

Planetary Ultraviolet Spectroscopy

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The emission spectra of a planetary dayglow are produced by the resonance scattering of atoms, the fluorescence scattering of molecules, and the photoelectron excitation of the atoms and molecules that are the major constituents of the atmosphere. The absorption spectra of a planetary atmosphere are the result of the combination of ground reflection, atmospheric scattering, and atmospheric absorption. The observation of these spectra from a planetary spacecraft is accomplished by observing the bright limb, disk, terminator, and dark limb of the planet with a telescope and scanning uv spectrometer. Ultraviolet spectroscopy can determine if the atoms and molecules basic to life are present in a planetary atmosphere: in particular, molecular nitrogen and the photodissociation products of water vapor. Ultraviolet spectrometer experiments can also tell if the atmosphere has been changed by the presence of life such as the production of oxygen from photosynthesis. Local regions of photosynthetic oxygen production will produce ozone which is detectable by uv spectroscopy.

Introduction

Ultraviolet spectroscopy can contribute answers to two important questions relative to exobiology: Are the basic chemical ingredients present on a planet for the formation of the organic compounds that are necessary for the development of life? And has the chemical environment of the planet been modified by the presence of life? Ultraviolet spectrometer measurements of planetary atmospheres are able to detect the presence of molecular nitrogen which until now has not been measured in any atmosphere other than that of the earth. The lack of atmospheric nitrogen on Mars, for example, would indicate that it may be difficult to form the amino acids that are necessary for the origin of life. Ultraviolet spectroscopy can determine if a planetary atmosphere is not in chemical equilibrium with its radiation and thermal environment. On the earth, for example, molecular oxygen is present in the atmosphere as a result of the existence of life. The detection of substantial amounts of oxygen in a planetary atmosphere may be interpreted as evidence of life. The measurement of ozone by uv spectroscopy is a sensitive technique to determine the presence of molecular oxygen.

Theoretical Interpretation of Planetary Ultraviolet Spectra

The airglow of a planetary atmosphere produces emission spectra. Emissions that occur by the direct action of the sun on the day side of the planet are

known as the day airglow or dayglow. Atmospheric atoms and molecules are excited by both the resonance scattering of solar radiation and by photoelectrons that are produced by solar uv radiation. The measurement of the dayglow produced by resonance-fluorescence scattering provides a very sensitive technique to detect and measure certain atmospheric atoms and molecules even though they may be extremely minor constituents. The observation of the photoelectron-excited dayglow, on the other hand, is a powerful method to measure the major constituents of a planetary upper atmosphere, no matter what they may be.

Emission spectra also appear in the atmosphere on the night side of a planet. This night airglow or nightglow is the result of chemical and ionic reactions that occur in the upper atmosphere. The measurement of the nightglow provides information on the physical processes occurring in the planetary upper atmosphere, which, in turn, may be used to determine the abundance of certain atmospheric constituents.

The twilight airglow which may be observed at the terminator of the planet includes some of the emission spectra from both the dayglow and the nightglow.

Absorption spectra that appear in planetary atmospheres are the result of the combination of ground reflection, atmospheric scattering, and absorption.

Resonance Scattering—Atoms

Resonance scattering occurs when an atom in a planetary atmosphere absorbs a solar photon in a discrete spectral transition and then reemits a photon at the same wavelength. Fluorescence scattering includes the cases where the excited atom reemits a photon at longer wavelengths.

For scattering in the resonance lines of atoms, the incident solar radiation usually contains emission lines

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Table I. Atomic Emission Rate Factors^a

	λ (Å)	f	πF^{\oplus} (photons $\text{cm}^{-2} \text{sec}^{-1} \text{Å}^{-1}$)	g (photons/sec ⁻¹ atom ⁻¹)/sec ⁻¹	
Hydrogen	1216	0.4162	4.0×10^{11}	2.1×10^{-3}	9.2×10^{-4}
Oxygen	1302	0.031	2.3×10^9		
	1304	0.031	5.5×10^9		
	1306	0.031	9.0×10^9		
	1302, 4, 6			1.5×10^{-6}	6.7×10^{-7}
Nitrogen	1200	0.35	8×10^8	4×10^{-6}	2×10^{-6}
Carbon	1657	0.17	5×10^{10}	2×10^{-4}	9×10^{-5}

^a Wavelength, oscillator strength, solar flux at 1 a.u., and the resonance scattering emission rate factors appropriate to earth and Mars are given.

Table II. Molecular Emission Rate Factors^a

Emission bands		Wavelength (Å)	Emission rate factor (photons sec ⁻¹ molecule ⁻¹)	
Molecules			\oplus	\ominus
Nitric oxide	(1,0) gamma	2149	3.9×10^{-6}	1.7×10^{-6}
Carbon monoxide	(1,0) fourth positive	1510	2.1×10^{-7}	9.0×10^{-8}
Hydroxyl	(0,0) ultraviolet	3064	8.6×10^{-4}	3.7×10^{-4}
Cyanogen	(0,0) violet	3876	7.3×10^{-2}	3.1×10^{-2}
Ions				
Nitrogen	(0,0) first negative	3914	4.9×10^{-2}	2.1×10^{-2}
Carbon monoxide	(2,0) comet tail	4264	1.3×10^{-3}	5.6×10^{-4}
Carbon monoxide	(0,0) first negative	2190	1.2×10^{-4}	5.2×10^{-5}

^a Wavelength and fluorescence scattering emission rate factors are given for the strongest band of a number of molecular systems.

of the same atoms. The volume emission rate which is the number of photons scattered per unit volume per unit time is directly proportional to the flux of incident solar photons, the oscillator strength of the transition, and the volume density of the illuminated atoms:

$$R = \pi F \lambda^2 (\pi e^2 / mc^2) f n.$$

The units of volume emission rate R are photons $\text{cm}^{-3} \text{sec}^{-1}$; of solar flux πF , photons $\text{cm}^{-2} \text{sec}^{-1} \text{Å}^{-1}$; of wavelength λ , angstroms; and of the ground state atom density n , atoms/ cm^{-3} . The value of the physical constant $\pi e^2 / mc^2$ is $8.829 \times 10^{-13} \text{cm}$.

