

ABSORPTION CROSS SECTIONS OF HCl AND DCl AT 135–232 NANOMETERS: IMPLICATIONS FOR PHOTODISSOCIATION ON VENUS

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ABSTRACT

Cross sections for photoabsorption of HCl and DCl are determined in the spectral region of 135–232 nm using radiation from a synchrotron light source. At wavelengths near the onset of absorption ($\lambda > 200$ nm), cross sections of HCl are approximately 5–10 times larger than those of DCl. These data are used to calculate rates of photodissociation of HCl and DCl in the Venusian atmosphere. For the entire wavelength region measured, the rate of photodissociation of DCl is only 16% that of HCl. The difference in rates of photodissociation contributes to the exceptionally large [D]/[H] ratio of the Venusian atmosphere.

Subject headings: planets and satellites: individual (Venus)—ultraviolet: solar system

1. INTRODUCTION

HCl is a minor constituent of the Venusian atmosphere, but it plays an important role in the photochemistry and atmospheric evolution (Connes et al. 1967; Prinn 1971, 1985; McElroy et al. 1973; Yung & DeMore 1982; von Zahn et al. 1983). Photodissociation of HCl by solar UV produces H and Cl atoms that lead to the odd-hydrogen cycle (OH and HO₂) and the reactive chlorine cycle (ClO, ClCO, and ClCO₃; Yung & DeMore 1982). HCl has been observed at altitudes above the clouds. Because CO₂ strongly absorbs solar radiation at wavelengths less than 200 nm, HCl is dissociated by solar light mostly at wavelengths greater than 200 nm.

The [D]/[H] ratio in the Venusian atmosphere has a value about 100 times as large as those for terrestrial and other astronomical bodies (McElroy, Prather, & Rodriguez 1982; Donahue et al. 1982; Prinn 1985; Yung & DeMore 1999). An understanding of such a large isotopic enhancement is of current interest. Water vapor in the Venusian atmosphere is trapped below 60 km mainly by H₂SO₄. The species that carries hydrogen to the upper atmosphere is HCl, not H₂O. An H atom produced from photodissociation of HCl may subsequently escape from the atmosphere. In contrast, DCl is less dissociated, so that the D atom is retained. If the difference between rates of photodissociation of HCl and DCl is large, this might contribute to the enhancement of the [D]/[H] ratio in the Venusian atmosphere. Hence, it is important to determine accurately the absorption cross sections of HCl and DCl, especially near the absorption onset.

It is generally difficult to measure photoabsorption cross sections in the onset region accurately, because the values are small and easily susceptible to distortion from impurities that absorb more strongly in that region. To remove impurities from the

sample gas requires special attention. As Inn (1975) pointed out, the data of Myer & Samson (1970) are distorted by impurities in this way so that their absorption cross sections are much greater than those of Inn at wavelengths greater than 180 nm. We expended a special effort to assure the purity of the sample and extended accurate measurements to 232 nm for HCl and 220 nm for DCl.

No photoabsorption cross section of DCl is reported in the vacuum UV region. The threshold wavelength for DCl absorption is expected to be smaller than that for HCl, because the zero-point energy of DCl is less than that for HCl. A shift to shorter wavelength upon deuteration is commonly observed for many molecules, such as water (Cheng et al. 1999), methane and ethane (Lee et al. 2001), and methanol (Cheng et al. 2001). However, taking into account the singlet-triplet mixing effect, Lambert, Dagdigan, & Alexander (1998) predicted that the photoabsorption cross section of DCl has a maximum at a wavelength greater than that of HCl. For further theoretical interpretations, the reader is referred to Yung & Miller (1997) and C. G. Morgan et al. (2001, in preparation).

