

## STRATOSPHERIC HCl FROM INFRARED SPECTRA

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**Abstract.** HCl has been observed in the stratosphere from balloon borne spectroscopic measurements of a portion of the fundamental band in the 3 microns wavelength region. The observation of absorption lines using the sun as a source at solar zenith angles larger than  $90^\circ$  indicates an HCl volume mixing ratio equal to  $(3.8 \pm 1.5) \times 10^{-10}$  at 20 km increasing with altitude at least up to 30 km where the value is  $(1.4 \pm 0.6) \times 10^{-9}$ . The total zenith amount above 21 km is found to be  $(10 \pm 3.5) \times 10^{14} \text{ cm}^{-2}$  in agreement with previous observations performed up to this altitude. A maximum number density equal to  $(7.2 \pm 3) \times 10^8 \text{ cm}^{-3}$  is observed at  $24 \pm 2 \text{ km}$  altitude.

### Introduction

Since the indication has been given by Stolarsky and Cicerone (1974) that chlorine from industrial and natural sources can play a role in the odd oxygen balance in the stratosphere, the interest in this species has become evident. It has grown considerably when Molina and Rowland (1974) have drawn the attention to the stratospheric problem associated with the release of chlorofluoromethanes. The main removal process of Cl from the stratosphere to the troposphere is considered to be through HCl rainout. Measurements of the vertical distribution of hydrochloric acid in the stratosphere are essential for the understanding of the chemical and physical sources and sinks of this molecule at the various altitudes (for a review, see Rowland and Molina (1975) and Nicolet (1975)). Specific determination of HCl by the spectroscopic method has recently been performed up to 21 km by Farmer, Raper and Norton (1975). The measurements reported here extend the data up to 34 km.

### Observation

A grille spectrometer (Girard, 1963) similar to the instrument flown previously for the determination of vertical distributions of stratospheric NO and NO<sub>2</sub> (Ackerman *et al.*, 1975) has been used on board of a balloon gondola equipped with an azimuth control unit and with a servocontrolled

plane mirror for elevation and fine azimuth sun tracking. The flight took place in the afternoon of October 2, 1975, from the CNES range in Aire sur l'Adour (France). A Zodiac 100.000 m<sup>3</sup> balloon was used to carry the 217 kg payload at the ceiling altitude of 35 km which was reached at 1623 GMT, the solar elevation angle being  $13^\circ$ . The intensity of the solar radiation was then measured in the spectral interval:  $2916 \text{ cm}^{-1} - 2970 \text{ cm}^{-1}$  with a scanning time of 6.5 minutes. The spectra recorded when the sun was well above the horizon showed no absorption feature in the solar continuum occurring at the positions of the lines used in this work.

HCl absorption features become detectable for a solar elevation equal to  $1^\circ$ . Telluric absorptions became more and more pronounced as the solar radiation was traversing denser and denser atmospheric layers. Sun tracking ended at 1806 GMT. The spectral interval is dominated by methane absorption lines due to the 3 micron band. The resolution achieved is  $0.22 \text{ cm}^{-1}$  and allows the investigation of small absorptions features in narrow methane windows. Six pairs of HCl lines occur in the wavelength range considered. As shown in figure 1, the four R<sub>1</sub> and R<sub>2</sub> components due to the HCl<sup>37</sup> and HCl<sup>35</sup> isotopic molecules have been observed.

### Results

The HCl<sup>35</sup> R<sub>1</sub> and R<sub>2</sub> lines at  $2925.91 \text{ cm}^{-1}$  and  $2944.92 \text{ cm}^{-1}$  respectively are insignificantly contaminated by other absorbers. Their integrated absorptions have been measured and plotted versus the minimum altitude reached in the atmosphere by the solar rays corresponding to the solar depression angle occurring at the time of recording of the individual lines. The curve of growth has been inverted with layers of 2 km thickness to deduce a vertical distribution of HCl from 18 to 34 km. The values of integrated absorption cross sections used are those published by Toth *et al.* (1970). They have been adapted to the stratospheric temperatures. The effects due to the Voigt profiles of the lines have been taken into account (Whitting, 1968) in the inversion process with a Lorentz half width of  $0.1 \text{ cm}^{-1}$  at NTP conditions (Rank *et al.* 1963). Figure 2 shows the deduced volume

