

Table S1 X-ray powder diffraction pattern of $\text{TlF}_3 \cdot \text{AsF}_5$

$d / \text{\AA}$	I/I_o
5.0052	60
4.0995	100
3.7919	20
3.6509	20
3.3625	90
2.7171	10
2.6031	20
2.5191	10
2.1607	20
2.0648	10
2.0082	40
1.8844	10

X-ray powder diffraction pattern was obtained using the Debye-Scherrer technique with Ni-filtered CuK_α radiation. Sample was loaded into quartz capillaries (0.3 mm) in a dry box. Intensities were estimated visually.

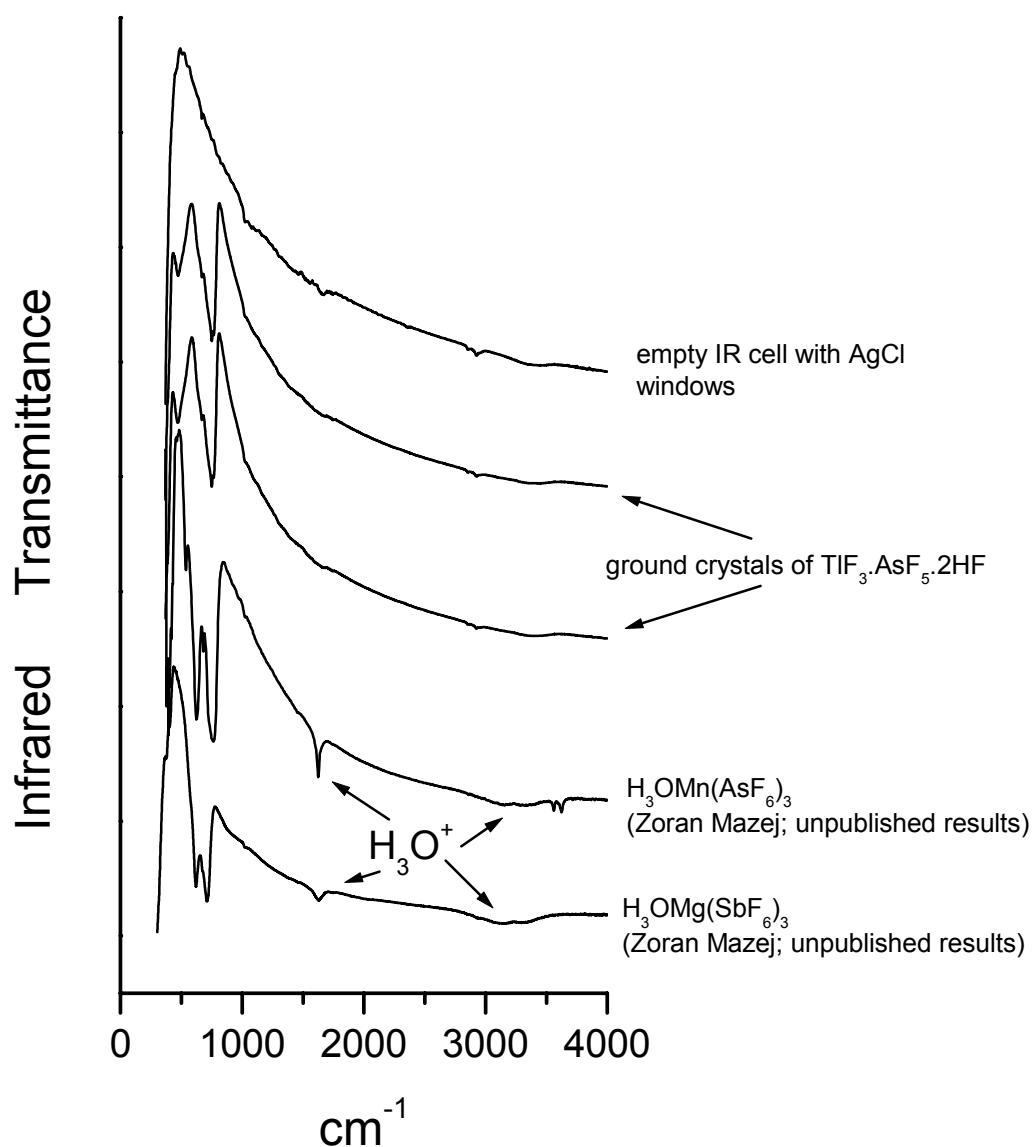


Fig. S1 Infrared spectra of ground crystals of $\text{TlF}_3 \cdot \text{AsF}_5 \cdot 2\text{HF}$ together with infrared spectrum of empty IR cell and IR spectra of two H_3O^+ salts.