The emission rate factor, g , directly relates the volume emission rate of an individual spectral emission to the volume density of the emitter:

$$R = gn.$$

Because of its dependence on the solar flux, g is a function of distance from the sun and the time in the solar cycle:

$$g = \pi F \lambda^2 (\pi e^2 / mc^2) f.$$

Emission rate factors for atmospheric atoms of particular relevance to exobiology are listed in Table I. These factors were calculated for solar activity appropriate to solar maximum. Since the solar flux varies as r^{-2} , the emission rate factors appropriate to Mars and the earth are in the ratio 0.433.

The resonance lines of neutral atoms in the solar spectrum are usually reversed since they are formed in the photosphere. The solar flux used in the calculation

of emission rate factors must be measured at the center of these lines. The atomic hydrogen Lyman-alpha line which has been observed at high resolution on a number of rocket flights¹ shows a deep reversal. A rocket flight on 19 October 1967 measured the flux at the center of the line as 4×10^{11} photons $\text{cm}^{-2} \text{sec}^{-1}$ at a distance of 1 a.u. from the sun.² The resonance triplet of atomic oxygen at 1302 Å, 4 Å, and 6 Å was measured on the same flight and found to be reversed as well. Since the atomic nitrogen and carbon lines at 1200 Å and 1675 Å, respectively, are formed at the same level in the solar atmosphere, it may be expected that their line shapes are similar. The solar fluxes in Table I for atomic oxygen, nitrogen, and carbon were calculated using the values for integrated line intensities measured by the NRL group³ and applying the atomic oxygen line shape to all the lines. The oscillator strengths for these lines are taken from Wiese *et al.*⁴

Emission rate factors have been calculated for a number of other airglow lines such as atomic and ionized helium and the metallic atoms and ions.⁵

Fluorescence Scattering—Molecules

Molecules in planetary atmospheres absorb solar radiation while undergoing electronic transitions. When the energy is reradiated, also in an electronic transition, it is distributed over various vibrational bands and rotational lines depending on the structure of the particular molecule. The emission rate of fluorescence scattering for a molecular band system may be related to the density of atmospheric molecules

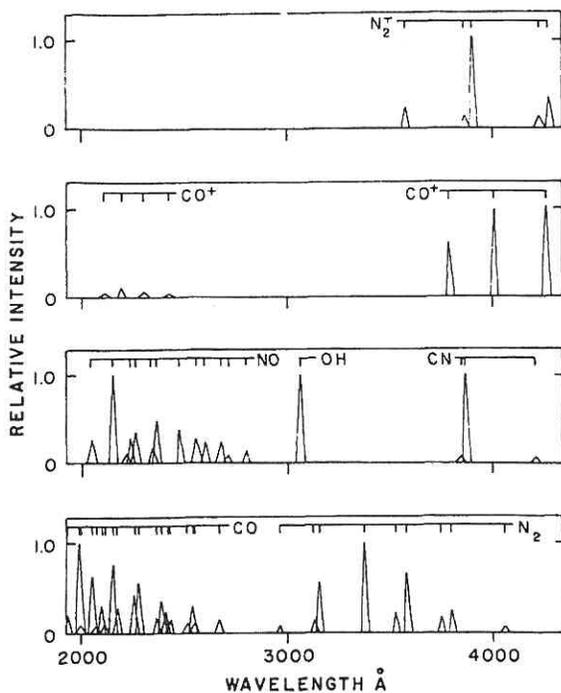


Fig. 1. Planetary airglow molecular band systems, 1900–4300 Å. The upper three spectrograms show the nitrogen first negative, carbon monoxide fourth positive and comet tail, nitric oxide gamma, hydroxyl uv, and cyanogen violet bands as they appear in fluorescence scattering. The lower spectrogram shows the carbon monoxide Cameron and nitrogen second positive bands as they appear from photoelectron excitation.

in a way analogous to that used for the resonance scattering of atoms. The volume emission rate is proportional to the solar flux, band oscillator strength, and molecular volume density because of the absorption process, and to the band branching ratios because of the subsequent emission:

$$R_{v'v''} = \pi F_{0v'} \lambda_{0v'}^2 \frac{\pi e^2}{mc^2} f_{0v'} \sum_{v''} \frac{A_{v'v''}}{A_{v'v''}} n_0$$

For a particular electronic transition, the upper vibrational level is designated v' and the lower level v'' . The volume emission rate for the transition v', v'' at a wavelength $\lambda_{v'v''}$ is $R_{v'v''}$. The absorption of solar flux $\pi F_{0v'}$ takes place at a wavelength $\lambda_{0v'}$ from the lowest vibrational level $v'' = 0$ of the ground electronic state. The band oscillator strength $f_{0v'}$ applies to absorption, while the transition probability $A_{v'v''}$ pertains to emission. The branching ratio $A_{v'v''}/\sum_{v''} A_{v'v''}$ is the ratio of the number of transitions occurring in the band under consideration to all of the transitions leaving the upper vibrational level. The volume density of molecules n_0 applies to the number in the ground vibrational state which for atmospheric molecules is approximately equal to the total density. Since the molecular absorption occurs over a range of wavelengths, it is usually the solar continuum that is applicable to calculations of the volume emission rate.

