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Purpose of the visit

The aim of the visit was to study low-energy electron driven synthesis of molecules in astrophysical ice analogues. The obtained results can give more information about electron controlled chemistry within interstellar ice analogues.

One of chosen system to investigate was binary ice mixture composed of methanol (CH_3OH) and ammonia (NH_3) molecules. The mixed molecular films were prepared at temperature about 20 K then they were irradiated with electron beam of energy up to 100 eV. The possibly occurring chemical modifications in ices were investigated *in situ* by Fourier transformed infrared (FTIR) spectroscopy.

Description of works carried out during the visit

The investigation of electron-induced reactivity has to be carried out in ultra high vacuum (UHV) conditions. Unfortunately, at the beginning the pressure obtained in vacuum chamber was of 10^{-5} Torr magnitude at room temperature. After changing of gaskets and leak precision valve, a new arrangement of gas line, and a few days of pumping the reached pressure was equal to $2x10^{-7}$ Torr at 300 K. A pressure of $5x10^{-9}$ Torr was obtained during the experimental run at 30 K.

The pure (NH_3 and CH_3OH) and mixed films (NH_3:CH_3OH) were deposited at 30-50 K onto ZnSe substrate mounted on the cold finger of cryostat (which can be heated up to 400 K). After deposition of molecules an infrared spectrum was recorded using FTIR spectrometer in the 4000-600 cm^{-1} region with 4 cm^{-1} resolution. As apparatus was mainly designed for high energy electron irradiation the investigated molecular films were irradiated with 1 keV electrons by using conventional electron gun. (The purpose of this investigation was also to compare the obtained results with existing literature data.) Further study with electron irradiation at 100 eV was also performed. The IR spectra were recorded during irradiation in order to detect the formation of new molecules.

A commercially supplied sample of NH_3 (Argo International, 99.996%) was used directly from container. Methanol sample with 99.9% (Aldrich) purity was used after several freeze-pump-thaw degassing cycles.

Description of the main results obtained

Pure methanol and ammonia films

Lower part of figure 1a shows 4000 - 600 cm^{-1} range IR spectrum recorded at 30K for pure CH_3OH film condensed at the same temperature. Positions of all observed bands are in good agreement with previous study [1]. Upper part of figure 1a displays spectrum recorded after 1 hour irradiation with 1 keV electrons (current ~10 μA). The main modifications of IR spectrum consist of following new peaks (marked with star in Fig. 1a): 2341 cm^{-1} (2276 cm^{-1}) ascribed to CO_2 ($^{13}CO_2$) molecules formation, 2138 cm^{-1} – CO molecules, 1721 cm^{-1} – H_2CO, and finally 1303 cm^{-1} assigned to CH_4 synthesis. Fig. 1b shows zoom of modified region.

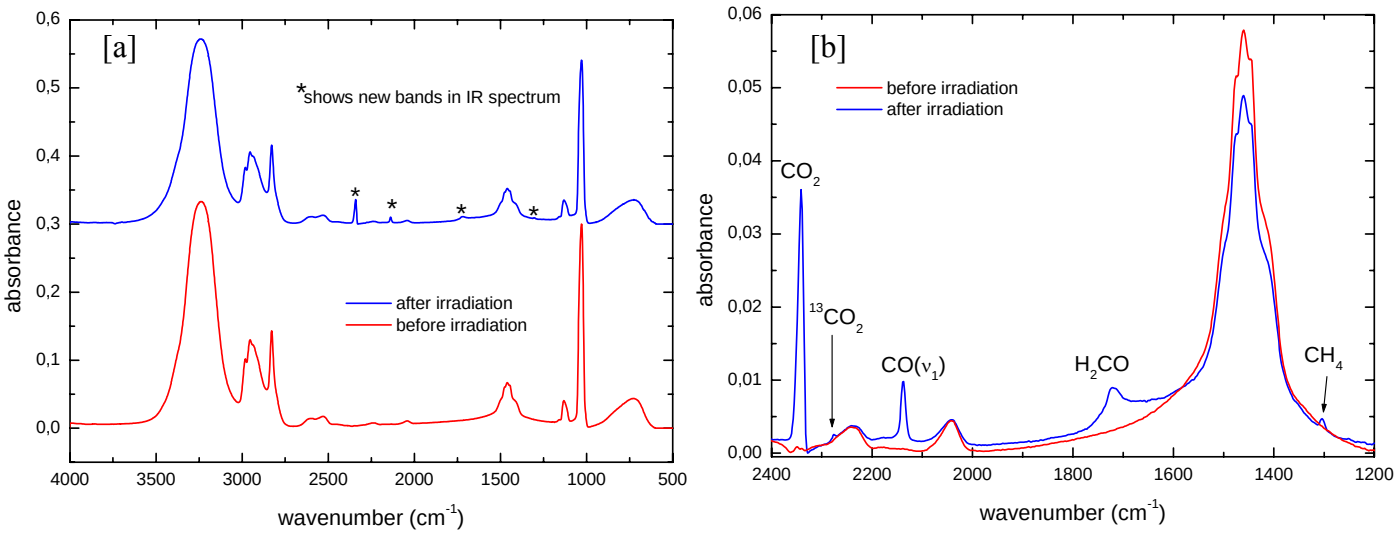

Figure 1: IR absorbance spectra of a CH_3OH film at 30 K before and after 1 keV electron irradiation: a) 4000-600 cm^{-1}; b) zoom of Fig.1a graph in wavenumber range where chemical modifications are observed.

