INSTITUT D'AERONOMIE SPATIALE DE BELGIQUE
3 - Avenue Circulaire
B - 1180 BRUXELLES

AERONOMICA ACTA

A - N° 184 - 1977

Stratospheric CH_4, HCl and ClO and the chlorine-ozone cycle

by

M. ACKERMAN, D. FRIMOUT and C. MULLER

BELGISCH INSTITUUT VOOR RUIMTE-AERONOMIE
3 - Ringlaan
B - 1180 BRUSSEL

FOREWORD

Stratospheric CH_4, HCl and ClO and the Chlorine-Ozone cycle has been accepted for publication in Nature.

AVANT-PROPOS

Stratospheric CH_4, HCl and ClO and the Chlorine-Ozone cycle paraîtra dans la revue Nature.

VOORWOORD

Stratospheric CH_4, HCl and ClO and the Chlorine-Ozone, werd voor publicatie in het tijdschrift Nature aanvaard.

VORWORT

Stratospheric CH_4, HCl and ClO and the Chlorine-Ozone, wird in der Zeitschrift Nature herausgegeben werden.

STRATOSPHERIC CH_4, HCl and ClO AND THE CHLORINE-OZONE CYCLE

by

M. ACKERMAN, D. FRIMOUT and C. MULLER

Abstract

The ratio of the measured HCl and ClO abundances is in good agreement with the computed values if the recently determined methane concentrations are introduced in the computation with the measured O, OH, O_3, NO and H_2 concentrations.

Résumé

Le rapport des abondances de HCl et ClO stratosphériques est en accord avec les valeurs calculées si les concentrations de méthane déterminées récemment sont introduites dans le calcul associées à celles de O, OH, O_3, NO et H_2 mesurées.

Samenvatting

De verhouding van de gemeten stratosferische HCl en ClO hoeveelheden, komt overeen met deze van de berekende waarden indien de onlangs bepaalde methaan concentraties in acht genomen worden samen met de gemeten waarden voor O, OH, O_3, NO en H_2.

Zusammenfassung

Das Verhältnis der gemessenen stratosphärischen Dichten von HCl und ClO stimmt mit den gerechtneten Werten überein, wenn die neuen festgestellten Methandichten sowie die gemessenen Werten von O, OH, O_3, NO und H_2 in den Rechnungen eingeführt werden.

Since it has been suggested[1] that chlorine can play a role on the stratospheric ozone balance, much attention has been paid to the subject, particularly when it has been realized that halocarbons can contribute significantly to the stratospheric chlorine content[2,3,4]. In addition to atomic chlorine two main species of the chlorine-ozone cycle have been measured in the stratosphere, namely HCl[5] and ClO[6], of which the ratio of abundances can be expressed by the relation[3]

$$n\,HCl/n\,ClO = (k_1\,n\,CH_4 + k_2\,n\,H_2 + k_3\,n\,HO_2)\,(k_4\,n\,O + k_5\,n\,NO)/$$

$$k_6\,n\,O_3 \times k_7\,n\,OH \qquad (1)$$

where n A represents the number density of species A and k's expressed below in cm^3 $molecule^{-1}$ s^{-1}, represent the rate constants[7] of the reactions

$CH_4 + Cl \rightarrow CH_3 + HCl$	$k_1 = 5 \times 10^{-12}\,e^{-1114/T}$
$H_2 + Cl \rightarrow H + HCl$	$k_2 = 5.6 \times 10^{-11}\,e^{-2250/T}$
$HO_2 + Cl \rightarrow O_2 + HCl$	$k_3 = 10^{-11}$
$ClO + O \rightarrow Cl + O_2$	$k_4 = 5.3 \times 10^{-11}$
$ClO + NO \rightarrow Cl + NO_2$	$k_5 = 1.7 \times 10^{-11}$
$Cl + O_3 \rightarrow ClO + O_2$	$k_6 = 3.6 \times 10^{-11}\,e^{-318/T}$
$HCl + OH \rightarrow Cl + H_2O$	$k_7 = 3 \times 10^{-12}\,e^{-400/T}$

The $H_2O_2 + Cl \rightarrow HCl + HO_2$ reaction has been neglected due to its low rate constant[8].

All species in very low stratospheric concentration, HO_2 excepted which plays a minor role, intervening in relation (1) have been measured : H_2[9], NO[10,11], O[12,13] and OH[14]. The abundance of ozone is known[15] and most studies have relied on CH_4 data obtained in the stratosphere by in situ sampling[9].