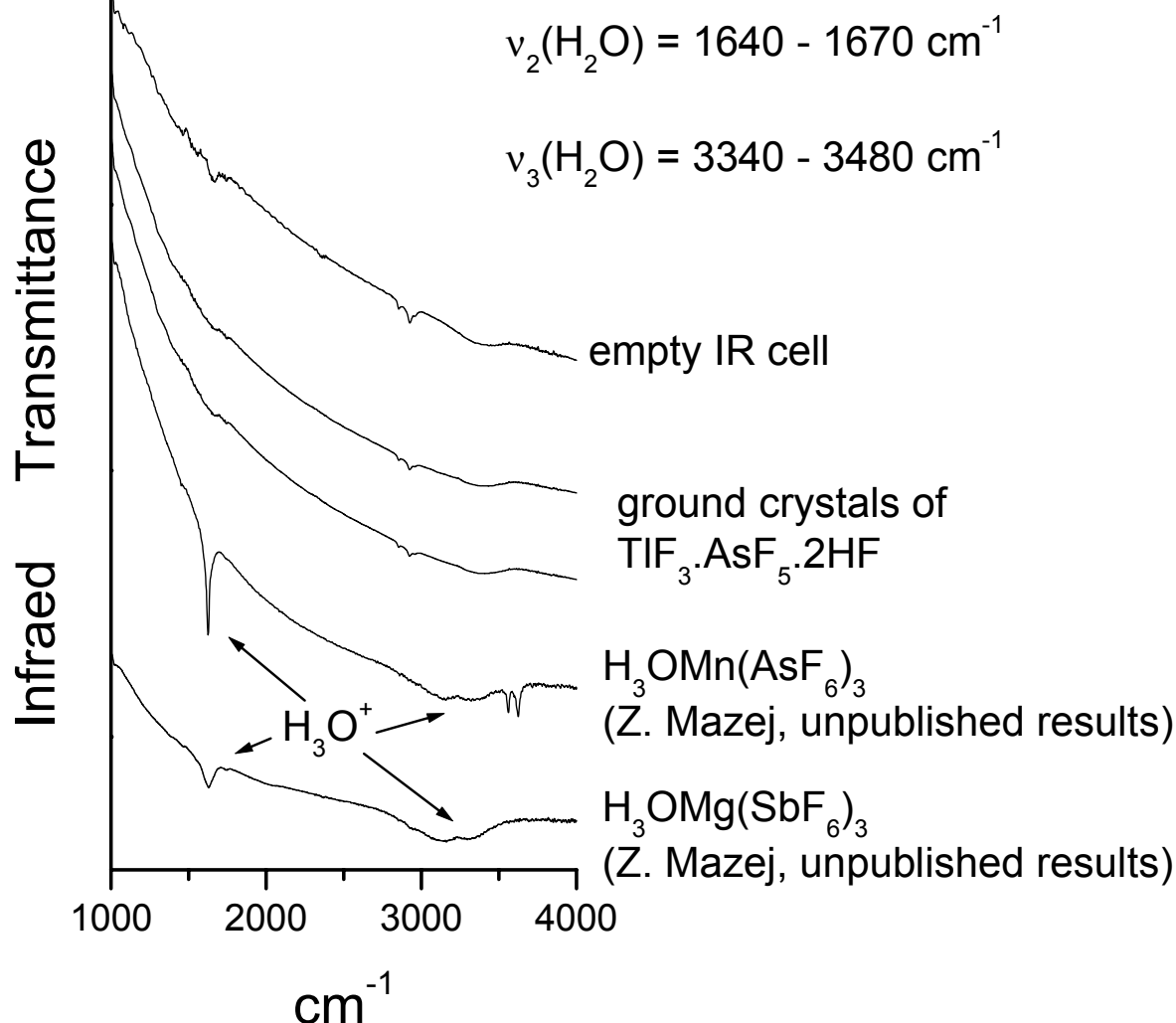


Fig. S2 Detail of infrared spectra of ground crystals of $\text{TlF}_3 \cdot \text{AsF}_5 \cdot 2\text{HF}$, infrared spectrum of empty IR cell, IR spectra of two H_3O^+ salts and infrared data for water.

Remark:

During the preparation of the sample of ground crystals of $\text{TlF}_3 \cdot \text{AsF}_5 \cdot 2\text{HF}$ for infrared measurement in a glove-box, sample was warmed to ambient temperature and it could decompose to $\text{TlF}_3 \cdot \text{AsF}_5$.

Compounds with coordinated water or oxonium salts are much more stable than HF containing compounds. Hypothetical $\text{TlF}_3 \cdot \text{AsF}_5 \cdot 2\text{H}_2\text{O}$ or $(\text{H}_3\text{O})\text{Tl}(\text{F})\text{F}_2(\text{AsF}_6)$ could release water and water/HF, respectively, at their decomposition. In that case, liberated water could not evaporate so quickly and it should be still detected in the infrared spectra. Additionally, it was observed that when Tl^{3+} salts were exposed to moisture in the atmosphere, they immediately turned brown.