Emission rate factors have been calculated for a number of band systems which may be found in the airglow of Mars. The emission rate factor at 1 a.u. and 1.52 a.u. for the strongest band in each system is listed in Table II.^{6,7} The relative intensity of the several bands in each of these systems is shown in Figs. 1 and 2. The band system is normalized to the strongest band for each molecule or ion within that system. Each band system has a distinct signature with the emission rate of the strongest band providing a direct relationship with the molecular density. The upper three spectrograms in Fig. 1 and the upper spectrogram in Fig. 2 are calculated for fluorescence scattering. Table II identifies the wavelength of the principal band in each system.

The nitric oxide gamma bands have been observed in the dayglow of the earth.⁸ The hydroxyl uv band and the cyanogen violet bands have been observed in the spectra of comets.⁹ The carbon monoxide fourth positive bands are predicted to be present in the airglow of Mars.⁶

The first negative bands of ionized molecular nitrogen have been observed on earth—in the twilightglow from the ground¹⁰ and in the dayglow from rockets.¹¹ The comet tail bands of ionized carbon monoxide have been observed in emission from the tails of comets, as their name indicates.⁹ The first negative bands of ionized carbon monoxide are predicted to have one-tenth the intensity of the comet tail bands when they are produced by fluorescence scattering.⁶

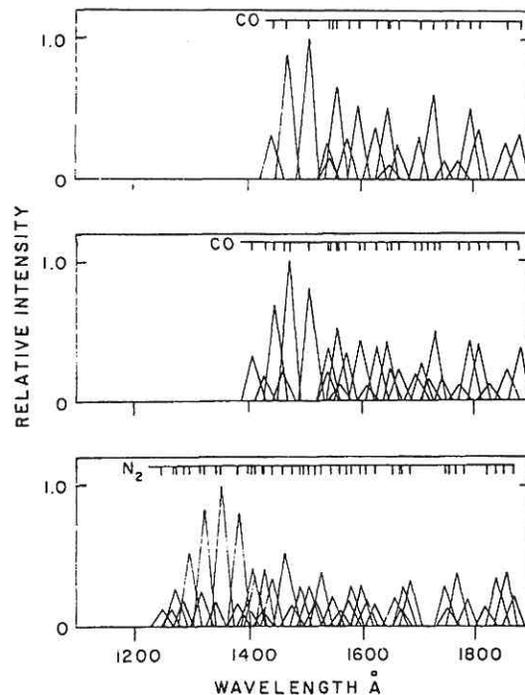


Fig. 2. Planetary airglow molecular band systems, 1100–1900 Å. The lower two spectrograms show the nitrogen Lyman-Birge-Hopfield and carbon monoxide fourth positive bands as they appear from photoelectron excitation. The upper spectrogram shows the carbon monoxide fourth positive bands as they appear in fluorescence scattering.

Table III. Cometary Fluorescence Spectra^a

Molecule or Ion	Wavelength (Å)
CO ₂ ⁺	2882
	3509
C ₃	4052
C ₂	2732
	5165
CH	4313
	3871
	3143
CH ⁺	4238
NH	3360
NH ⁺	2886
OH ⁺	3562

^a Wavelengths of a number of molecular bands that appear in cometary spectra and may appear in planetary spectra are given.

Emissions from neutral carbon monoxide are expected from the upper atmosphere of Mars. Ionized carbon monoxide may be a constituent of the ionosphere of Mars, and hence, emissions from this molecular ion are possible. Another likely candidate for the Martian ionosphere is ionized carbon dioxide. This molecular ion has an emission band at 2882 Å and its presence should be expected in the airglow of Mars.

The emission spectra of nitric oxide, cyanogen, and hydroxyl are sensitive indicators of the presence and chemical form of the biologically important chemical constituents: hydrogen, carbon, nitrogen, and oxygen. Molecular hydrogen, which might be present in the Martian atmosphere, fluoresces in the Lyman and Werner bands. This fluorescence is produced by solar radiation shortward of 1100 Å, with the fluorescence spectrum extending up to 1600 Å.

The possibility of fluorescent scattering from a number of other molecular band systems has been investigated.⁶ The following prospective fluorescence band systems are found to be too weak because of predissociation or small band oscillator strength: oxygen—Schumann-Runge and Herzberg; nitrogen—Vegard-Kaplan; ionized nitrogen—second negative; ionized nitric oxide—first negative; and ionized oxygen—second negative. There is the possibility of fluorescence in planetary atmospheres of the ions and molecules that are present in comets. Table III lists a number of such species together with wavelengths of principal bands which either exist or are predicted to exist in cometary spectra.¹²

Photoelectron Excitation

The extreme uv radiation from the sun produces energetic photoelectrons when ionizing atoms and molecules in a planetary upper atmosphere. Photoelectrons produced by solar radiation between 31 Å and 1027 Å, that have energies between 10 eV and 100 eV, are capable of exciting uv emissions from atmospheric atoms and molecules. Calculations have been made of the electron impact excitation of the earth's dayglow.^{13,14}

The volume emission rate of the transition from *j* to *k* of the *l*th atom or molecule is proportional to the atomic or molecular density, the production rate of photoelectrons, and the atomic or molecular excitation cross sections through the following approximate expression:

$$R_{l,jk} = n_l \left[\sum_{E_p} Q(E_p) \int_{W_j}^{E_p} \frac{\sigma_{lj}(E)}{dE/dx} dE \right] \frac{A_{jk}}{\sum_k A_{jk}}$$

where *n_l* is the number density of atoms or molecules, *σ_{lj}* is the electron impact cross section for excitation of the *j*th level of the *l*th constituent, *W_j* is the threshold energy of *j*th level, and *A_{jk}* is the transition probability of the *jk* transition. The approximation lies in the assumption that effects due to the loss of energy in discrete quanta may be ignored; the errors arising are small if *W_j* is larger than a few volts.¹⁴ The electron energy loss rate *dE/dx* is a function of the density and composition of the gas. The rate of production of photoelectrons *Q* is a function of the solar extreme uv flux, the ionization cross sections, the density of the atoms and molecules being ionized, and the optical depth of the solar flux:

$$Q(E_p) = \sum_{l,i} n_l \sigma_{li} \pi F \exp\left(-\sum_l \sigma_{la} \int_h^\infty n_l \sec \theta dz\right),$$

where *σ_{la}* is the total absorption cross section of the *l*th species, *σ_{li}* is the ionization cross section of the *i*th ionization level, and *θ* is the solar zenith angle. The primary energy of the photoelectron *E_p* is related to the wavelength of the incident solar flux by

$$E_p = (hc/\lambda) - I_{li}$$

where *I_{li}* is the ionization threshold of the *l*th constituent.

