



## Exploring the Secrets of Venus and Mars

A key issue in understanding the atmosphere and climate of an extraterrestrial body and their variations is the extent of isotopic fractionation, such as D/H,  $^{18}\text{O}/^{16}\text{O}$ , and  $^{15}\text{N}/^{14}\text{N}$ . For instance, the isotopic fractionations of D/H on Mars and Venus are 6 and 100, respectively, times the terrestrial value. A mechanism proposed to explain variations in isotopic fractionation on these planets is the photoinduced fractionation effect (PHIFE). The idea is that the rates of photolysis differ greatly for various isotopomers near their respective photodissociation threshold regions. Corresponding electronic structures typically vary only slightly among isotopomers, but their cross sections for photoabsorption leading to dissociation might vary greatly near a threshold region because of different zero-point energies of the ground electronic states. If the threshold of wavelength lies in a region in which the solar radiant flux decreases with decreasing wavelength (130-220 nm), a variation in the dissociation rates of isotopomers might be significant such that the PHIFE must be taken into account in modeling the photochemistry of these species in planetary atmospheres.

Photodissociation rates for planetary isotopomers with solar radiation are calculated according to the integral,

$$R = \int I \sigma d\lambda,$$

in which  $I$  is the solar flux,  $\sigma$  is the cross section of photodissociation, and  $\lambda$  is the wavelength. If the planetary molecule excited in the band is subject to only dissociation, the cross section for photodissociation is equal to the cross

section for photoabsorption. To assess the potential for photochemically induced changes in stellar and upper planetary atmospheres, it is necessary to know the absolute absorption cross sections of pertinent stellar and planetary species in the VUV range. Photoabsorption cross sections of gaseous interstellar molecules have been extensively measured in the VUV range, but such data for their deuterated isotopomers are lacking and need to be established.

We measured the absorption cross sections using a double-beam absorption gas cell. The VUV light is dispersed with a 6-m monochromator on the High-Flux beamline or the 1-m Seya-Namioka beamline. The intensity of light, partially reflected from a window placed  $45^\circ$  to the incident beam before the gas cell, was monitored to serve as a reference. LiF/CaF<sub>2</sub> windows transmitting light at  $\lambda > 105/123$  nm, respectively, were used to seal the gas cell. The VUV light was converted to visible light with sodium salicylate coated on a glass window, and detected with a photomultiplier tube in a photon-counting mode. The absorption cross section is determined from absorbance according to the equation

$$\ln(I_0/I) = n \sigma l + \alpha,$$

in which  $I_0$  and  $I$  are reflected and transmitted light intensities, respectively;  $n$  is the number density of the sample,  $\sigma$  is the absorption cross section, and  $l$  is the length of absorption path of the gas cell. The offset  $\alpha$  was determined with no sample in the gas cell. At each wavelength, the absorption cross section was obtained by fitting with linear least squares 5-15 absorbance values measured at various pressures.

Generally, it is difficult to accurately measure photoabsorption cross sections in the onset region, because the values are small and susceptible to distortion from any impurity that absorbs more strongly than the subject gas in that region. To remove impurities from the sample and their isotopic species deserves special attentions. The extension of accurate measurements to large wavelengths requires high purity. Some samples need special efforts to attain this sufficiently high purity.

We have measured photoabsorption cross sections of  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{HCl}$ ,  $\text{CH}_3\text{OH}$ , and their deuterated isotopomers in the VUV range. The results for  $\text{H}_2\text{O}$  and  $\text{HOD}$  can be applied to Mars, those for  $\text{HCl}$  and  $\text{DCl}$  to Venus, those for  $\text{CH}_4$ ,  $\text{CH}_3\text{D}$ ,  $\text{C}_2\text{H}_6$ , as well as  $\text{C}_2\text{H}_5\text{D}$ , to the giant planets and Titan, and those for deuterated  $\text{CH}_3\text{OH}$  to comets.

Photoabsorption cross sections of  $\text{HCl}$  and  $\text{DCl}$  determined in the spectral region of 135-230 nm are shown in Fig. 1. Our data of  $\text{HCl}$  agree with earlier reports. As the data of  $\text{DCl}$  are reported for the first time, no prior experimental data exist for comparison.

$\text{HCl}$  is a minor constituent of the Venusian atmosphere, but it plays an important role in the photochemistry of the Venusian atmosphere and its evolution. Water vapor in the Venusian atmosphere is trapped below 60 km mainly by  $\text{H}_2\text{SO}_4$ . As shown in the sketch of Fig. 2, the major species that carries hydrogen to the upper atmosphere is  $\text{HCl}$ , not  $\text{H}_2\text{O}$ . Photodissociation of  $\text{HCl}$  by solar light produces  $\text{H}$  and  $\text{Cl}$  atoms. The light  $\text{H}$  atoms escape and are lost forever to the depths of space.