In the altitude range (32-36 km) where data are available for computation the n HCl/n ClO ratio is observed to be about 0.8 while values ranging from 4.5 to 3.5 result from model calculations[4].

A new determination[16] of CH_4 has been performed by means of infrared absorption spectrometry from a balloon platform wich leads to methane mixing ratios above 25 km lower than currently used in stratospheric models. The results, shown in figure 1, have been derived from spectra of the 3.3. μm CH_4 band obtained simultaneously with HCl absorption spectra[17]. They have been used in conjunction with all other measurements to evaluate the n HCl/n ClO ratio from equation (1) in order to deduce the effect of these new data on the chlorine-ozone cycle. The number densities used in the computation are listed in table 1 with the results. The computed values of the n HCl/n ClO ratio appear to be in good agreement with the observed ones while the model calculated ratios are, especially at the lowest altitude, in marked disagreement. Part of this disagreement is due to the use in models of high methane concentrations which have already been considered as being surprisingly large by Wofsy and McElroy[19]. A similar opinion has been expressed by Rowland and Molina[3] who have considered the possibility of lower methane concentrations leading to an enhancement by a factor of 2 or 3 of the chlorine atom chain.

In conclusion, it turns out that introducing high methane concentrations[9] into model calculations[4] has lead to a computed n HCl/n ClO ratio, for the case considered here, 2.3 times higher, lowering the effect of chlorine on ozone.

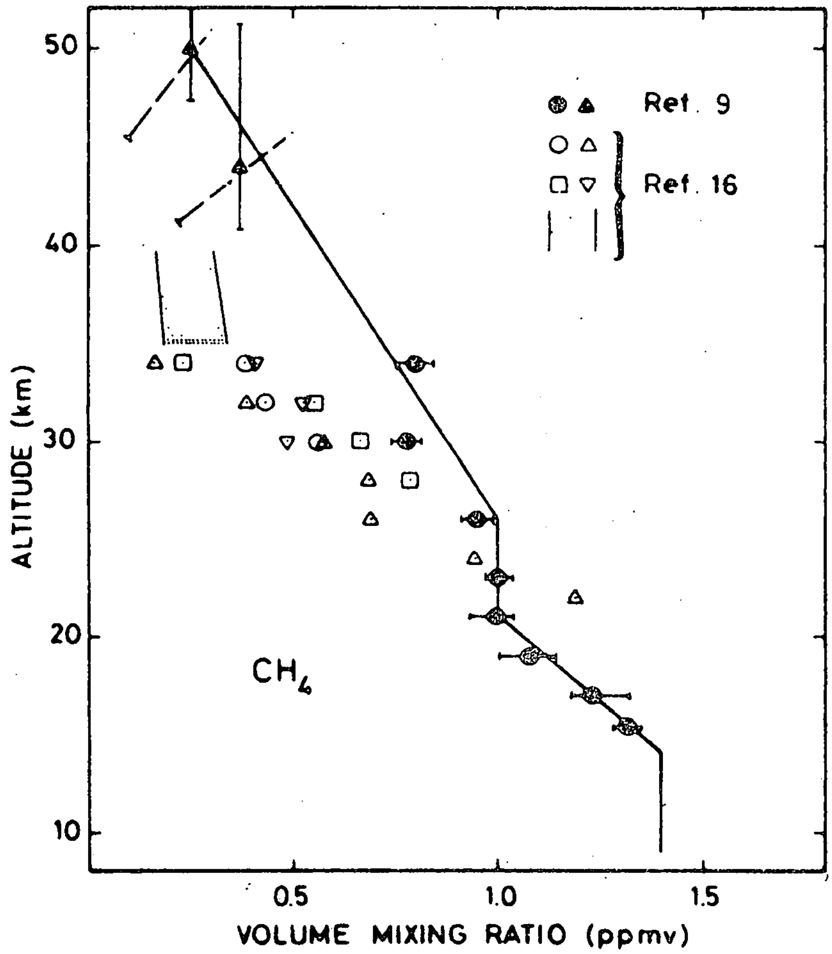

Fig. 1.- Vertical distribution of the volume mixing ratio of methane. The in situ sampling results[9] are shown with the values recently determined[16] by means of infrared spectrometry of the P_5 to P_8 multiplets of the 3.3 μm band. The solid curve represents the values used in model calculations[4]. The envelope above 35 km corresponds the methane absorptions at zenith angle, χ, smaller than 90°.