The volume emission rate may be directly related to the volume density by a function we may call the emission rate factor, in analogy with the earlier treatment of resonance-fluorescence scattering:

$$R = g_n n.$$

The photoelectron excitation emission rate factor *g_e* approaches a constant value at altitudes in the planetary atmosphere where the attenuation of the extreme uv solar flux may be neglected, and where the electron loss rate is proportional only to the neutral atmospheric density.

Photoelectrons excite the major constituents of the atmosphere, no matter what they may be. For an

Table IV. Planetary Photoelectron-Excited Spectra^a

Molecular band system		Wavelength (Å)
Nitrogen	(0,0) second positive	3371
Nitrogen	(3,0) Lyman-Birge-Hopfield	1354
Carbon monoxide	(1,0) Cameron	1993
Carbon monoxide	(2,0) fourth positive	1478

^a Wavelengths of the strongest bands of a number of planetary molecules are given.

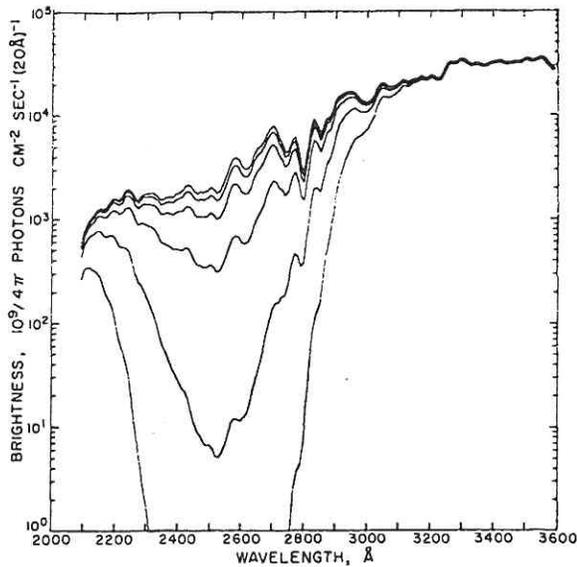


Fig. 3. Spectra of disk of Mars, 2000–3600 Å. The several spectra from top to bottom are calculated from a 9-mbar CO₂, 200 K model atmosphere with the following amounts of ozone: 0 cm, 0.0003 cm, 0.001 cm, 0.003 cm, 0.01 cm, and 0.03 cm.

atmosphere of unknown composition, the emission rates of the photoelectron-excited dayglow give the ratio of the major constituents to one another. Once the relative composition is determined, then the electron energy loss rate may be calculated. The emission rate for any species may then be related to the density of that species quantitatively on an individual basis.

The wavelengths of the strongest bands for two nitrogen and two carbon monoxide systems that may be present in the atmosphere of Mars are given in Table IV. The relative intensity of a number of the bands in the systems are shown in the lower spectrogram of Fig. 1 and the lower two in Fig. 2. In the figures, the band system is normalized to the strongest band. The spectra are distinct and easily identified as to the molecule and the process exciting the band system. The upper two spectrograms of Fig. 2 show the carbon monoxide from the fourth positive bands as excited by photons in the upper spectrogram and by photoelectrons in the middle one.

The second positive bands of molecular nitrogen have been observed in the dayglow of the earth from a rocket.¹⁵ The Lyman-Birge-Hopfield bands have been observed, as well, in a recent rocket experiment employing a similar technique.

Absorption Spectra

Absorption features appear in the uv spectrum of a planet as a result of ground reflection, atmospheric scattering, and absorption by atmospheric constituents. The equation that describes the surface brightness of an atmosphere undergoing molecular scattering and absorption, simultaneously, with only single scattering occurring is

$$B(\lambda) = (3/16\pi)(1 + \cos\varphi)\pi F(\lambda)/\mu \int_0^\infty \sigma_s(\lambda)n_s \\ \times \exp \left\{ -(\mu_0^{-1} + \mu^{-1}) \int_z^\infty [\sigma_a(\lambda)n_a + \sigma_s(\lambda)n_s] dz' \right\} dz,$$

where πF is the solar flux as a function of wavelength, μ_0 and μ are the cosines of the solar and instrument zenith angles, φ is the phase angle, σ_s the Rayleigh scattering cross section, n_s the number density of molecules participating in the Rayleigh scattering, σ_a the absorption cross section, and n_a the number density of absorbers. Both cross sections are functions of wavelength. A prominent absorber in the uv whose presence is of biological interest is ozone. If it is present in only minute amounts, it will absorb solar radiation between 2000 Å and 3000 Å with a maximum at 2550 Å. A second term needs to be added to the equation to take into account the surface reflectivity:

$$+ (\Lambda/\pi)\mu_0\pi F(\lambda) \exp \left\{ -(\mu_0^{-1} + \mu^{-1}) \right. \\ \left. \times \int_0^\infty [\sigma_a(\lambda)n_a + \sigma_s(\lambda)n_s] dz' \right\},$$

where Λ is the surface albedo.

