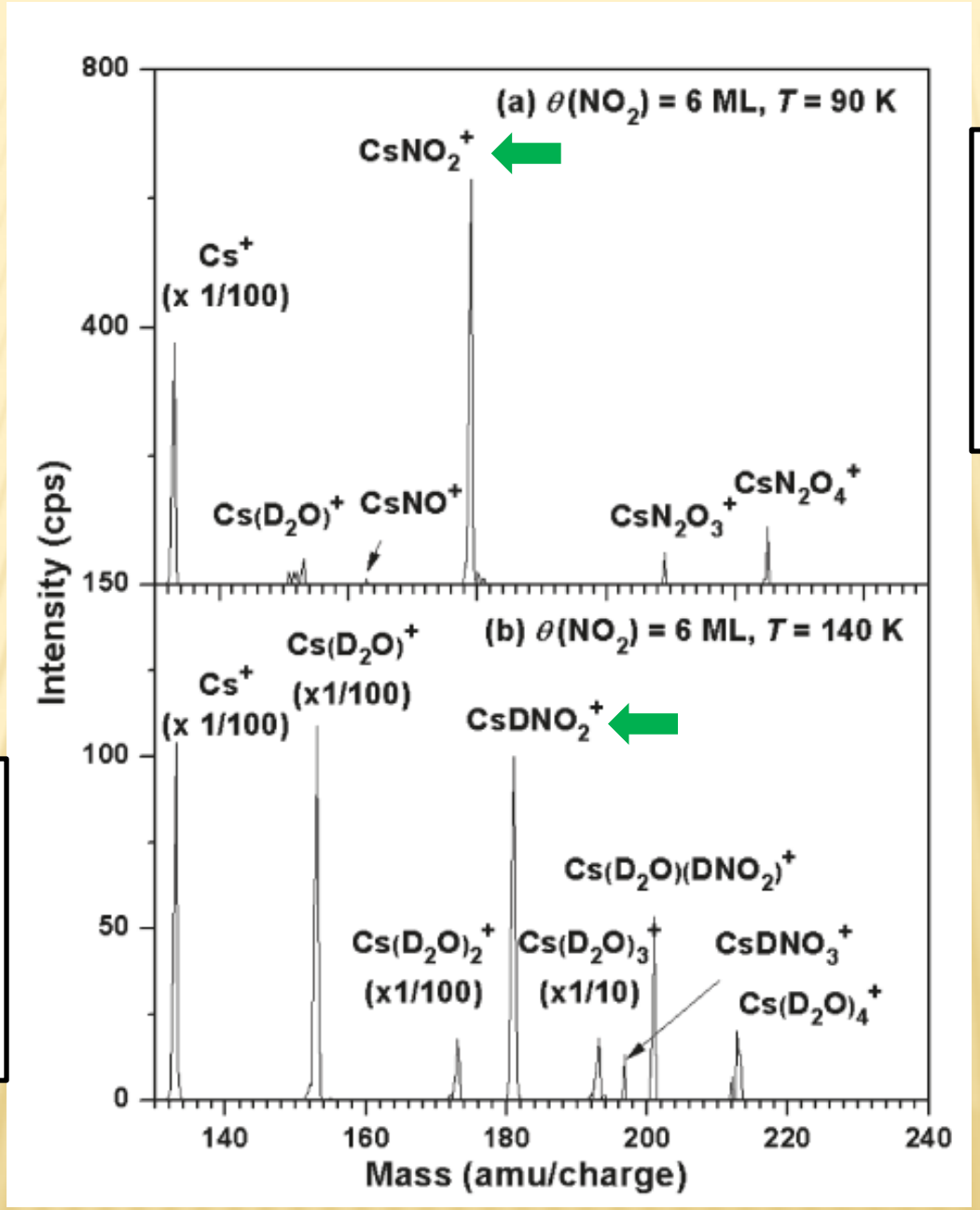
1. Experiments were performed in the above instrument.
2. Ice film (D_2O) was grown on the Ru(0001) surface.
3. The ice film was typically 4 BL (BL= bi-layer).
4. The ice film presented in the paper is polycrystalline in nature, it was prepared by maintaing temperature at 135 K and post annealing at 140 K for 5 minutes.
5. NO_2 was deposited at 90 K and at the partial pressure 1 10^{-9} torr.
6. Chemical species present on the ice films were identified by reactive ion scattering (RIS).