TABLE 1.- Data used in the evaluation of n HCl/n ClO and results.

	Altitude (km)		
	32	34	36
n O_3[15]	2.5×10^{12}	1.9×10^{12}	1.4×10^{12}
n CH_4[16]	1.2×10^{11}	7.0×10^{10}	4.2×10^{10}
n H_2[9]	2.0×10^{11}	1.4×10^{11}	1.0×10^{11}
n HO_2[3]	2.2×10^{7}	1.9×10^{7}	1.5×10^{7}
n OH[14]	1.1×10^{7}	1.1×10^{7}	1.5×10^{7}
n O[13]	1.3×10^{8}	2.6×10^{8}	3.9×10^{8}
n NO[11]	1.3×10^{9}	1.1×10^{9}	7.0×10^{8}
T(K)[18]	228	234	239
n HCl (observed)[17]	4.2×10^{8}	3.0×10^{8}	2.4×10^{8}
n ClO (observed)[6]	5×10^{8}	4×10^{8}	3×10^{8}
n HCl/n ClO (equation 1)	1.2	1.2	0.8
n HCl/n ClO (observed)	0.84	0.75	0.8
n HCl/n ClO (model)[4]	4.5	3.9	3.5

REFERENCES

[1] STOLARSKI, R.S. and CICERONE, R.J. *Canad. J. Chem.* 52, 1610-1615, (1974).

[2] MOLINA, M.J. and ROWLAND, F.S. *Nature* **249**, 810-812 (1974).

[3] ROWLAND, F.S. and MOLINA, M.J. *Rev. Geophys. Sp. Phys.* 13, 1-35 (1975).

[4] HALOCARBONS : Effects on Stratospheric Ozone, National Academy of Sciences, Washington, D.C. September (1976).

[5] EYRE, J.R. and ROSCOE, H.K. *Nature* **266**, 243-244 (1977).

[6] ANDERSON, J.G. NASA Conference on the Stratosphere and Related Problems, Logan, Utah, September (1976).

[7] NICOLET, M. *Rev. Geophys. Sp. Phys.* 13, 593-636 (1975).

[8] HAMPSON, R.F. and GARVIN, D. Chemical Kinetic and Photochemical Data for Modelling Atmospheric Chemistry, Addenda of June 1975, NBS Technical Note 866.

[9] EHHALT, D.H., HEIDT, L.E., LUEB, R.H. and POLLACK, W. *Pageoph* 113, 389-402 (1975).

[10] ACKERMAN, M., FRIMOUT, D., MULLER, C., NEVEJANS, D., FONTANELLA, J.C., GIRARD, A. and LOUISNARD N. *Nature* **245**, 205-206 (1973).

[11] ACKERMAN, M. *J. Atmos. Sciences* 32, 1649-1657 (1975).

[12] ANDERSON, J.G. *G.R.L.* 2, 231-234 (1975).

[13] ANDERSON, J.G. in ref. 4.

[14] ANDERSON, J.G. *G.R.L.* 3, 165-168 (1976).

[15] KRUEGER, A.J. *Pageoph* **106-108**, 1272-1280 (1973).

[16] ACKERMAN, M., FRIMOUT, D. and MULLER, C. *Aeronomica Acta n*° **180**, (1977) to be published in Pageoph.

[17] ACKERMAN, M., FRIMOUT, D., GIRARD, A., GOTTIGNIES, M. and MULLER, C. *G.R.L.* 3, 13-16 (1976).

[18] U.S. Standard Atmosphere Supplements, 1966, U.S. Government Printing Office Washington D.C. 20402.

[19] WOFSY, S.C. and McELROY, M.B. *J. Geophys. Res.* 78, 2619-2624 (1973).

115 - LEMAIRE, J. and M. SCHERER, Kinetic models of the solar and polar winds, 1973.

116 - NICOLET, M., La biosphère au service de l'atmosphère, 1973.

117 - BIAUME, F., Nitric acid vapor absorption cross section spectrum and its photodissociation in the stratosphere, 1973.

118 - BRASSEUR, G., Chemical kinetic in the stratosphere, 1973.

119 - KOCKARTS, G., Helium in the terrestrial atmosphere, 1973.

