Hunt for Molecules
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MOLECULES IN PLANETARY ATMOSPHERES

Lellouch, E.[1]

Abstract. Molecules in planetary atmospheres trace chemical processes, atmospheric dynamics, external sources, and bear information on the origin and evolution and planets. Examples are given, and some of the historical or spectacular detections are shown. Millimeter-wave spectroscopy is playing its role in these achievements.

1 Some very brief history

The first molecules in planets have been discovered exactly a century ago. In 1905, V.M. Slipher (Lowell Observatory) obtained photographic spectra of Saturn and Jupiter in which he found strong absorption bands. It was not until 1932, however, that these bands were identified as methane and ammonia (see Wildt 1969). One year before Pierre Encrenaz was born, Kuiper (1944) discovered methane in the photographic infrared spectra of Uranus, Neptune and Titan, as well as other weak bands that were shown by Herzberg to be due to molecular hydrogen. Fig. 1 shows Kuiper's detection of methane on Titan. About this and the other planetary observations, Kuiper wrote: "The only reason why I happened to observe the planets and the ten brightest satellites was that they were nicely lined up in a region of the sky where I had run out of programs stars...". Yet, methane is now recognized to be the second in abundance but first in importance molecule in Titan's atmosphere, controlling both the tropospheric meteorology and the stratospheric chemistry.

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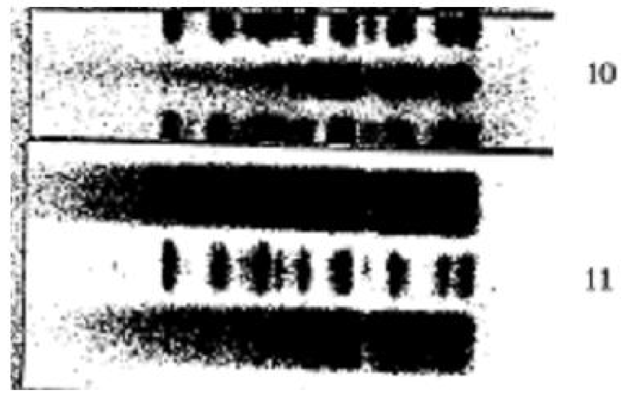

Fig. 1. The detection of methane in Titan (Kuiper 1944)

As far as the millimeter range is concerned, the first results were the detection of CO in Venus and Mars (Kakar et al. 1976, 1977). It was quickly noted (Wilson et al. 1981) that CO is more abundant on Venus's nightside than on the dayside (Fig. 2), a result that is now understood to be due to day-to-night transport in the upper atmosphere of Venus (80-110 km) probed by the millimeter observations.

2 Why study molecules in planetary atmospheres?

There are numerous reasons to hunt for molecules in planets, and particularly atmospheres. A first, esthetic rather than scientific, reason is that planetary spectra can be beautiful. Particularly spectacular (in my taste) spectra include the detections of CH_3CN on Titan in the millimeter range (obtained at IRAM in 1992 and published in Marten et al. 2002, Fig. 3), of C_6H_6 in Saturn, obtained in the IR with ISO (Bézard et al. 2001), and of S_2 in Io's volcanic plume Pele, achieved in the UV by HST (Spencer et al. 2000).

Although they probably do not rival the ISM, molecules in planetary atmospheres are too numerous to be extensively discussed in this review, and it is more useful to illustrate the kind of information they provide. In

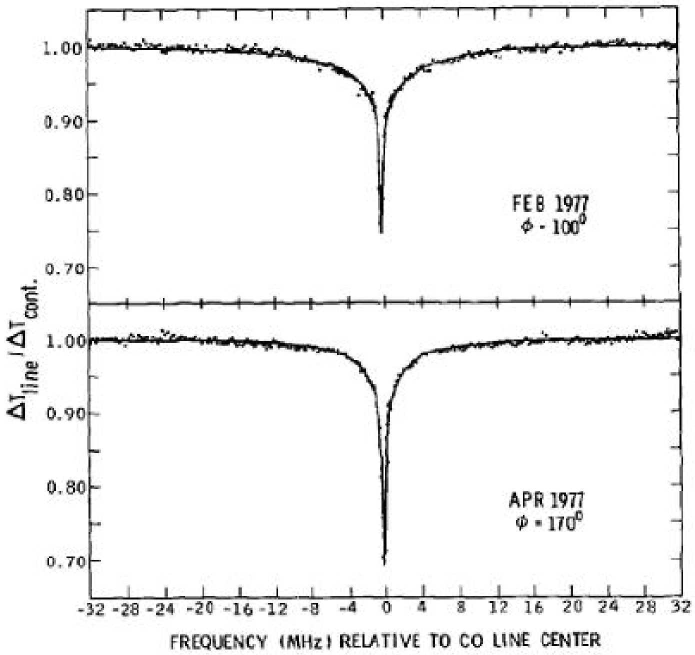

Fig. 2. The CO(1-0) millimeter line on the dayside (top) and nightside of Venus (Wilson et al. 1978)

the first place, detecting new species is useful to constrain chemical pathways, whose complexity can be frightening (see Moses et al. 2000). This is particularly true, e.g. for Giant Planet's and Titan's atmospheres, in which the detection of numerous hydrocarbons up to C_6 (CH_4, CH_3, C_2H_2, C_2H_4, C_2H_6, CH_3CCH (propyne), C_3H_4 (allene), C_3H_8, C_4H_2, C_6H_6) has been achieved. Titan's methane chemistry is even more complex, since it is coupled with the nitrogen photochemistry, giving rise to the presence several nitriles. Another example is the recent detection of hydrogen peroxide (H_2O_2) in the martian atmosphere (Fig. 4). Hydrogen peroxide has long been predicted to be present as a result of the water photochemistry. The main production mechanism of H_2O_2 is $HO_2 + HO_2 \longrightarrow H_2O_2$, and is main