Since no vibrational bands belonging to water or to H_3O^+ were observed and since sample, after recording IR spectra, was still snow white, it could be concluded that H_2O and H_3O^+ were neither present or neither liberated (H_3O^+ as H_2O) from grown crystals obtained after crystallization of $\text{TlF}_3/\text{AsF}_5/\text{aHF}$ mixture.

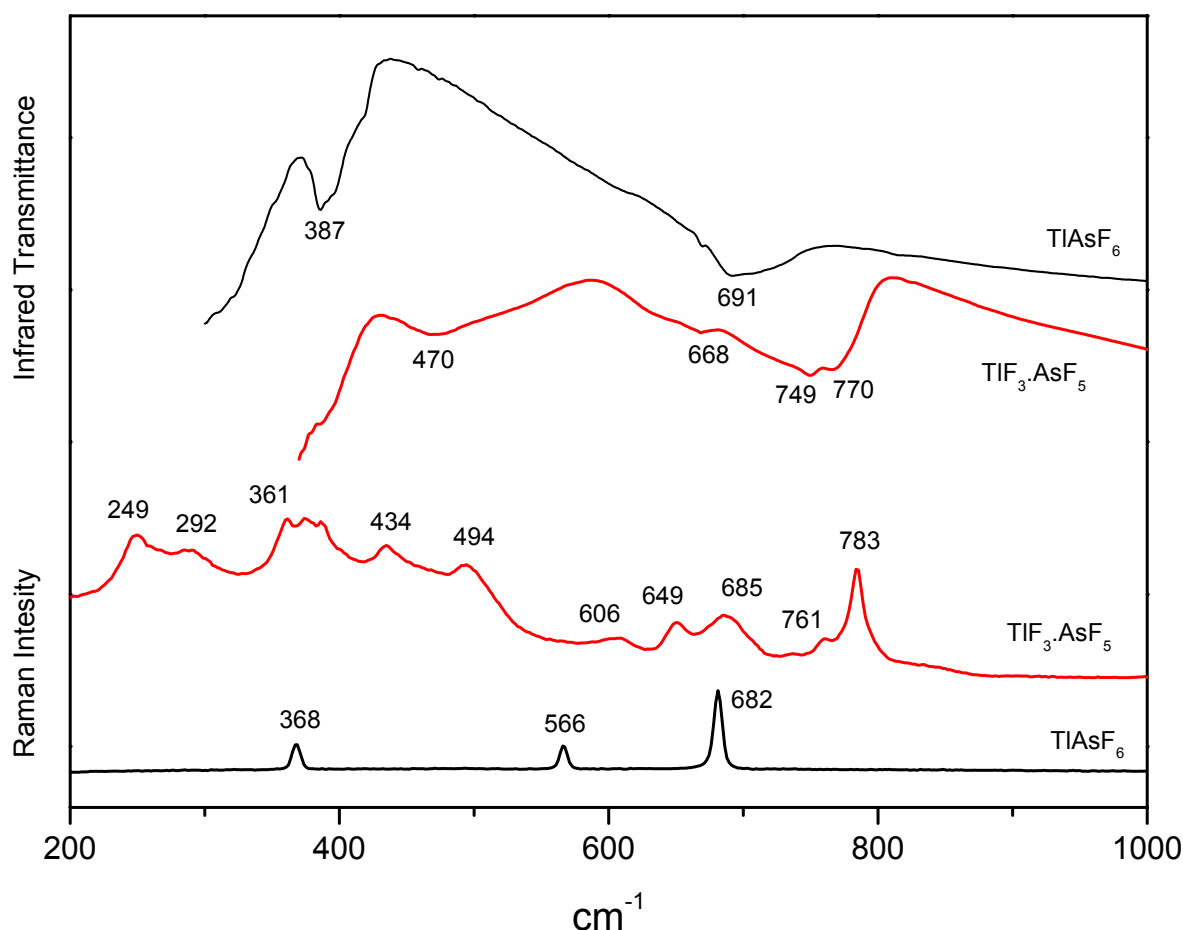


Fig. S3 Vibrational spectra of $\text{TlF}_3 \cdot \text{AsF}_5$ and Raman spectrum of TlAsF_6

Infrared spectra of $\text{TlF}_3 \cdot \text{AsF}_5 \cdot 2\text{HF}$ were taken on a Perkin-Elmer Spectrum GX spectrometer on powdered samples between AgCl windows in a leak tight brass-cell. Raman spectra of $\text{TlF}_3 \cdot \text{AsF}_5 \cdot 2\text{HF}$ were obtained with a HORIBA JOBIN YVON LabRam-HR Raman micro-spectrometer. The sample was excited by the 632.8 nm emission line of a He-Ne-laser (17 mW).