Planetary spectra expected for a model with a surface albedo of 0.04¹⁶ and an atmospheric pressure of 9 mb with varying amounts of ozone have been calculated and the results are shown in Fig. 3. The concentrations of ozone used in these calculations are less than the amount present in the earth's atmosphere. The uppermost curve in the figure shows a spectrum at 20-Å resolution that occurs for a model with no ozone. All of the spectral features are due to Fraunhofer lines in the incident solar spectrum. With increasing amounts of ozone, less and less radiation is scattered back into space in the 2000-Å to 3000-Å region until with 0.03 cm atm of ozone, the scattered intensity drops to zero in the center of this region. The amount of ozone present in the atmosphere can be determined from spectral observations of the type shown in Fig. 3 by a mathematical inversion. This technique has been developed and used on satellite observations of ozone in the earth's upper atmosphere.^{17,18}

Atmospheric Structure

The altitude distribution of gases in a planetary atmosphere is determined by a balance between their kinetic and potential energy in the gravitational field in the manner indicated by this version of the barometric equation:

$$n = n_0(T_0/T) \exp \left(- \int_0^h (mg/kT) dz \right).$$

The volume density n as a function of altitude h is proportional to the density and temperature at a reference level and inversely proportional to the temperature at the level h ; m is the molecular mass of the gas, g the gravitational acceleration, k Boltzmann's constant, and T the temperature. Both T and g may vary as a

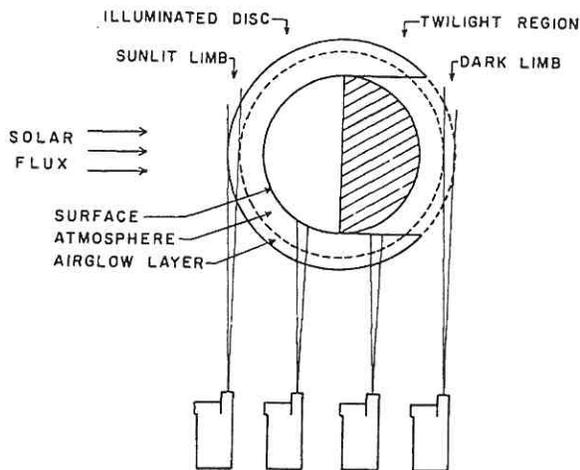


Fig. 4. Planetary observing geometry from a flyby spacecraft. Observations are made of the sunlit limb, the illuminated disk, the twilight region, and the dark limb.

function of altitude. The quantity kT/mg is the scale height H , which for an isothermal, constant gravity atmosphere is a measure of the exponential decrease in density:

$$n = n_0 \exp(-h/H).$$

The scale height of an atmosphere may be determined at any level by measuring the atmospheric density at closely spaced altitudes:

$$H_l = (h_2 - h_1) / (\ln n_1 - \ln n_2)$$

The local scale height H_l applies to the level l midway between h_1 and h_2 . When the atmosphere is isothermal, the local height may be used to determine the temperature of the atmosphere, if the molecular mass m has been identified and the gravitational acceleration g is known [$T = (mg/k)H_l$]. When the atmosphere is not isothermal, the temperature may still be determined from measurements of the scale height gradient, $\beta = dH_l/dh$, and the local scale height, H_l .

$$T = (1 + \beta)(mg/k)H_l.$$

In the lower levels of a planetary atmosphere, motions and turbulence produce a mixing equilibrium where the atmospheric constituents are in a fixed ratio to one another. When the preceding equations are applied to such an atmosphere, the molecular mass that needs to be used is the average molecular mass. At high levels in the atmosphere, when the density is sufficiently low, diffusive separation causes each of the atmospheric constituents to follow its own scale height. When other forces and motions are absent, each individual atom or molecule is distributed according to its individual kinetic and potential energy in the gravitational field. All of the preceding equations may be applied by identifying the density and molecular mass of each individual species:

$$n_i = n_{i0} \exp(-h/H_i),$$

where the scale height of species i , $H_i = kT/m_i g$.

In particular altitude regions of planetary atmospheres, photodissociation and photoionization take place. These processes and the ensuing chemical reactions change the composition of the atmosphere. A particular atmospheric constituent may be in photochemical equilibrium, where the rate of local production of a species is balanced by the rate of recombination. There may also be regions where photochemical and mixing or photochemical and diffusion processes are occurring concurrently.

Observational Techniques

Ultraviolet spectra of a planetary atmosphere may be observed in emission or in absorption. The emission spectra are observed best by looking at the brightly illuminated limb of the planet. Depending on the spectral region, some emission features may be observed when looking at the fully illuminated planetary disk and others can be observed only in the twilight region when the lower atmosphere is in shadow. The weak emissions from the night side of the planet are most intense on the dark limb. Absorption spectra which in the uv are very broad features, may easily be measured by observing the illuminated planetary disk.

Observing geometry appropriate to a flyby spacecraft is shown in Fig. 4. A uv spectrometer and telescope are shown viewing the planetary atmosphere in four different locations: the sunlit limb, the illuminated disk, the twilight region, and the dark limb. The advantage of observing an airglow layer edgewise instead of vertically is the increased intensity of light that comes from the geometrically longer pathlength of emitters. For molecular emissions in the earth's upper atmosphere, this enhancement may be a factor as large as eighty.