120 - ACKERMAN, M., J.C. FONTANELLA, D. FRIMOUT, A. GIRARD, L. GRAMONT, N. LOUISNARD, C. MULLER and D. NEVEJANS, Recent stratospheric spectra of NO and NO_2, 1973.

121 - NICOLET, M., An overview of aeronomic processes in the stratosphere and mesosphere, 1973.

122 - LEMAIRE, J., The "Roche-Limit" of ionospheric plasma and the formation of the plasmapause, 1973.

123 - SIMON, P., Balloon measurements of solar fluxes between 1960 A and 2300 A, 1974.

124 - ARIJS, E., Effusion of ions through small holes, 1974.

125 - NICOLET, M., Aëronomie, 1974.

126 - SIMON, P., Observation de l'absorption du rayonnement ultraviolet solaire par ballons stratosphériques, 1974.

127 - VERCHEVAL, J., Contribution à l'étude de l'atmosphère terrestre supérieure à partir de l'analyse orbitale des satellites, 1973.

128 - LEMAIRE, J. and M. SCHERER, Exospheric models of the topside ionosphere, 1974.

129 - ACKERMAN, M., Stratospheric water vapor from high resolution infrared spectra, 1974.

130 - ROTH, M., Generalized invariant for a charged particle interacting with a linearly polarized hydromagnetic plane wave, 1974.

131 - BOLIN, R.C., D. FRIMOUT and C.F. LILLIE, Absolute flux measurements in the rocket ultraviolet, 1974.

132 - MAIGNAN, M. et C. MULLER, Méthodes de calcul de spectres stratosphériques d'absorption infrarouge, 1974.

133 - ACKERMAN, M., J.C. FONTANELLA, D. FRIMOUT, A. GIRARD, N. LOUISNARD and C. MULLER, Simultaneous measurements of NO and NO_2 in the stratosphere, 1974.

134 - NICOLET, M., On the production of nitric oxide by cosmic rays in the mesosphere and stratosphere, 1974.

135 - LEMAIRE, J. and M. SCHERER, Ionosphere-plasmasheet field aligned currents and parallel electric fields, 1974.

136 - ACKERMAN, M., P. SIMON, U. von ZAHN and U. LAUX, Simultaneous upper air composition measurements by means of UV monochromator and mass spectrometer, 1974.

137 - KOCKARTS, G., Neutral atmosphere modeling, 1974.

138 - BARLIER, F., P. BAUER, C. JAECK, G. THUILLIER and G. KOCKARTS, North-South asymmetries in the thermosphere during the last maximum of the solar cycle, 1974.

139 - ROTH, M., The effects of field aligned ionization models on the electron densities and total flux tubes contents deduced by the method of whistler analysis, 1974.

140 - DA MATA, L., La transition de l'homosphère à l'hétérosphère de l'atmosphère terrestre, 1974.

141 - LEMAIRE, J. and R.J. HOCH, Stable auroral red arcs and their importance for the physics of the plasmapause region, 1975.

142 - ACKERMAN, M., NO, NO_2 and HNO_3 below 35 km in the atmosphere, 1975.

143 - LEMAIRE, J., The mechanisms of formation of the plasmapause, 1975.

144 - SCIALOM, G., C. TAIEB and G. KOCKARTS, Daytime valley in the F1 region observed by incoherent scatter, 1975.

145 - SIMON, P., Nouvelles mesures de l'ultraviolet solaire dans la stratosphère, 1975.

146 - BRASSEUR, G. et M. BERTIN, Un modèle bi-dimensionnel de la stratosphère, 1975.

147 - LEMAIRE, J. et M. SCHERER, Contribution à l'étude des ions dans l'ionosphère polaire, 1975.

148 - DEBEHOGNE, H. et E. VAN HEMELRIJCK, Etude par étoiles-tests de la réduction des clichés pris au moyen de la caméra de triangulation IAS, 1975.

149 - DEBEHOGNE, H. et E. VAN HEMELRIJCK, Méthode des moindres carrés appliquée à la réduction des clichés astrométriques, 1975.

150 - DEBEHOGNE, H. et E. VAN HEMELRIJCK, Contribution au problème de l'abérration différentielle, 1975.

151 - MULLER, C. and A.J. SAUVAL, The CO fundamental bands in the solar spectrum, 1975.

152 - VERCHEVAL, J., Un effet géomagnétique dans la thermosphère moyenne, 1975.

