Table 1. Molecules with absorption bands near 4.73 μ.

Molecule	Band	Wavelength (μ)	Reference
HCN	$3\nu_2$	4.73	(*8*)
C_2N_2	ν_3	4.63	(*8*)
CH_3D	ν_2	4.54	(*9*)
GeH_4	ν_3	4.73	(*10*)
SiH_4	ν_3	4.56	(*11*)

mosphere, are listed in Table 1, together with the wavelengths of their band origins. Although only the HCN and GeH_4 bands can strictly be considered as coincidences, the unknown background of the jovian spectrum would not entirely rule out the other molecules listed in Table 1. Objections against the presence in Jupiter of the molecules listed in Table 1 can be raised on the basis of calculations of chemical equilibrium (*5*) or consideration of elemental abundance. Such calculations, however, may not strictly apply to Jupiter.

The feature observed at 4.73 μ could also be produced by the absorption of solid particles, such as ammonium hydrosulfide or ammonium polysulfides [NH_4SH or $(NH_4)_2S_x$], recently postulated (*6*) to be the condensable materials forming a cloud layer in Jupiter at about 225°K. No information regarding the absorption of these ammonium salts seems to be available. However, Woeller and Ponnamperuma (*7*) have recorded the time development of the spectrum of a reaction involving HCN and NH_3. The polymer formed as the end product of the reaction, after removal of unreacted gases, shows an absorption feature at about 4.72 μ which is in fact more conspicuous than the HCN band in the unreacted mixture. The 5-μ spectrum of Jupiter presented here has thus brought into new relevance laboratory experiments of the kind that Woeller and Ponnamperuma (*7*) have performed.

The spectrum of Jupiter presented in Fig. 1 also shows the following characteristics:

1) The spectral gradient corresponds to a color temperature of 300°K if the color temperature of α Boo is taken to be 3600°K. The brightness temperature implied by the measured irradiance at 4.8 μ is ~ 250°K. The difference between these color and brightness temperatures is not considered significant.

2) The intensity decreases sharply at wavelengths below 4.7 μ. This decrease is probably the result of absorption in the extremely strong ν_3 band and in the weaker combination bands $2\nu_4$ and $\nu_2 + \nu_4$ of CH_4. The energy emitted by Jupiter in the entire 5-μ window would be between 10 and 15 percent higher if this absorption were not present. Inferences (that is, brightness temperatures) from broadband photometry of standard stars and Jupiter should thus allow for their different spectral energy distributions. The incomplete compensation for terrestrial H_2O absorption and the insufficient signal-to-noise ratio have precluded the detection of any extraneous feature in the jovian spectrum at wavelengths greater than 4.9 μ.

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Particle Formation during Water-Vapor Photolysis

Abstract. *Micrometer-sized particles have been produced by the photolysis of water vapor at wavelengths between 1500 and 1700 angstroms. Although the composition of the particles was not determined, the rate of particle production is consistent with the efficient conversion of water photolysis products to particulate matter. Such a process may be of importance in planetary atmospheres.*

This report describes our observation of the formation of particles when H_2O vapor at unsaturated pressure is exposed to ultraviolet (UV) light at a wavelength between 1500 and 1700 Å. Each particle has spheroidal shape, low density, unit positive charge, and a diameter that is determined by competition between the rate of H_2O vapor absorption and the rate of particle sedimentation. When H_2O vapor at a pressure of 10 torr (one-half the saturation vapor pressure) is photolyzed, each UV photon that is absorbed results in an increase in particle mass equal to that of approximately one H_2O vapor molecule. The mass added to particles per photon absorbed is about an order magnitude greater when a mixture of H_2O vapor at a pressure of about 10^{-2} torr in He at a pressure of 300 torr is photolyzed. Presently accepted concepts of H_2O chemistry do not appear capable of accounting for these observations.