As absorption features shown in Fig. 1 are broad and continuous, photoexcitation into this region results in dissociation. The onset of absorption by  $\text{HCl}$  occurs at a wavelength  $\sim 10$  nm greater than that for  $\text{DCl}$ , as expected from relative zero-point energies. The results in Fig. 1 serve to evaluate the effect of photolysis of  $\text{HCl}$  versus that of  $\text{DCl}$  in the Venus model. Fig. 3 shows a comparison of the photolysis rates ( $\text{cm}^{-3} \text{s}^{-1}$ ) of  $\text{HCl}$  and  $\text{DCl}$  in the atmosphere of Venus based on Model C of Yung and DeMore in Icarus **51**, 199 (1982). On the per molecule basis,

photolysis of  $\text{DCl}$  is about 0.67 times that of  $\text{HCl}$  in the upper atmosphere. At these altitudes most photons are absorbed slightly longward of the maximum cross sections at about 180 nm, where there is relatively small difference between absorption by  $\text{HCl}$  and that by  $\text{DCl}$ . In the lower atmosphere photolysis of  $\text{DCl}$  is 0.1-0.2 times as efficient as that of  $\text{HCl}$ ; in this region shielding of VUV radiations by  $\text{CO}_2$  becomes important. Photons that can penetrate the Venusian atmosphere to reach these levels are in the long wavelength tail longward of 200 nm, where the difference between absorption by  $\text{HCl}$  and that by  $\text{DCl}$  is large. The column integrated rate of photolysis of  $\text{HCl}$  is about 6 times that of  $\text{DCl}$ . An  $\text{H}$  atom produced from photodissociation of  $\text{HCl}$  might subsequently escape from the atmosphere. In contrast, because  $\text{DCl}$  is less dissociated,  $\text{D}$  atoms tend to be conserved in the planetary atmosphere. By this means solar dissociation of  $\text{HCl}$  and  $\text{DCl}$  contributes to enhancing the  $\text{D}/\text{H}$  ratio observed in the Venusian atmosphere.

According to the same idea, major differences in VUV absorption cross sections for isotopomers of planetary molecules would imply fundamental differences in the rates of photodissociation for these isotopic molecules, hence major differences in the abundance of deuterated species that are formed from photolytic products. We expect PHIFE to be a common phenomenon in planetary atmospheres throughout the solar system and to provide the key to understanding the history and evolution of the planets.

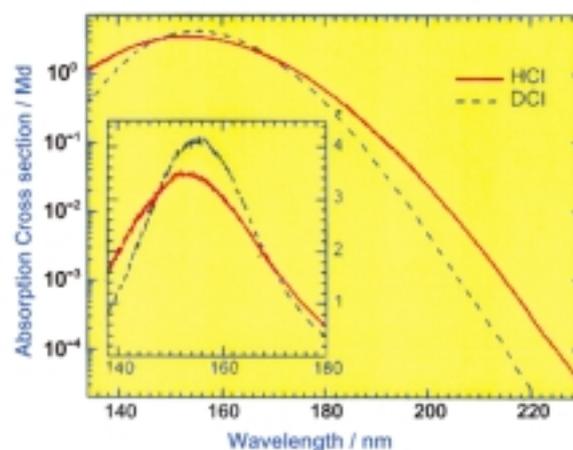


Fig. 1: Absorption cross sections of  $\text{HCl}$  and  $\text{DCl}$  in the region 135-230 nm.

