

cording to the deposition-embryo mechanism, requires a contact nucleation threshold of about -6°C . However, the deposition threshold and the contact angle of $\alpha=78^{\circ}$ lead to a predicted value for $\cos\theta_2$ of about 3.2, requiring that PbI_2 be a perfect immersion nucleus, with a threshold immersion freezing temperature of near 0°C . This indicates either a failure of the nucleation theory or an error in the experimental values, but does not indicate a failure of the proposed deposition-embryo mechanism. In this regard, it is also important that the experimental *condensation* threshold for PbI_2 differ significantly from the threshold predicted from the measured contact angle (Koutsky *et al.*, 1965).

There have been no quantitative experimental tests of the classical nucleation theory as it applies to heterogeneous freezing. The required relationship (1) between θ_1 , θ_2 and α provides one such test. This analysis of Dr. Fukuta's new results must await their availability, but should shed light not only on the contact nucleation mechanism, but on classical nucleation theory as well. However, an apparent failure in the usual applications of the classical theory (as in PbI_2)

should not be construed as a failure of the proposed deposition-embryo mechanism.

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Absorption Coefficient of HCl in the Region 1400 to 2200 Å

EDWARD C. Y. INN

Ames Research Center, NASA, Moffett Field, Calif. 94035

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ABSTRACT

The results of absorption coefficient measurements of HCl in the region 1400 to 2200 Å are reported and compared with those previously published. It is concluded that the present results represent the best compromise of all measurements and should be used for any calculations on the photodissociation rate of HCl in planetary atmospheres.

1. Introduction

Photodissociation of HCl in the wavelength region 1900 to 2200 Å is an important process in the photochemistry of this minor constituent in the atmosphere of Venus. Thus, to account for the stability of CO_2 in the atmosphere of Venus, Prinn (1971) has suggested that HCl is the source of Cl atoms, which catalytically convert CO and O_2 into CO_2 . On the other hand, McElroy *et al.* (1973) show that H atoms, derived from the photodissociation of HCl, catalyze the recombination of CO_2 on Venus.

Absorption coefficient measurements of HCl for the spectral region 1400 to 2100 Å appear to have been reported only by Romand and Vodar (1948), Romand (1949), and Myer and Samson (1970). Comparison of these measurements shows a rather marked difference in the reported absorption coefficients, particularly at

about 1400 Å and above 1800 Å. The author here reports a set of measurements of the absorption coefficient of HCl in the region 1400 to 2200 Å that resolves this discrepancy.

2. Experiment

The absorption measurements were carried out using a 1 m vacuum ultraviolet spectrometer (McPherson Model 217), a 10.0 cm long absorption cell with LiF windows at the spectrometer exit slit, and an EMR 542F-08-18 photomultiplier tube. The latter is a "solar blind" detector, that is, it is insensitive to wavelengths >3500 Å, hence no correction for scattered light above 3500 Å was required. The detector output was fed into a picoammeter (Keithley Model 417) and the signal was displayed on a strip-chart recorder. Two background light sources were used: a high-pressure krypton

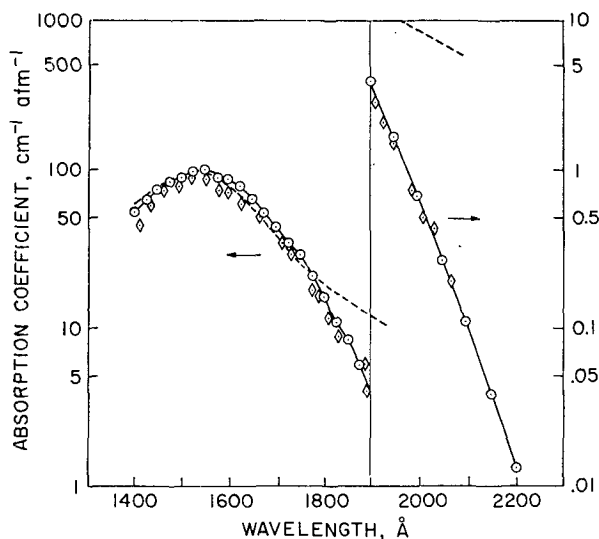


FIG. 1. Absorption coefficients of HCl: Romand (1949), diamond points; Myer and Samson (1970), dashed line; this work, circles.

continuum for the region 1400 to 1700 Å and a H₂ continuum for the region 1700 to 2200 Å.