2. EXPERIMENTS

The experimental setup is described in a previous paper (Cheng et al. 1999). Briefly, vacuum ultraviolet (VUV) photons produced in the synchrotron radiation facility in Taiwan are dispersed with a 1 m Seya-Namioka monochromator with a grating blazed at 140 nm and with 600 grooves mm⁻¹. Two slits of 4 × 2 mm are installed along the beam path before the absorption cell to reduce scattered light. The beam size is 3.5 × 1 mm at the entrance of the absorption cell and increases to 4.5 × 1.5 mm at the exit window. Both entrance and exit windows are CaF₂, which also serves to eliminate second-order

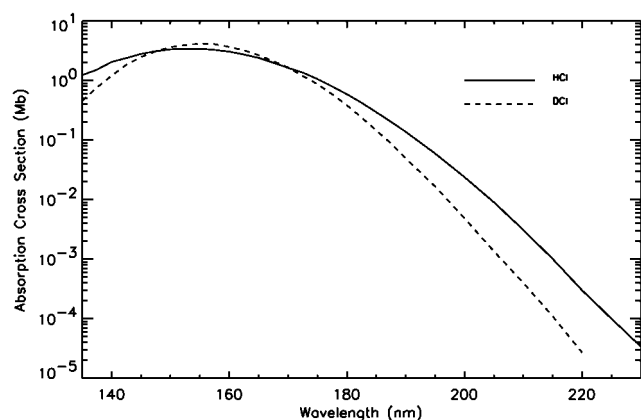


FIG. 1.—Photoabsorption cross sections of HCl and DCl in the 135–232 nm region.

light. Spectra were recorded at 0.1 nm intervals; uncertainty of wavelength measurement is limited by the scan step.

The absorption cross section was measured with a double-beam apparatus. The light was monitored before the gas cell by reflection from an LiF plate placed at 45° from the beam line. The VUV light was converted to visible light with sodium salicylate coated on a glass window and detected with a photomultiplier tube (Hamamatsu R955) in a photon-counting mode. The absorption cross section is determined from the absorbance A ,

$$A = \ln(I_0/I) = n\sigma l, \quad (1)$$

where I_0 is the reflected light intensity, I is the transmitted light intensity, n is the gas density, σ is the absorption cross section, and $l = 385.73$ mm is the length of the absorbing path through the gas sample. The absorbance was adjusted to zero with the gas cell evacuated to less than 5×10^{-7} torr. The density of gas sample at room temperature was determined from its pressure monitored with a capacitance manometer (MKS-Baratron). A reservoir of 600 cm³ in volume was connected to the sample cell so as to reduce possible interference resulting from surface desorption, photofragmentation, and variation in gas temperature. At each wavelength, the absorption cross section was determined from a linear fit of five to 13 absorbance values measured at varied pressures. The gas pressures, 0.097–900 torr for HCl and 0.169–217 torr for DCl, are chosen such that maximum absorbance was less than 2, to avoid saturation effects. At 232 nm, the absorbance of HCl is linearly dependent on gas pressure up to 900 torr, implying that dimers and polymers do not contribute to the cross section measured.

HCl of purity 99.999% was purchased from AGA Inc. DCl with a listed isotopic purity of 99% was obtained from Cambridge Isotope Laboratories. Each sample was further purified by a freeze-pump-thaw procedure two times; the sample was frozen at 77 K and pumped for 20 minutes each time. DCl was further purified by vacuum distillation from 168 to 77 K. The sample gas was introduced into the cell while maintaining the sample cylinder at ~190 K. After this purification procedure, absorption of possible contaminants such as O₂ and H₂O became undetectable in the VUV spectrum.

3. PHOTOABSORPTION CROSS SECTIONS AND PHOTODISSOCIATION PROCESSES

Photoabsorption cross sections of HCl and DCl in the spectral region of 135–232 nm are determined at a spectral reso-