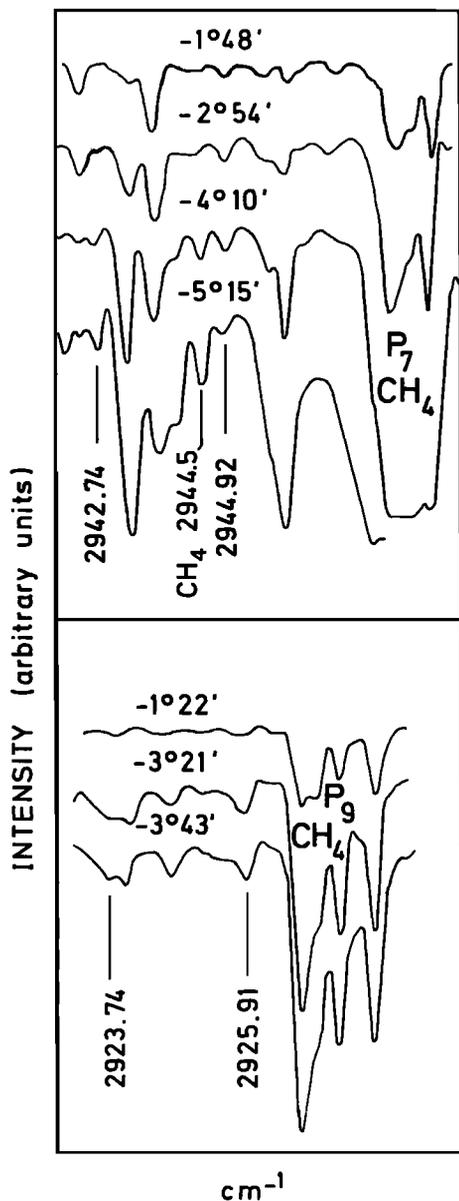


Figure 1. Portions of spectra observed from 35 km altitude in the spectral regions of the  $P_7$  and  $P_9$  multiplets of  $\text{CH}_4$ . The astronomical solar depression angles are indicated for each spectrum. The  $R_1$  and  $R_2$   $\text{HCl}^{35}$  lines at  $2925.91 \text{ cm}^{-1}$  and  $2944.92 \text{ cm}^{-1}$  respectively exhibit a very different growth with increasing solar zenith angle from the neighbouring methane lines (see for instance the  $\text{CH}_4$  feature at  $2944.5 \text{ cm}^{-1}$ ). The  $R_1$  and  $R_2$   $\text{HCl}^{35}$  lines at  $2923.74 \text{ cm}^{-1}$  and  $2942.74 \text{ cm}^{-1}$  appear smaller as expected and less well separated from the  $\text{CH}_4$  components at the achieved resolution of  $0.22 \text{ cm}^{-1}$ .

mixing ratios versus altitude with the uncertainty limits which include the uncertainties in the measurement of the absorptions, these being always smaller than 10% at the line center for the altitude range covered and the uncertainties arising from the inversion process.

### Discussion and conclusion

The HCl volume mixing ratios obtained from this balloon experiment are lower than those of Farmer *et al.* (1975) in the narrow altitude range where they can be compared. The small disagreement can be due to geographic or time variability. It could also be due to the rather important amount of hydrochloric acid above the top flight altitude of the aircraft used which did not give the full use of the large solar zenith angle effect to obtain the maximum atmospheric path. The total vertical amount of HCl above 21 km found by means of the balloon borne spectrometer is however equal to  $(10 \pm 3.5) \times 10^{14} \text{ cm}^{-2}$ , in agreement with the value deduced by Farmer *et al.* (1975), supporting their conclusion that the maximum mixing ratio is located somewhere above the maximum aircraft flight level. It appears now to be above 30 km but close to this altitude since the measurements at 35 km indicate that the total vertical amount of HCl above this altitude is  $(2.2 \pm 0.7) \times 10^{14} \text{ cm}^{-2}$ . This leads also to the conclusion that balloon flights at 45 km are required to better define the stratospheric vertical distribution of HCl in order to compare experimental data with theoretically evaluated amounts of HCl in the actual stratosphere.

*Acknowledgements.* Thanks are due to Mr. Fergant from ONERA and to Mr. Van Ransbeeck from IASB for their contribution to the success of the experiment. The help of

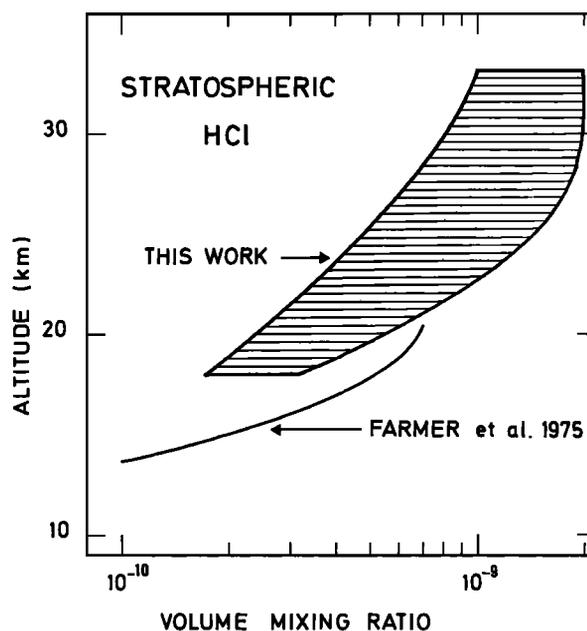


Figure 2. Volume mixing ratio computed from the observed number densities of HCl and from the total atmospheric densities taken from the Mi-Latitude Spring/Fall model of the U.S. Standard Atmosphere Supplements, 1966 versus altitude. The stratospheric aircraft measurements of Farmer *et al.* (1975) are also shown.

the CNES balloon division in Toulouse and the skill of the operations and launching teams in Aire sur l'Adour are gratefully acknowledged. This work was partly supported by COVOS.

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(Received October 20, 1975;  
accepted January 13, 1975.)