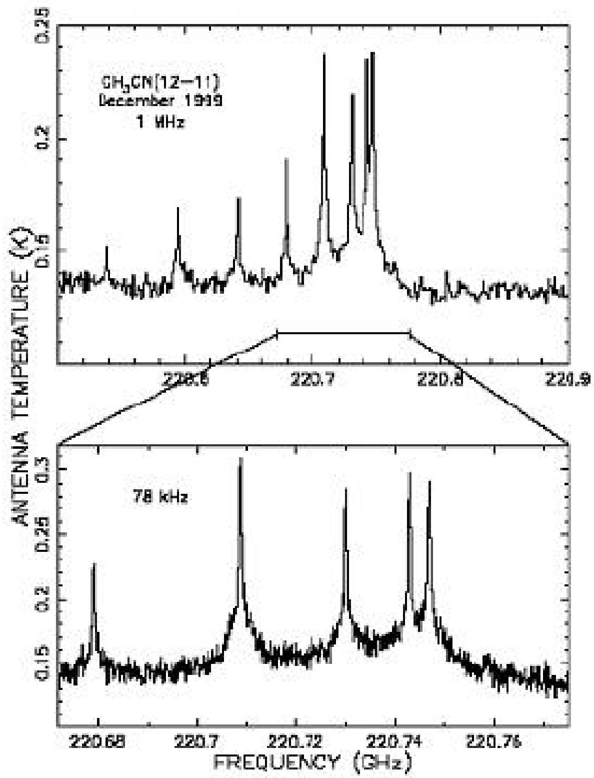

Fig. 3. The detection of CH_3CN on Titan, achieved at the 30-m telescope. From Marten et al. 2002

loss process is photolysis. After long searches, H_2O_2 was finally detected during the 2003 opposition, both in the sub-millimeter by Clancy et al. 2004) and in the IR range by T. Encrenaz et al. (2004).

The second general field is that of planetary atmosphere dynamics and their couplings with chemistry. Molecules trace dynamics in different manners. First, line spectroscopy (especially line-resolved, as in the case at millimeter wavelengths) provides information on the species vertical profile,

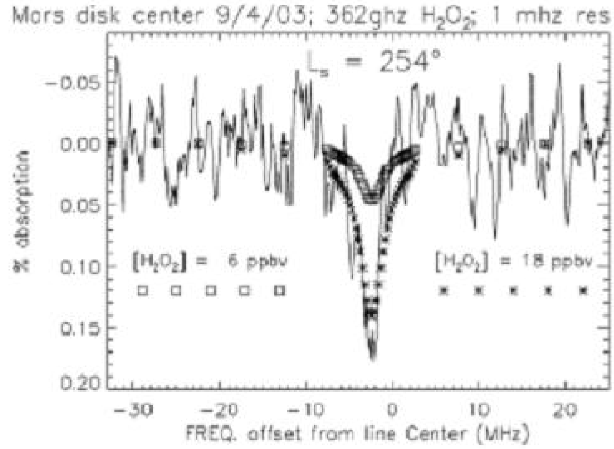

Fig. 4. The submillimeter detection of H_2O_2 on Mars, obtained at JCMT. From Clancy et al. 2004

which is often diagnostic of vertical transport (eddy diffusion and vertical winds). Second, molecular profiles bear information on thermal profiles and on horizontal winds. Winds are related to the global thermal field, and can also be measured directly from Doppler shift. Finally, the horizontal distribution (especially in latitude) of minor species constrains horizontal transport processes, especially horizontal advection by meridional winds and horizontal eddy mixing. Examples can be found in the mapping of CO millimeter lines in Venus atmosphere (Lellouch et al. 1994), or the direct measurement of mesospheric winds at 300 and 450 km in Titan's atmosphere (Moreno et al. 2005, Fig. 5).