TABLE 1
ABSORPTION CROSS SECTIONS (IN UNITS OF 10^{-18} cm²) OF HCl AND DCl IN THE 135–230 nm REGION

Wavelength λ (nm)	DCl (This Work)	HCl (This Work)	HCl (Inn 1975)	HCl (Nee et al. 1986)
135.0	0.455	1.23	...	1.2
137.5	0.759	1.52	...	1.6
140.0	1.20	2.05	2.11	2.0
142.5	1.84	2.38	2.51	2.4
145.0	2.48	2.79	2.81	2.7
147.5	3.08	3.11	3.24	2.9
150.0	3.64	3.34	3.45	3.1
152.5	3.93	3.42	3.72	3.2
155.0	4.15	3.43	3.82	3.3
157.5	4.07	3.27	3.47	3.2
160.0	3.67	3.06	3.32	3.1
162.5	3.21	2.73	2.97	2.7
165.0	2.67	2.40	2.48	2.3
167.5	2.11	1.99	2.04	1.9
170.0	1.66	1.63	1.63	1.6
172.5	1.19	1.36	1.31	1.3
175.0	0.871	1.06	1.09	1.0
177.5	0.589	0.796	0.808	0.7
180.0	0.385	0.589	0.588	0.5
182.5	0.239	0.423	0.432	...
185.0	0.145	0.294	0.313	...
187.5	0.0880	0.203	0.215	...
190.0	0.0493	0.138	0.145	...
195.0	0.0167	0.0596	0.0618	...
200.0	0.00485	0.0239	0.0256	...
205.0	0.00136	0.00903	0.00983	...
210.0	0.00040	0.00310	0.00395	...
215.0	0.00011	0.00101	0.000137 ^a	...
220.0	0.000027	0.00030	0.000048 ^a	...
225.0	...	0.00010
230.0	...	0.000034

^a Likely to be 10 times the listed value; see text.

lution of 0.1 nm, as shown in Figure 1. The uncertainty is estimated to be 5% of each measurement. This is an estimate of 1 σ error including all possible systematic errors, such as temperature, pressure, path length, and curve fitting. Data at 2.5 nm intervals are listed in Table 1 for comparison with those of Inn (1975) and of Nee, Suto, & Lee (1986). A complete listing of absorption cross sections at 0.1 nm resolution is available. As earlier data of Romand (1949) and of Myer & Samson (1970) were compared by Inn (1975), they are not listed here. Our values are generally smaller than values of Inn (1975) but slightly greater than those of Nee et al. (1986), but they agree within experimental uncertainties. Values for $\lambda > 215$ nm of Inn (1975) are likely erroneous. According to absorption coefficients of HCl shown in Figure 1 of Inn's paper, these values should be 10 times as large. Our data agree better with these corrected values (see Table 1). There are no experimental data for comparison with our DCl measurements, but Lambert et al. (1998) reported theoretical values; for example, calculated values are 3.5, 1.2, 0.05, and 0.0003 Mbarn (1 Mbarn = 10^{-18} cm²) at 150, 170, 190, and 210 nm, respectively, comparable with our measurements listed in Table 1.

As absorption features shown in Figure 1 are broad and continuous, photoexcitation into this region results in dissociation. The onset of absorption by HCl occurs at a wavelength ~10 nm greater than for DCl, as expected from consideration of relative zero-point energies. Such a phenomenon is observed for many molecules upon deuteration (Cheng et al. 1999, 2001; Lee et al. 2001). For the same reason, the absorption maximum of DCl is expected to shift to a wavelength smaller than that of HCl. However, this is not observed in our data: the absorption maximum lies near 154 nm for HCl and 156 nm for DCl.

Furthermore, in contrast to HCl, the absorption band contour for DCI is symmetric, as shown in Figure 1.

Without the singlet-triplet interaction, the absorption feature of HCl is expected to be symmetric as calculated by van Dishoeck, van Hemert, & Dalgarno (1982). The observed asymmetry was previously suspected to be a measurement error, but sufficient experimental measurements exist to establish that the asymmetric band contour is real.

This difference likely reflects a mixing of the ground ($X^1\Sigma^+$) state with the $^3\Pi_0$ state of HCl through spin-orbit coupling; therefore, HCl has a component of transition to the repulsive excited state, $a^3\Pi_0$, which lies near the predominant state $A^1\Pi_1$ (Givertz & Balint-Kurti 1986; Lambert et al. 1998). This singlet-triplet mixing serves to explain the asymmetric absorption band contour of HCl (Givertz & Balint-Kurti 1986) and the unusual direction of shift of absorption maximum upon deuteration.