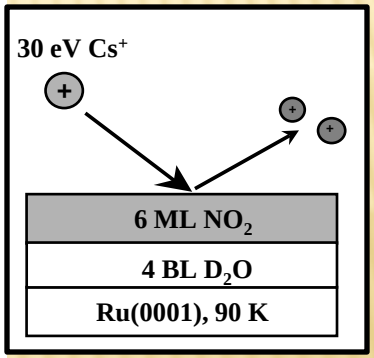
Results:

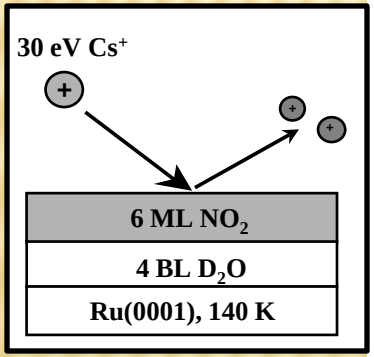

(a) θ(NO2) = 0.8 ML, T = 90 K
Cs(D2O)+
Cs+
(x 1/100)
Cs(D2O)2+
CsNO2+
(b) θ(NO2) = 0.8 ML, T = 140 K
Cs(D2O)+(x1/100)
Cs+
(x 1/100)
Cs(D2O)2+
(x1/10)
CsDNO2+
Cs(D2O)3+
Cs(D2O)(DNO2)+
Intensity (cps)
Mass (amu/charge)
0
50
100
150
140
160
180
200
220
240