Since the present measurements were carried out in an absorption continuum of HCl, a moderately wide spectral slit width of 0.3 Å was used. Furthermore, measurements were made at fixed wavelengths throughout the spectral region and, at each wavelength, absorption was recorded for at least three widely different pressures of HCl. Pressure measurements were made with a transducer, which was calibrated against an oil manometer for the lower pressures and a mercury manometer for the higher pressures.

Matheson technical grade HCl (99.0% minimum purity) was further purified by bulb-to-bulb fractional distillation, discarding the first and last fractions. Three cycles of fractional distillation were carried out and the purified HCl stored in a 1-liter flask. No attempt was made to determine the ultimate purity of the stored sample. Since the absorption coefficients varied over a range of about 10⁴, the HCl pressures used varied from 0.084 to 645 torr.

3. Results

The absorption spectrum of HCl in the region 1400 to 2200 Å is a continuum. Accordingly, the results of the present measurements have been plotted in Fig. 1, a smooth curve being drawn through the measured points (circles). Table 1 lists the absorption coefficients obtained for the various wavelengths at which the measurements were made. Error limits for the reported values in Table 1 are conservatively estimated to be ±10%. Uncertainty in the wavelength position is ±0.5 Å.

Fig. 1 also displays the published results of Romand (1949). The dashed curve in Fig. 1 reproduces the published curve of Myer and Samson (1970). Note that, in the region 1450 to 1800 Å, there is good agreement among all three measurements. However, below 1450 Å, the present measurements agree quite well with those of Myer and Samson (1970), whereas those of Romand (1949), at about 1400 Å, are about 35% lower. On the other hand, for wavelengths >1800 Å, there is good agreement between the present results and those of Romand (1949), whereas those of Myer and Samson (1970) deviate quite markedly. For example, at 2100 Å the latter's result is about 50 times larger.

It is difficult to determine the cause of the large discrepancy in the long-wavelength absorption coefficients reported by Myer and Samson (1970). Much of this discrepancy may be due to the fact that the absorption coefficient of HCl is very small in this spectral region, thus requiring very high pressures to obtain measurable absorption. The absorption due to the presence of any relatively strongly absorbing impurity could far out-

TABLE 1. Absorption coefficients of HCl.

λ (Å)	α^a (cm ⁻¹ atm ⁻¹)	σ^b (×10 ¹⁸ cm ²)
1400	56.8	2.11
1425	67.4	2.51
1450	75.6	2.81
1475	87.0	3.24
1500	92.7	3.45
1525	100.0	3.72
1550	102.5	3.82
1575	93.3	3.47
1600	89.1	3.32
1625	79.9	2.97
1650	66.7	2.48
1675	54.9	2.04
1700	43.7	1.63
1725	35.1	1.31
1750	29.3	1.09
1775	21.7	0.808
1800	15.8	0.588
1825	11.6	0.432
1850	8.41	0.313
1875	5.79	0.215
1900	3.90	0.145
1950	1.66	0.0618
2000	0.688	0.0256
2050	0.264	0.00983
2100	0.106	0.00395
2150	0.0369	0.000137
2200	0.0129	0.0000480

^a α , the absorption coefficient, is defined by $I/I_0 = \exp[-(\alpha p T_0 l)/(p_0 T)]$, where I and I_0 are the transmitted and incident intensity, respectively, p and T the pressure and absolute temperature, respectively, p_0 and T_0 refer to the gas at standard conditions, namely 1 atm and 273.15K, and l is the absorption path length.

^b σ , the absorption cross section, is defined by $\sigma = \alpha/N_0$, where N_0 is Loschmidt's number.

weigh the weak absorption due to HCl at these higher pressures.

4. Conclusions

Fig. 1, which compares the three different measurements of the absorption coefficient of HCl in the region 1400 to 2200 Å, shows that the present results represent the best compromise among the measurements. The absorption coefficients listed in Table 1 should be used for calculations on the photodissociation rate of HCl in planetary atmospheres, with simple interpolation for intermediate wavelengths.

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