153 - AMAYENC, P., D. ALCAYDE and G. KOCKARTS, Solar extreme ultraviolet heating and dynamical processes in the mid-latitude thermosphere, 1975.

154 - ARIJS, E. and D. NEVEJANS, A programmable control unit for a balloon borne quadrupole mass spectrometer, 1975.

155 - VERCHEVAL, J., Variations of exospheric temperature and atmospheric composition between 150 and 1100 km in relation to the semi-annual effect, 1975.

156 - NICOLET, M., Stratospheric Ozone : An introduction to its study, 1975.

157 - WEILL, G., J. CHRISTOPHE, C. LIPPENS, M. ACKERMAN and Y. SAHAI, Stratospheric balloon observations of the southern intertropical arc of airglow in the southern american aera, 1976.

158 - ACKERMAN, M., D. FRIMOUT, A. GIRARD, M. GOTTIGNIES, C. MULLER, Stratospheric HCl from infrared spectra, 1976.

159 - NICOLET, M., Conscience scientifique face à l'environnement atmosphérique, 1976.

160 - KOCKARTS, G., Absorption and photodissociation in the Schumann-Runge bands of molecular oxygen in the terrestrial atmosphere, 1976.

161 - LEMAIRE, J., Steady state plasmapause positions deduced from McIlwain's electric field models, 1976.

162 - ROTH, M., The plasmapause as a plasma sheath : A minimum thickness, 1976.

163 - FRIMOUT, D., C. LIPPENS, P.C. SIMON, E. VAN HEMELRIJCK, E. VAN RANSBEECK et A. REHRI, Lâchers de monoxyde d'azote entre 80 et 105 km d'altitude. Description des charges utiles et des moyens d'observation, 1976.

164 - LEMAIRE, J. and L.F. BURLAGA, Diamagnetic boundary layers : a kinetic theory, 1976.

165 - TURNER, J.M., L.F. BURLAGA, N.F. NESS and J. LEMAIRE, Magnetic holes in the solar wind, 1976.

166 - LEMAIRE, J. and M. ROTH, Penetration of solar wind plasma elements into the magnetosphere, 1976.

167 - VAN HEMELRIJCK, E. et H. DEBEHOGNE, Réduction de clichés de champs stellaires pris par télévision avec intensificateur d'image, 1976.

168 - BRASSEUR, G. and J. LEMAIRE, Fitting of hydrodynamic and kinetic solar wind models, 1976.

169 - LEMAIRE, J. and M. SCHERER, Field aligned distribution of plasma mantle and ionospheric plasmas, 1976.

170 - ROTH, M., Structure of tangential discontinuities at the magnetopause : the nose of the magnetopause, 1976.

171 - DEBEHOGNE, H., C. LIPPENS, E. VAN HEMELRIJCK et E. VAN RANSBEECK, La caméra de triangulation de l'IAS, 1976.

172 - LEMAIRE, J., Rotating ion-exospheres, 1976.

173 - BRASSEUR, G., L'action des oxydes d'azote sur l'ozone dans la stratosphère, 1976.

174 - MULLER, C., Détermination de l'abondance de constituants minoritaires de la stratosphère par spectrométrie d'absorption infrarouge, 1976.

175 - VANCLOOSTER, R., First and second order approximation of the first adiabatic invariant for a charged particle interacting with a linearly polarized hydromagnetic plane wave, 1976.

176 - VERCHEVAL, J., Détermination des conditions de lancement de Spacelab en vue de rencontrer les exigences d'un projet d'expérience par spectrométrie d'absorption, 1977.

177 - LEMAIRE, J., Impulsive penetration of filamentary plasma elements into the magnetospheres of the Earth and Jupiter.

178 - SIMON, P.C. and D. SAMAIN, Solar flux determination in the spectral range 150-210 nm, 1977.

179 - SIMON, P.C., Le rayonnement ultraviolet du soleil et ses relations avec l'aéronomie, 1977.

180 - ACKERMAN, M., D. FRIMOUT and C. MULLER, Stratospheric methane-measurements and predictions, 1977.

181 - ACKERMAN, M., Stratospheric pollution related ultraviolet radiation phenomena, 1977.

182 - BRASSEUR, G., Un modèle bidimensionnel du comportement de l'ozone dans la stratosphère, 1977.

183 - SIMON, P.C., Irradiation solar flux measurements between 120 and 400 nm. State of the art and future needs, 1977.