Stratospheric HCl from infrared spectra

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FOREWORD

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STRATOSPHERIC HCl FROM INFRARED SPECTRA

by

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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° 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 $(10 \pm 3.5) \times 10^{14}$ cm$^{-2}$ in agreement with previous observations performed up to this altitude. A maximum number density equal to $(7.2 \pm 3) \times 10^{8}$ cm$^{-3}$ is observed at $24 \pm 2$ km altitude.

Résumé

HCl a été observé dans la stratosphère par mesure spectroscopique en ballon d'une partie de la bande fondamentale à 3 microns de longueur d'onde. L'observation de raies d'absorption en utilisant le soleil comme source à des distances zénithales supérieures à 90° indique une concentration volumique égale à $(3.8 \pm 1.5) \times 10^{-10}$ à 20 km croissant avec l'altitude au moins jusqu'à 30 km où la valeur est de $(1.4 \pm 0.6) \times 10^{-9}$. La quantité zénithale au-dessus de 21 km est trouvée égale à $(10 \pm 3.5) \times 10^{14}$ cm$^{-2}$ en accord avec des observations antérieures effectuées jusqu'à cette altitude. Un maximum de concentration de $(7.2 \pm 3) \times 10^{8}$ cm$^{-3}$ est observé à $24 \pm 2$ km d'altitude.
Samenvatting

HCl werd per ballon waargenomen in de stratosfeer door de spectroscopische meting van een gedeelte van de fundamentele band bij een golflengte van 3 micron. De waarneming van absorptielijnen, waarbij de zon als bron werd gebruikt voor zenithale afstanden groter dan 90°, geeft een volumetrische dichtheid van \((3,8 \pm 1,5) \times 10^{-10} \text{ cm}^{-3}\) bij 20 km. Deze waarde stijgt met de hoogte minstens tot 30 km waar de waarde \((1,4 \pm 0,6) \times 10^{-9} \text{ cm}^{-3}\) is. De zenithale hoeveelheid boven de 20 km wordt gelijk gevonden aan \((10 \pm 3,5) \times 10^{14} \text{ cm}^{-2}\) in overeenstemming met de waarnemingen vroeger verricht tot op deze hoogte. Een dichtheidsmaximum van \((7,2 \pm 3) \times 10^{8} \text{ cm}^{-3}\) werd waargenomen bij 24 ± 2 km hoogte.

Zusammenfassung

HCl wurde durch Ballon spektroskopische Messungen in einem Teil der \(3\mu\) fundamen-
talen Band beobachtet. Mit der Sonne als Lichtquelle auf einer Zenitdistanz grösse

rer als 90°, wird ein HCl Mischungsverhältnis von \((3,8 \pm 1,5) \times 10^{-10}\) auf einer Höhe von 20 km fest-
gestellt. Das Mischungsverhältnis steigt mit der Höhe wenigstens bis zu 30 km, wo eine Wert

von \((1,4 \pm 0,6) \times 10^{-9}\) beobachtet ist. Der gesamte senkrechte Gehalt oberhalb 21 km ist

\((10 \pm 3,5) \times 10^{14} \text{ cm}^{-2}\) in Übereinstimmung mit anderen Beobachtungen auf dieser Höhe.

Die maximum Konzentration von \((7,2 \pm 3) \times 10^{8} \text{ cm}^{-3}\) ist auf einer Höhe von 24 ± 2 km

beobachtet.
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\textsubscript{2} (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\textsuperscript{3} 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°. The intensity of the solar radiation was then measured in the spectral interval 2916 cm\textsuperscript{-1} - 2970 cm\textsuperscript{-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°. 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 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 \(R_1\) and \(R_2\) components due to the HCl\(^{37}\) and HCl\(^{35}\) isotopic molecules have been observed.

**RESULTS**

The HCl\(^{35}\) \(R_1\) and \(R_2\) lines at 2925.91 cm\(^{-1}\) and 2944.92 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 \textit{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 cm\(^{-1}\) at NTP conditions (Rank \textit{et al.} 1963). Figure 2 shows the deduced volume 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 \textit{et al.} (1975) in the narrow altitude range where they can be compared. The
Fig. 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 \( R_2 \) HCl\(^{35}\) lines at 2925.91 cm\(^{-1}\) and 2944.92 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 cm\(^{-1}\)). The \( R_1 \) and \( R_2 \) HCl\(^{37}\) lines at 2923.74 cm\(^{-1}\) and 2942.74 cm\(^{-1}\) appear smaller as expected and less well separated from the \( \text{CH}_4 \) components at the achieved resolution of 0.22 cm\(^{-1}\).
Fig. 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.
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.

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