Molecules can also trace interaction between Solar System objects. A highlight of the ISO observations was the discovery of an external source of water in the upper atmosphere of the Outer Planets (Feuchtgruber et al. 1997). This source may include interplanetary dust, planetary environments (icy satellite surfaces, rings), and cometary impacts. The role of cometary impacts was amply demonstrated by the dramatic and still observable modification of Jupiter's stratosphere composition following the comet Shoemaker-Levy 9 impacts. CO has been demonstrated to be present

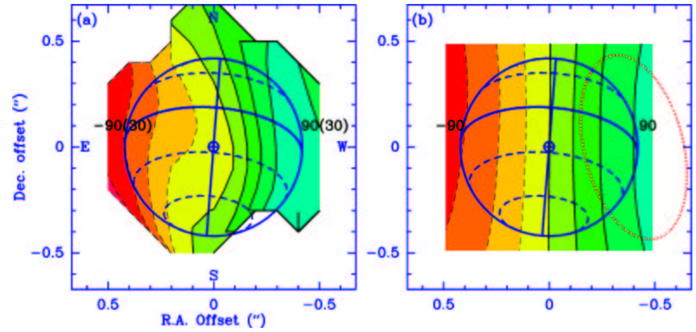

Fig. 5. Interferometric wind measurements in Titan's atmosphere. From Moreno et al. 2005

in the stratosphere of all Giant Planets (except possibly Saturn), and the possible existence of a dual – i.e. internal and cometary – source of CO in Neptune's atmosphere has been recently outlined (Lellouch et al. 2005).

High-resolution molecular spectroscopy is also a powerful means to study thin, exotic atmospheres. The best example here is Io's volcanic atmosphere, whose composition includes SO_2, SO, S_2, and NaCl (see review in McGrath et al. 2004). The latter species, which unlike SO_2, has a negligible equilibrium vapor pressure at Io's temperature, is a proof that volcanism directly injects species into the atmosphere, from which they can quickly escape into the neutral clouds and the plasma torus surrounding Io.

Finally, the molecular and isotopic content in planetary atmospheres bears information on the origin and evolution of planets. The most popular example is deuterium abundance in the Giant Planets, which can be viewed as resulting from the mixing (with variable relative weights for the different planets) of two reservoirs: (i) the gaseous nebula and (ii) the D-enriched icy grains that were embedded in the nebula. The abundance of deuterium in secondary atmospheres (the telluric planets and Titan) trace escape processes and indicate generally denser (and wetter, for Venus and Mars) atmospheres in the past. A more recent and less known result is that while the $^{12}C/^{13}C$ ratio in Titan's atmosphere has a terrestrial value, the $^{14}N/^{15}N$ ratio is depleted by a factor of 1.5 in N_2 and a factor of 4.5 in HCN (Waite et al. 2005). This indicates that (i) Titan's atmosphere was probably denser in the past by a factor of 4-20 (ii) fractionation processes exist that selectively enrich ^{15}HCN and (iii) carbon is constantly replenished to Titan's atmosphere to maintain a telluric isotopic content.

3 Remerciements

C'est un plaisir de remercier Pierre Encrenaz pour le soutien qu'il m'a apporté avec tant de gentillesse tout au long des années. Je lui sais gré en particulier (i) de m'avoir conseillé de faire ma thèse avec Thérèse (ii) de m'avoir donné des avis précieux (notamment "N'écoute pas les astronomes qui te diront que les observations millimétriques des planètes n'ont aucun intérêt !" (il y en eut)). Les meilleurs souvenirs remontent à l'année 1990, avec les observations au 30-m ayant abouti à la détection de SO_2 dans l'atmosphère de Io (Pierre était présent) et l'école des Houches que Pierre avait organisée cette année-là.

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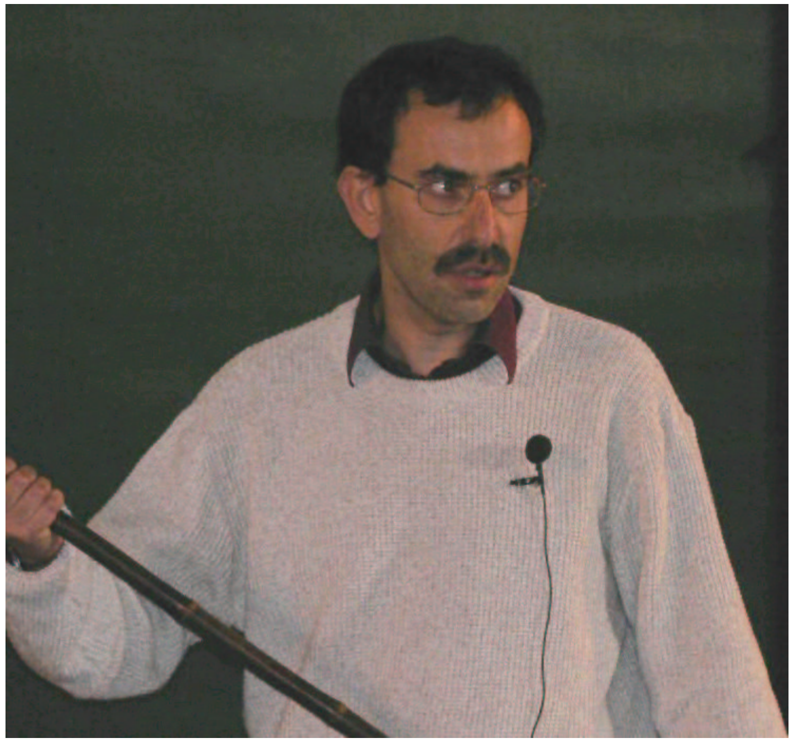

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