Irradiated film was slowly warmed to room temperature and IR spectra were recorded regularly. Around 130 K we have observed the phase change from amorphous to crystalline (not shown here). In case of non irradiated methanol film desorption of all condensed molecules occurs at 160-170 K (no thermally activated reaction was seen). Spectra obtained after warming to 170 K and 200 K of irradiated CH_3OH film are presented in Figure 2. The spectrum is very similar to spectrum reported by Bennett *et al.* [1] for ethylene glycol ($HOCH_2CH_2OH$) molecule.

A similar experimental procedure was used for irradiation with 100 eV electron (1.5 hour, 40 μA). However, only a couple of peaks were visible after irradiation: 2341 cm^{-1} and 2138 cm^{-1} assigned respectively to CO_2 and CO synthesis. There is no evidence of ethylene glycol formation during warming.

Whereas 1 keV (1 hour, 10 μA) electron irradiation of the pure methanol film leads to formation of few new molecules, no significant modification of IR spectrum was observed in case of ammonia film irradiated in the same conditions.

Methanol:ammonia films

The IR spectrum of NH_3 and CH_3OH mixture condensed at 30 K (ratio 1:1 in gas phase) contains peaks associated with absorption bands ascribed to NH_3 and CH_3OH, respectively; indicating that no spontaneous reaction took place during deposition. Such prepared sample was irradiated with 100 eV electrons energy for 1.5 hour with 40 μA current. The only products

noticed in IR spectrum after irradiation at 30 K were CO_2 and CO. However during warming of sample, a new absorption feature appeared at 2165 cm^{-1} indicating the presence of OCN^- [2].

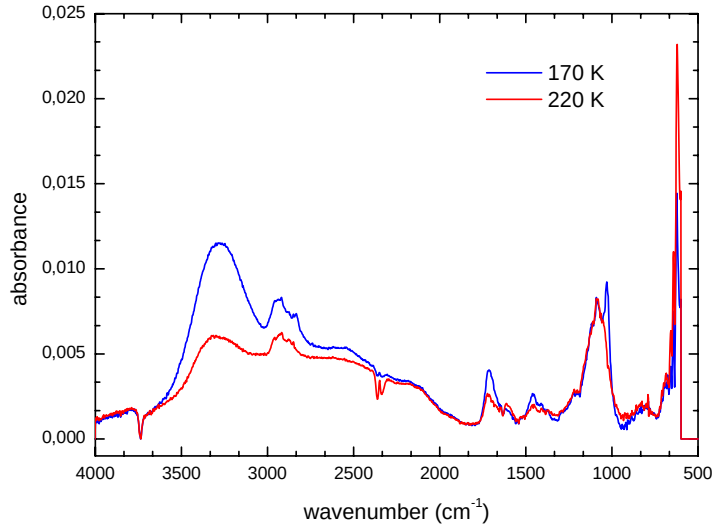

Figure 2: Infrared spectra of the residue irradiated methanol warming to 170 and 200 K.

The experiment with 100 eV electron irradiation was repeated with another NH_3:CH_3OH gas composition (ratio 4:7 Torr) deposited onto substrate; again only CO_2 and CO bands were observed (fig.3, red curve). The same sample was irradiated once more, but with 1 keV electrons for 15 minutes (current of 40 μA). The comparison of IR spectra before and after irradiation is shown in figure 3; the change of IR spectra is significant:

- H_2CO, CH_4 synthesis is observed (like in case of pure methanol film);
- the absorbance band for OCN^- is visible without need of heating;
- additional modifications are noticed which are associated with $HCOO^-$ and CH_2OH creation within ice.

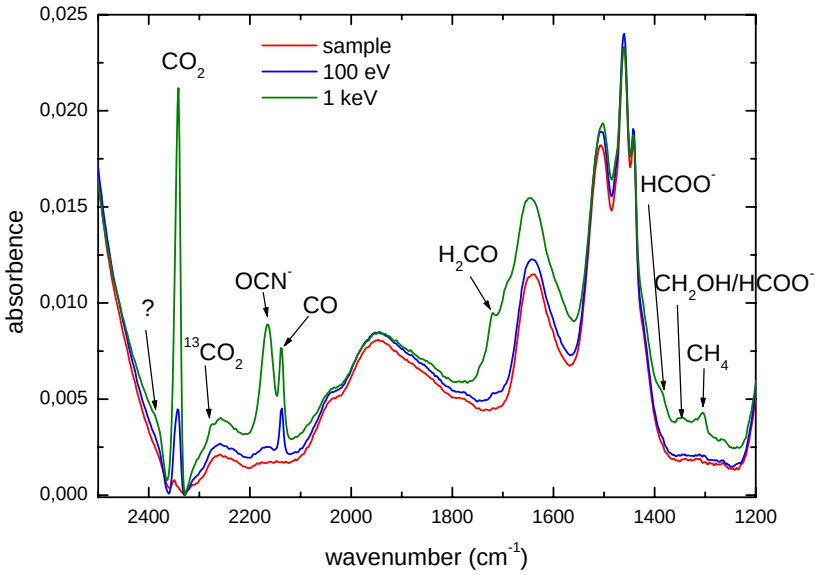

Figure 3: IR spectrum of deposited NH_3:CH_3OH film (ratio 4:7 in gas phase) at 30 K, in red; spectrum after irradiation with 100 eV electrons for 1.5 hour with a current of 40 μA, in blue; spectrum obtained after additional irradiation of 1 keV (15 min, 40 μA), in green.

1. C.J. Bennett, S.-H. Chen, B.-J. Sun, A.H.H. Chang, R.I. Kaiser, ApJ **660** (2007) 1588
2. S. Raunier, T. Chiavassa, F. Marinelii, A. Allouche, J.-P. Aycard, J. Chem. Phys. A **107** (2003) 9335