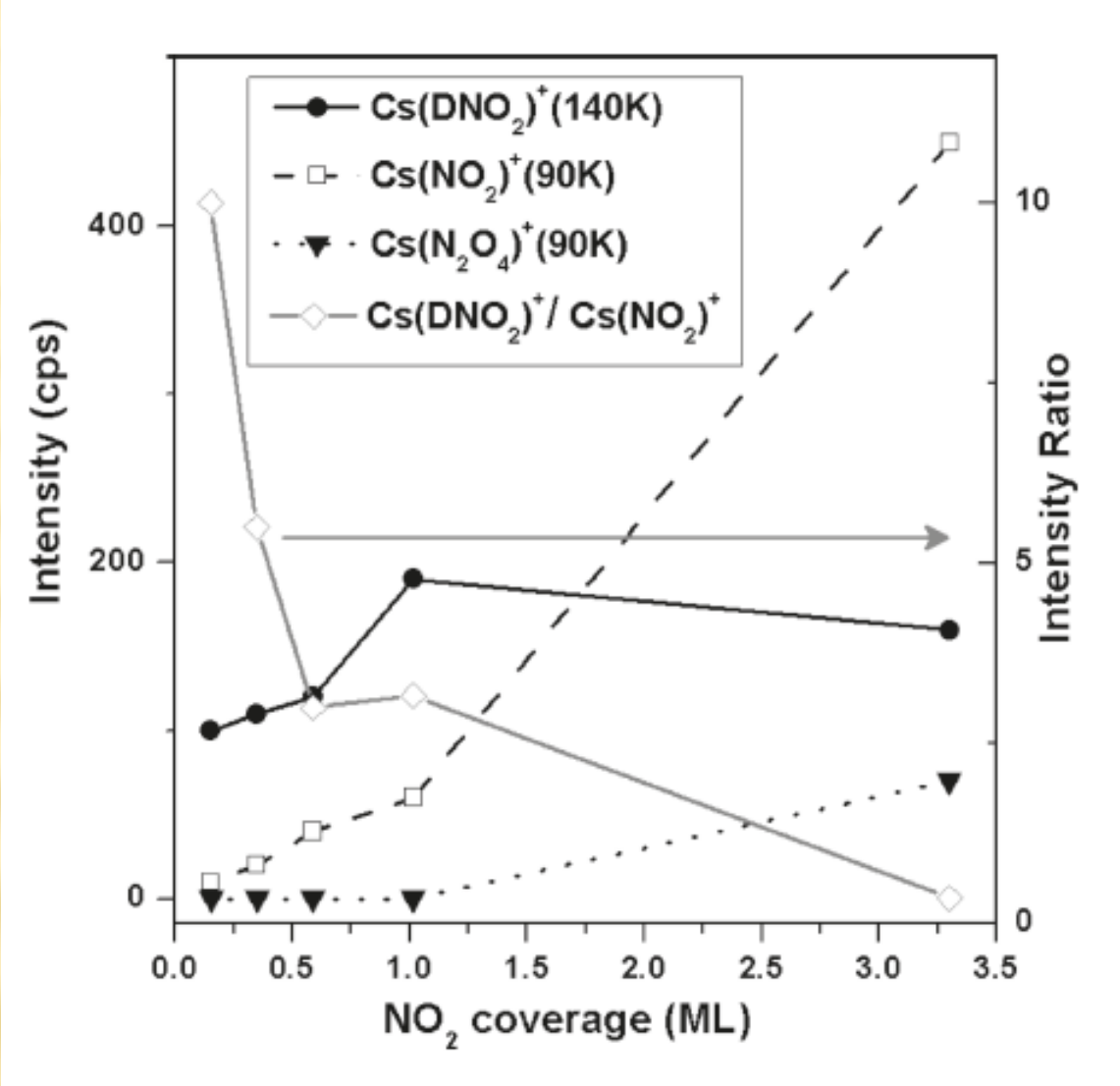

30 eV Cs+
0.8 ML NO2
4 BL D2O
Ru(0001), 90 K

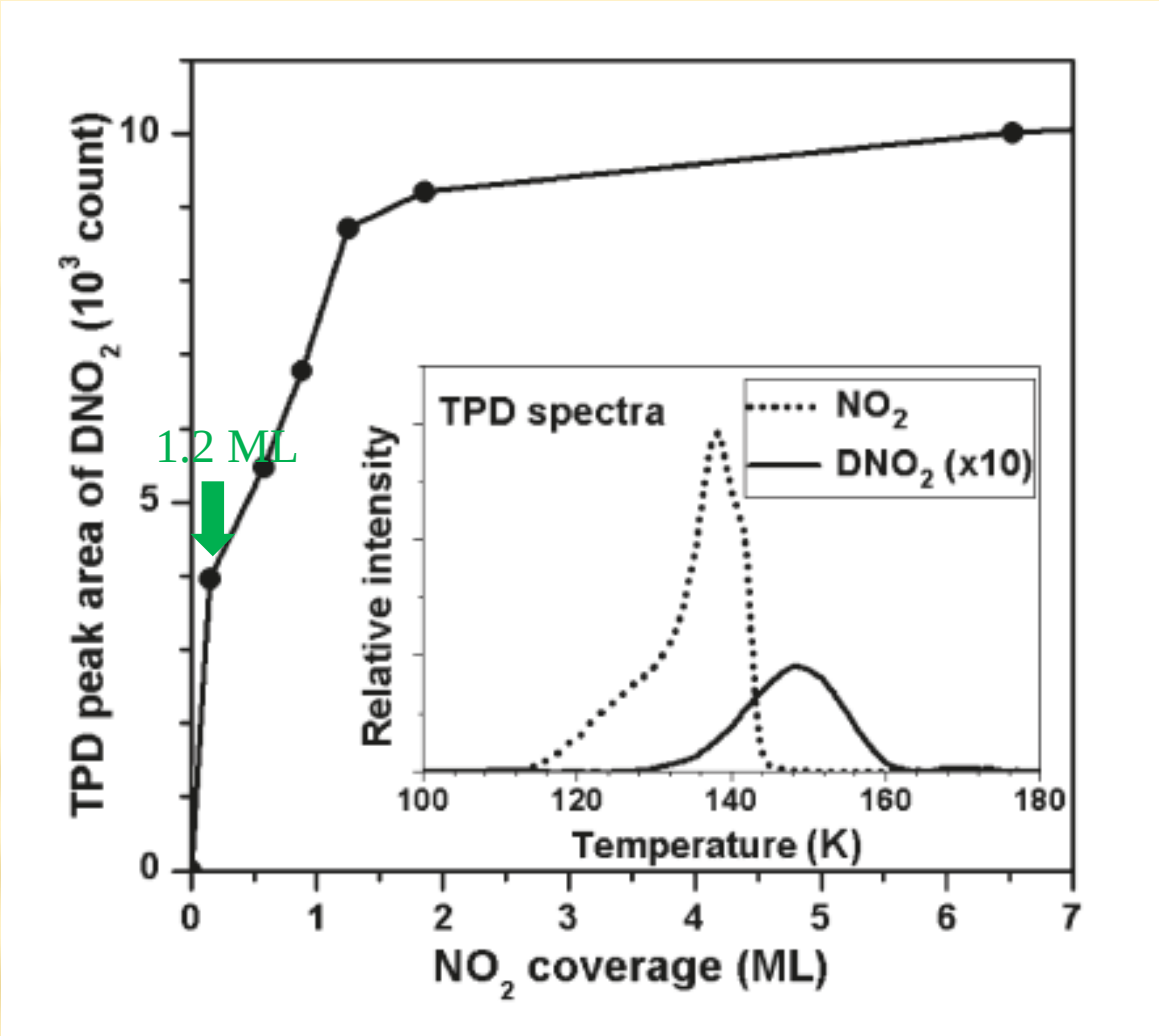

30 eV Cs+
0.8 ML NO2
4 BL D2O
Ru(0001), 140 K


(a) θ(NO2) = 6 ML, T = 90 K
CsNO2+
Cs+
(x 1/100)
Cs(D2O)+
CsNO+
CsN2O3+
CsN2O4+
(b) θ(NO2) = 6 ML, T = 140 K
Cs+
(x 1/100)
Cs(D2O)+
(x1/100)
CsDNO2+
Cs(D2O)(DNO2)+
Cs(D2O)2+
(x1/100)
Cs(D2O)3+
(x1/10)
CsDNO3+
Cs(D2O)4+
Intensity (cps)
Mass (amu/charge)
800
400
150
100
50
0
140
160
180
200
220
240


30 eV Cs+
6 ML NO2
4 BL D2O
Ru(0001), 90 K


30 eV Cs+
6 ML NO2
4 BL D2O
Ru(0001), 140 K


Cs(DNO2)+(140K)
Cs(NO2)+(90K)
Cs(N2O4)+(90K)
Cs(DNO2)+/ Cs(NO2)+
Intensity (cps)
Intensity Ratio
NO2 coverage (ML)
0
200
400
0
5
10
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5



TPD peak areas of DNO_2 as a function of NO_2 coverage for 0.15-6.5 ML on a D_2O-ice film. The inset displays the TPD spectra of NO2 (dashed line) and DNO_2 (solid line) measured on the ice film at $\theta(NO_2)$ = 0.8 ML

Discussion:

❖ It is known that NO_2 hydrolysis is difficult to occur in the gas phase and requires a substantially high activation energy (~120 kJ mol^{-1}).

❖ Kinetic studies had shown that the rate of NO_2 hydrolysis is accelerated in the presence of liquid water films.

❖ The present work revealed that once NO_2 molecules are accommodated onto the ice surface, they can be converted into nitrous acid almost spontaneously.

❖ Plausible mechanism

$$NO_2 + D_2O\text{-ice} \rightarrow NO_2\text{-}(D_2O)_n \text{ complex} \rightarrow DONO(D_2O)_{n-1}OD$$

Summary:

❖ The hydrolysis of NO_2 on an ice surface produces nitrous acid as a major product at 140 K. A nitrous acid product is formed regardless of whether NO_2 coverage is small or multilayer.

❖ A large portion of surface nitrous acids desorb intact at a high temperature.

❖ At high temperatures, nitric acid is produced in small amount.

❖ N_2O_3 and N_2O_4 species are formed only when a NO_2 multilayer exists on the ice film at 90 K.

❖ Nitrous acid is not formed under these conditions, and the surface populations of nitrous acid and N_2O_4 exhibit inverse correlation as a function of NO_2 coverage.

Importance:

❖ Collision can be made by using low energy proton ~ 90 K and sputtering can be done to check the activation energy of the reaction.

❖ Diffusion of the NO_2 through the ice layers can be checked.

❖ UV irradiation followed by sputtering can be measured at 90 K with the similar system.

Thank you