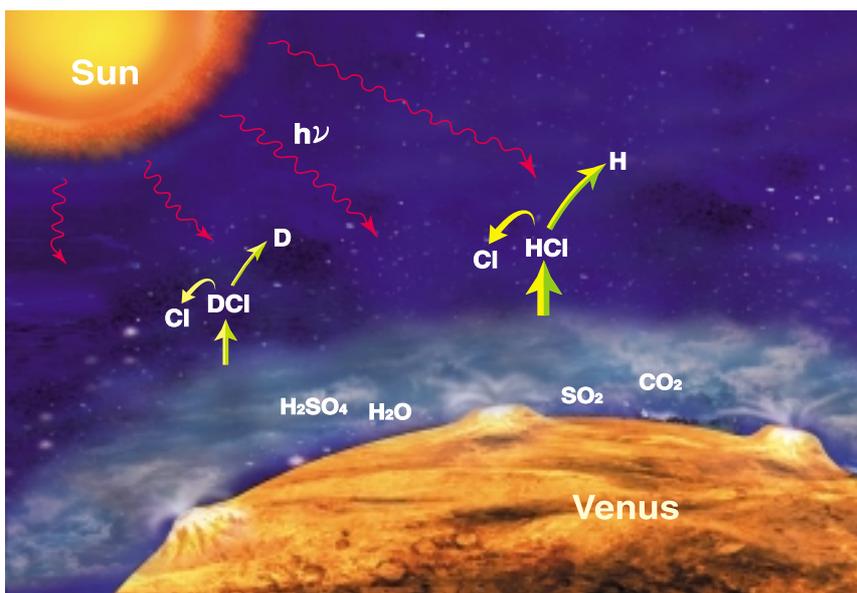


Fig. 2: Venus has an atmosphere of 96.5%  $\text{CO}_2$ , also has a thick layer of sulfuric acid clouds which might trap water. The major species that carries H to the upper atmosphere is HCl, which might be destroyed by VUV light. The photo-product of light H atom escapes and is lost forever to the depths of space.

Another example is the ratio D/H on Mars, which is 6 times the terrestrial value. As water is the ultimate source of atmospheric H on Mars, the D/H ratio provides a strong constraint on the amount of water that has escaped relative to what remains. For this purpose, we determined the absorption cross sections of  $\text{H}_2\text{O}$ , HOD, and  $\text{D}_2\text{O}$  in the region 140-195 nm, and carried out model calculations to evaluate the D/H fractionating effect based on the difference in photolytic rates of  $\text{H}_2\text{O}$  and HOD on Mars. The results indicate that PHIFE can reconcile the discrepancy between theory (model) and recent observations of the D/H

ratio. Thus, fractionation factor can be derived and can serve to estimate the water history. Based on this model, we conclude that Mars had an early warm atmosphere and has lost water in an amount equivalent to a global layer of 50 m in depth.

Data of  $\text{CH}_4$ ,  $\text{CH}_3\text{D}$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_2\text{H}_5\text{D}$  are incorporated in a photochemical model for deuterated hydrocarbons up to two carbons in the upper atmosphere of Jupiter. The model predicts the D/H ratio in deuterated ethane to be about 15 times that of the bulk atmosphere. Confirmation of this result would provide a sensitive test of the photochemistry of hydrocarbons in the atmosphere of Jupiter.

The photoabsorption cross sections of  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{OD}$ ,  $\text{CD}_3\text{OH}$ , and  $\text{CD}_3\text{OD}$  are determined in the spectral region 165-220 nm. These data are useful in calculating the photodissociation rates of these molecules by the solar flux at 1 AU (distance between sun and earth). The rates for  $\text{CH}_3\text{OD}$  and  $\text{CD}_3\text{OD}$  are only 80% and 82% of those for  $\text{CH}_3\text{OH}$  and  $\text{CD}_3\text{OH}$ , respectively. Excitation of these methanol isotopomers in this wavelength region results mainly in breaking the O-H and O-D bonds to form H and D, respectively. The enhancement factors for photoinduced isotopic fractionations calculated from rates of solar photodissociation are +199% for  $\text{CH}_3\text{OD}$ , -35% for  $\text{CD}_3\text{OH}$ , and +154% for

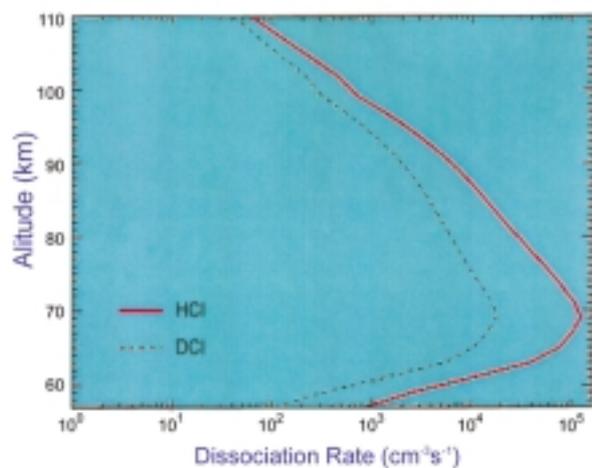


Fig. 3: Comparison of photolysis rates (in units of  $\text{cm}^{-3} \text{s}^{-1}$ ) of HCl and DCI in the atmosphere of Venus.

CD<sub>3</sub>OD. These large factors are detectable in cometary atmospheres, when comets enter the inner solar region in which photodissociation is important in controlling methanol chemistry. The current cross-section data are applicable also to calculating photodissociation rates in various regions of space, such as interstellar media, galaxies, and massive protostars in which methanol and its isotopomers exist.

#### Beamlines:

03A1 High Flux beamline

04B1 SEYA beamline

#### Experimental Station:

Dual-beam absorption end station

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