While the theoretical discussion centers about the volume emission rate R , the quantity that is observed is the integral of the emission rate along the line of sight. The column emission rate $4\pi I$ in photons $\text{cm}^{-2} \text{sec}^{-1}$ is related to the volume emission rate by the following integration:

$$4\pi I = \int_0^\infty R(r) ds,$$

where ds is the increment of length in the direction of view. The column emission rate is proportional to the volume density of atoms or molecules through the emission rate factor g :

$$4\pi I = g \int_0^\infty n(r) ds.$$

The volume density in a planetary atmosphere may be a function of only the planetocentric distance, while the line of sight of the observation may be in a different direction s . The column density of atoms in the direction of view may be related to the vertical column density by an integration using the Van Rhijn function:

$$\int_0^\infty n(r) ds = \int_0^\infty n(r) V(x, r) dr,$$

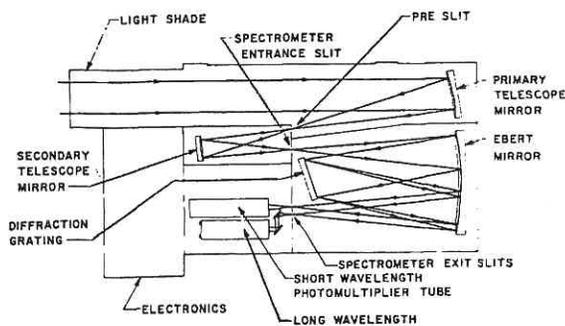


Fig. 5. Planetary uv spectrometer. A 0.25-m uv scanning spectrometer with a 0.25-m telescope and dual photomultiplier tube detectors.

where

$$V(\chi, r) = [1 - (r_0/r)^2 \sin^2 \chi]^{-\frac{1}{2}}$$

χ is the angle between the direction of observation and the planet vertical, and r_0 is the planetocentric distance of the point of observation. The ratio of the column density in the direction of view to the vertical column density is defined as the Chapman function $Ch(\chi)$, which is a function of χ and the atom density distribution $n(r)$. The column emission rate along the direction of observation is related to the volume density by

$$\begin{aligned} 4\pi I &= gCh(\chi) \int_{r_0}^{\infty} n(r) dr \\ &= gN_0Ch(\chi), \end{aligned}$$

where N is the vertical column density of atoms or molecules. For an isothermal atmosphere, the Chapman function is approximated by the following expression:

$$Ch(\chi, r_0/H) = \left(\frac{\pi r_0}{2H}\right)^{\frac{1}{2}} \exp\left(\frac{r_0}{2H} \cos^2 \chi\right) \operatorname{erfc}\left(\frac{r_0}{2H} \cos^2 \chi\right)^{\frac{1}{2}},$$

where $\operatorname{erfc} x$ is the complementary error function.¹⁹ This is the appropriate equation to use with observations of the illuminated planetary disk. For the limb observations, where the instrument is viewing from outside the atmosphere, the appropriate function to use is twice the value of the Chapman function at $\chi = 90^\circ$: $2(\pi r_0/2H)^{\frac{1}{2}}$ or $(2\pi r_0/H)^{\frac{1}{2}}$. In an extended planetary exosphere, the atom density distribution may be approximated by a power law

$$n(r) = n(r_0)(r_0/r)^k.$$

For observations made from outside of the exosphere, the observed column emission rate is related to the atom density by the use of the equation

$$4\pi I = gn(r_0)r_0 \frac{2(\pi)^{\frac{1}{2}}}{(k-1)} \frac{\Gamma[(k+1)/2]}{\Gamma[(k/2)]},$$

where $\Gamma(x)$ is the complete gamma function.²⁰

Instrumentation

The instrumentation required to measure planetary uv spectra is a scanning photoelectric spectrometer

with a small telescope. The outstanding spectrometer for measurements in the visible and uv regions of the spectrum from space vehicles is the Ebert system. The modern discovery and development of this optical system has been carried on by Fastie.²¹⁻²³ The useful characteristics of the Ebert spectrometer for use as a space instrument are the simplicity and compactness of the mechanical construction and the relatively high light-gathering power that results from using the curved slits and a short focal length. The photometric equation for the use of the instrument at fixed spectral resolution is^{7,22}

$$S = (4\pi I/4\pi)(h/f)(n/d)\Delta\lambda A_g T(\lambda),$$

where S is the signal at the exit slit, $4\pi I$ is the column emission rate, h the slit height, f the focal length, n and d the grating order and spacing, $\Delta\lambda$ the desired spectral resolution, A_g the area of the grating, and $T(\lambda)$ the transmission of the instrument due to grating efficiency and mirror reflectivity. This equation shows that after the selection of spectral resolution and the grating, the slits should be made as long as the detector system will allow and the focal length as short as the resolution will allow. In practice, focal ratios as small as five are found to be useful. Ebert spectrometers have been used in rocket experiments to measure the earth's day-glow in the far uv^{24,25} the middle and near uv,^{8,26,15} and the visible¹¹ portions of the spectrum.

Observations of the uv spectrum of a planetary disk require that the more intense visible radiation be rejected by the instrument. This is done best by the use of hard cathode photomultiplier tubes. Cesium iodide photocathodes placed on lithium fluoride windows respond to uv radiation between 1050 Å and 1750 Å and have rapidly falling sensitivity at larger wavelengths. Cesium telluride photocathodes are sensitive from short wavelengths that depend on the window material to about 2750 Å where the sensitivity begins to drop rapidly. The uv spectrometer on OGO-4 uses two photomultipliers, one cesium iodide and one cesium telluride, to measure the uv spectrum of the earth.²⁷ This Ebert scanning spectrometer is able to measure (with the cesium iodide tube) the airglow lines between 1050 Å and 1750 Å while looking at the brightly illuminated earth. Within the cesium telluride tube, the spectrometer measures the backscattered radiation that contains the absorption spectrum of ozone. Airglow lines between 1750 Å and 2750 Å are measured in the twilight region when the lower atmosphere is in the shadow. In order to observe planetary emission lines in the near uv between 3000 Å and 4000 Å, it is necessary to use a bialkali photocathode and to observe at the limb and in the twilight region.