Our observations might imply that the singlet ground state of DCI does not mix with the triplet state as much as for HCl. This assertion is supported with observations that the photodissociation yield of the excited $\text{Cl}^*(^2P_{1/2})$ atom from DCI is less than that of HCl. In the spectral region of 190–220 nm, the quantum yield for $\text{Cl}^*(^2P_{1/2})$ is about 0.41 for HCl (Zhang, Dulligan, & Wittig 1997; Lambert et al. 1998) but 0.28 for DCI (Ascenzi et al. 1999). Although theoretical calculations indicate that $\text{Cl}^*(^2P_{1/2})$ is dominantly produced through spin-orbit interaction at long range, its yield might be affected by the adiabatic excitation process; that is, initial excitation to the triplet state produces excited Cl^* atoms. A smaller yield of Cl^* indicates that DCI has a smaller component of the triplet state than HCl.

4. PHOTODISSOCIATION RATES

The rate of photodissociation is calculated from the photodissociation cross section and the solar flux, at the orbit of Venus, as described in Yung & DeMore (1999). We assume that the cross sections for photodissociation are equal to the cross section for photoabsorption. Rates of photodissociation computed by our model are shown in Figure 2. The total rates of photodissociation in the range 135–232 nm are 7.74×10^{10} and $1.27 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$ for HCl and DCI, respectively.

The results from Figure 1 are used in a Venus model to evaluate the effect of the photolysis of HCl versus that of DCI. Figure 2 shows a comparison of photolysis rates (in units of $\text{cm}^{-3} \text{ s}^{-1}$) of HCl and DCI in the atmosphere of Venus based on model C of Yung & DeMore (1982). The HCl rate is taken from their standard model. The DCI rate is computed by replacing the cross sections of HCl with those of DCI as measured in this work. On a per molecule basis, DCI photolysis is about 0.67 of HCl photolysis in the upper atmosphere. At these al-

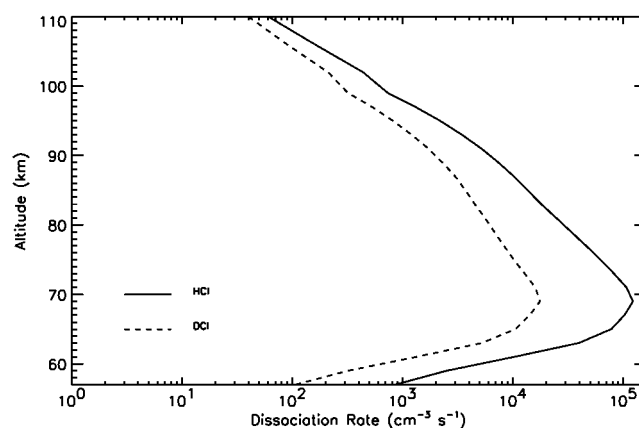


FIG. 2.—Comparison of photolysis rates (in units of $\text{cm}^{-3} \text{ s}^{-1}$) of HCl and DCI in the atmosphere of Venus based on the model of Yung & DeMore (1982). The HCl rate is taken from their model C. The DCI rate is computed by replacing the cross sections of HCl with those of DCI as measured in Fig. 1. The integrated rates are 7.74×10^{10} and $1.27 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$.

titudes, most of the photons are absorbed slightly longward of the peak of the cross sections around 180 nm, where there is relatively small difference between absorption by HCl and DCI. In the lower atmosphere, photolysis of DCI is 5–10 times less efficient than that of HCl. In this region, shielding of UV radiation by CO_2 becomes important. The photons that can penetrate to these levels are in the wavelength tail longward of 200 nm, where the difference between absorption by HCl and DCI is large. The column integrated rate for HCl photolysis is about 6 times that of DCI. Hence, solar dissociation of HCl and DCI contributes to enhancement of the $[\text{D}]/[\text{H}]$ ratio observed in the Venusian atmosphere.

5. CONCLUSION

Photoabsorption cross sections of HCl and DCI are determined in the 135–232 nm region. Onset of absorption of HCl occurs at a wavelength ~ 10 nm greater than that of DCI. The rate of photodissociation of HCl by solar light is much greater than that of DCI, especially at wavelengths greater than 200 nm. Hence, solar dissociation increases the loss of H relative to D and in turn enhances the $[\text{D}]/[\text{H}]$ ratio. The current data are useful for detailed modeling of the photochemistry and evolution of the Venusian atmosphere.

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