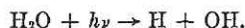
A diagram of the uv spectrometer that has been prepared for the Mariner Mars missions is shown in Fig. 5. The instrument consists of a small telescope, a scanning spectrometer, and two photomultiplier tubes with the associated electronics. The light enters the instrument through a long, baffled light shade and strikes a 250-mm primary telescope mirror. The light is focused through a preslit onto a secondary mirror

which focuses it in turn on the entrance slit of the spectrometer. The light shade baffling and the preslit are used to minimize the amount of off-axis light reaching the spectrometer while the instrument is viewing the planetary limb. After the light enters the spectrometer, the first half of the Ebert mirror collimates it onto the diffraction grating. The diffracted light leaving the grating is focused onto the exit slits by the second half of the Ebert mirror. The short wavelength light goes through the inner exit slit and strikes the short wavelength photomultiplier tube directly. The longer wavelength light after going through the outer exit slit is reflected by two mirrors onto the second photomultiplier tube. The mirrors and grating are coated with magnesium fluoride for higher reflectivity in the uv. The grating is scanned back and forth by a cam system driven by a motor in a sealed bellows. The electronics contain high voltage supplies and low current amplifiers for the photomultiplier tubes and a power supply for the grating drive system.

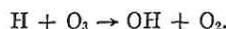
Are the Atoms and Molecules Basic to Life Present in the Mars Atmosphere?

Water Vapor

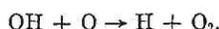
Atoms that are a fundamental part of the earth's biochemistry, and also part of the atmosphere, include hydrogen, oxygen, nitrogen, and carbon. On the earth, water vapor that is transported above the stratosphere is photodissociated into atomic hydrogen and the hydroxyl radical



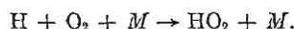
The hydrogen atoms react with ozone molecules that are present in the mesosphere to form hydroxyl radicals and molecular oxygen:



The hydroxyl radicals in turn react with atomic oxygen to reform the atomic hydrogen:



The atomic hydrogen reacts with molecular oxygen, as well, in a three-body reaction:



The perhydroxyl radicals that are formed react with atomic oxygen to form hydroxyl radicals:



Some of the atomic hydrogen is transported higher through the thermosphere until it reaches the base of the exosphere where, depending on the temperature of the thermosphere, some of it escapes. The flux of escaping atoms is strongly dependent upon the temperature at the escape level through the equation

$$F_{\text{esc}} = \frac{n_c}{2(\pi)^{1/2}} \left(\frac{2kT}{m} \right)^{1/2} \left(\frac{GMm}{r_c kT} + 1 \right) \exp\left(- \frac{GMm}{r_c kT} \right),$$

where n_c is the density of the escaping atom at the escape level r_c , m the mass of the escaping atom, M the mass of the planet, and G the gravitational constant.

The density at the escape level is determined by the rate of diffusion of hydrogen atoms through the thermosphere. This diffusive flux is controlled by the conditions at the bottom of the diffusion region. Atomic hydrogen is escaping at the top of the earth's atmosphere at the present time, but at a rate that is very small compared to the vast reservoir of hydrogen in the earth's oceans. The rate of escape is ultimately controlled by the rate of photodissociation of water vapor which in turn is controlled by the cold trap in the stratosphere. This series of processes has a large amount of inertia, and thus the escape rate of hydrogen does not vary widely.

On Mars, the situation may be quite different. The release of water vapor into the atmosphere may be controlled by the melting of the ice caps even if the bulk of the caps is carbon dioxide.²⁸ There may be strong seasonal changes in the amount of water vapor that reaches the photodissociation level. With only a small amount of molecular oxygen in the Martian atmosphere,²⁹ the water vapor photodissociation level will be controlled by carbon dioxide and will occur at higher ambient densities than on the earth. The small amount of oxygen and ozone at this level will allow a greater amount of atomic hydrogen to build up compared with the earth. Because of the higher density, the diffusion time upward for the atomic hydrogen will be no longer than it is in the earth's upper atmosphere. The thermospheric temperature of Mars is lower, perhaps much lower than is the earth's.³⁰ The lower Martian gravity in part offsets the lower temperature in the calculation of the escape rate from the top of the Martian atmosphere.

What then can uv spectroscopy tell us about water vapor and the escape of hydrogen from the Martian atmosphere? First, through resonance and fluorescence scattering, the presence of atomic hydrogen, atomic oxygen, and the hydroxyl radical in the upper atmosphere of Mars can be detected. Next, the distribution of atomic hydrogen as a function of altitude can be measured and the scale height and temperature of the Martian thermosphere calculated. From the density and temperature, the escape flux of atomic hydrogen can be calculated. Next, if atomic oxygen is present, its scale height and scale height gradient can be measured and the temperature profile determined down to the bottom of the thermosphere. At the altitude level where photodissociation takes place, it should be possible to measure the amount of the hydroxyl radical present in the atmosphere. Such a combination of related measurements should make it possible to understand the rate at which water vapor is currently being photodissociated in the upper atmosphere of Mars, and to determine at what rate the atomic hydrogen diffuses upward and is lost through atmospheric evaporation.

Nitrogen

Molecular nitrogen, which is the most abundant constituent of the earth's atmosphere, may or may not

be present in the atmosphere of Mars. The earth's atmosphere is the result of outgassing from the interior. Rubey³¹ has estimated that the primitive atmosphere of earth may have contained approx 7% of molecular nitrogen with the bulk of the remainder being gaseous carbon dioxide. The carbon dioxide has been removed by first dissolving in the oceans and then being deposited as carbonate rocks. The molecular nitrogen has remained to become the dominant gas. If the Martian atmosphere has resulted in a similar way from the outgassing of the interior, it may be expected to contain 5-10% molecular nitrogen, with the carbon dioxide remaining in the atmosphere because of the lack of oceans.

If the atmosphere of Mars is the remnant of the primordial gas that formed the solar system, an even larger abundance of molecular nitrogen is to be expected. A primitive planetary atmosphere that has lost its hydrogen and helium has been estimated to contain 15% molecular nitrogen, 25% neon, and 60% carbon dioxide.³²

If the amount of nitrogen on Mars is substantially less than these estimates, it means that somehow the nitrogen must have escaped preferentially leaving the carbon dioxide behind. Leighton and Murray²⁸ have suggested that the CO₂ might have been trapped or chemically combined on the surface while the nitrogen escaped. In this model the carbon dioxide would be released into the atmosphere after all of the nitrogen had escaped.

If nitrogen has not ever been present in the atmosphere of Mars either as molecular nitrogen or ammonia, then it will be difficult to imagine how the first amino acids could be formed. The Miller-Urey³³ mechanism requires that nitrogen compounds be present in a reducing atmosphere together with hydrocarbons and water vapor. An electric discharge, ionizing radiation, or uv light provides the energy to synthesize amino acids.

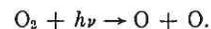
Molecular nitrogen can be measured in a planetary atmosphere with a mass spectrometer, but this technique requires that the mass spectrometer be carried into the atmosphere. Ultraviolet spectroscopy permits the measurement to be made from a flyby spacecraft at a much earlier time in the development of planetary exploration techniques and at a commensurately lower cost. Molecular nitrogen emissions are excited in the uv dayglow by photoelectron excitation. The observation of these emissions from the sunlit limb of the planet gives a detection sensitivity of approximately 1% for molecular nitrogen in the planetary upper atmosphere. The measurement must be made while discriminating against the bright disk of the planet.

Are there Signs of Life?

The oxygen that is present in the earth's atmosphere at the present time is the result of photosynthesis, and thus, its presence is evidence that life does exist on this planet. Berkner and Marshall^{34,35} have pointed out that although the photodissociation of water vapor

does lead to the formation of molecular oxygen, this mechanism can produce no more than 0.1% of the present atmospheric level because of the Urey self-regulating mechanism. Urey³⁶ showed that the molecular oxygen formed from the photodissociation of water vapor forms a protective layer above the water vapor slowing down the rate of photodissociation. This process is self-regulating and reaches an equilibrium at about 0.1% of the present amount of oxygen in the earth's atmosphere. In the Berkner-Marshall model, this amount of oxygen is compatible with early forms of life. With the beginning of photosynthesis, oxygen is produced at a rate that exceeds the losses due to surface oxidation, and molecular oxygen increases until the present abundance is reached.

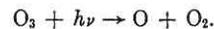
If photosynthesis is occurring on Mars, then oxygen should be produced. It is clear that such possible production is not as widespread as on the earth, since the spectroscopic observations which measure average composition over the planetary disk show a mixing ratio O₂ to CO₂ of not more than 0.26%.²⁹ There may, however, be local regions of photosynthetic oxygen production, such as warm, moist lowlands or in crater bottoms. Any oxygen produced would be photodissociated by solar radiation shortward of 2420 Å in the weak Herzberg continuum:



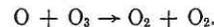
The atomic oxygen that is formed may react with molecular oxygen to make ozone:



The ozone will absorb solar radiation between 2000 Å and 3000 Å and shadow the environment below from this radiation:



Ozone may also be destroyed by reactions with the surface and with atomic oxygen:



The equilibrium level of ozone that is reached may be determined by taking into account the preceding equations plus additional loss mechanisms for atomic oxygen.³⁷

How then can uv spectroscopy look for signs of life? The ozone absorption spectrum between 2000 Å and 3000 Å may be used as a sensitive detector of ozone. An amount of ozone necessary to produce an optical depth of 0.1 at 2550 Å can be detected. This is equivalent to a 0.0003 cm atm of ozone or one-thousandth of the amount in the earth's upper atmosphere. The presence of localized concentrations of ozone in craters or lowlands will indicate the presence of molecular oxygen in that location. With the extreme sensitivity of the ozone measuring technique, it is possible to detect the presence of molecular oxygen of the order of a tenth of a percent. This is sufficient sensitivity to determine whether or not there is oxygen on Mars that is in excess of what is produced by photochemical equilibrium.

Conclusion

The emphasis in the preceding discussion has been on what uv spectroscopy might contribute to exobiology. Ultraviolet experiments will provide information on a number of other problems as well: the composition of the ionosphere, the presence of atmospheric phenomena produced by charged particle bombardment such as aurora, the pressure distribution of the atmosphere over the surface of Mars, for example. It is to be expected that the intensities of the spectral features of the dayglow will turn out to be quite different from the predictions listed in this paper. Most important, there will be features in the uv spectrum of the planets that will be quite unexpected. These may turn out to be the most important findings.

The ideas presented in this paper have been formulated over a number of years through collaboration with my co-experimenters on the Mariner uv experiments, and my colleagues at the University of Colorado: C. W. Hord, J. B. Pearce, G. E. Thomas, A. I. Stewart, and W. G. Fastie of The Johns Hopkins University.

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The 24th annual Symposium on Molecular Structure and Spectroscopy will be held in the Department of Physics, The Ohio State University, 2-6 September 1969. G. Herzberg (National Research Council of Canada), will be one of the principal speakers during the plenary sessions. The invited papers program will also include Robin M. Hochstrasser (Univ. of Pennsylvania) speaking on electronic spectra of large molecules, and T. Oka (NRCC) discussing microwave studies of collision-induced transitions between rotational levels. Seminars on special topics will also be featured. Some instrument companies will exhibit their latest products during the Symposium. Air-conditioned dormitory accommodations will be available for individuals as well as married couples. Write to K. Narahari Rao, Molecular Spectroscopy Symposium, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, Ohio, 43210, for further information