The phenomenon of particle formation induced by the illumination of a gas is not, in itself, unusual. In 1869 Tyndall (*1*) described experiments on the vapor of "nitrite of butyl" in which "the chemical action of light" served to "render . . . vapor visible." Since 1869 many observations of light-induced particle formation have been reported. The subject has been reviewed by Mohnen and Lodge (*2*). Observations of this kind can be divided into two classes, depending on whether or not the reaction system contains a species that is supersaturated. Where the reactants are not supersaturated, particles will be formed only if a product species produced by the light can form a polymeric compound with low vapor pressure. The number of gaseous molecules converted to the particle phase is thus of the same order of magnitude as the number of photons absorbed. Tyndall's observations and the formation of aerosols in photochemical smog from SO_2, NO_2, and hydrocarbons (*2*) appear to be in this category. In the second class of gas-to-particle-conversion phenomena, one species is present with a supersaturated pressure. The formation of a suitable condensation nucleus will induce rapid formation of droplets (particles). Since the condensation nucleus need only be a few molecular diameters in size, the absorption of a few photons can result in the transfer of millions of supersaturated vapor molecules to the particle phase. The multiplying effect of condensation nuclei in supersaturated water vapor has been employed (*2*) to detect extremely minute concentrations of trace gases when the trace species can be photochemically induced to form condensation nuclei.

The observations we describe here were made in highly unsaturated conditions that were not susceptible to the multiplying effect of simple condensation. The high efficiency of particle formation that we observed implies that either the particles are composed primarily of an undetected impurity whose reaction is catalyzed by H_2O photolysis or that the particles are composed primarily of H_2O vapor constituents that are bonded together in a totally unexpected fashion.

We first observed the effects of particle formation during studies of fluorescent emission from the products of the UV photolysis of CO_2 (*3*). Our observations consisted of photometric measurements of the light emitted from the gas at an angle of 90° to the UV beam. We discovered that the spectral features around 6300 and 5577 Å, which had previously been attributed to fluorescent emission from metastable oxygen atoms (*4*), were, in CO_2 photolysis, actually due to the scattering of visible emission lines from the UV source lamp.

The degree of light scattering we observed was about four orders of magnitude greater than that expected from species (like molecules) whose dimensions are much smaller than the wavelength of visible light. The magnitude of the light scattering from the volume of the photolysis cell can be characterized by a "90° scattering coefficient," ϕ. This coefficient can be deduced from B, the surface brightness observed at 90°, and I, the input (visible) radiant flux:

$$\phi = \frac{4\pi B}{I}$$

For isotropic scattering, ϕ is the fraction of the input radiation dispersed per centimeter and is equal to the product of the individual scattering cross section and the number density of the scattering species. We observed a value for ϕ of $\sim 10^{-4}$ cm^{-1}; that due to Rayleigh scattering from a gas at 50 torr is about $\sim 10^{-8}$ cm^{-1}.

The large value of ϕ implies that the scattering was due to particles with radii comparable to the 5000-Å wavelength of the light. This conclusion was confirmed by a visual examination of the light scattered at 90° to a focused tungsten lamp beam. With the aid of a lens, discrete scattering centers (particles) could be distinguished. A cloud containing about 10^4 particles per cubic centimeter was located in the center of the cell and rotated in response to convection currents set up by the photolysis lamp. When the UV lamp was turned off to reduce convective motion, the particles were observed to exhibit a net downward movement superposed on the erratic Brownian motion.

Experiments with other gases revealed that the critical component for particle formation was not CO_2 but rather H_2O vapor originating from the cell walls. We will show below that, although H_2O vapor does indeed appear to be the essential constituent for particle formation, the particles themselves are not composed of H_2O in its normal liquid or solid form.

We tested several reaction vessel designs. The nature of the vessel wall did not appear to be important; the phenomenon was reproduced in various well-cleaned Pyrex cells and with various UV window materials. Walls of any material appeared to inhibit particle formation since particles formed only in the center of the reaction cell. The thickness of the sharply defined particle-free layer adjacent to any surface decreased as the pressure of the buffer gas increased; this result suggests that the wall serves to remove reactive precursors of the particles. The walls appear to have two roles. The first is to provide a constant vapor pressure of "impurities," the only detectable species being H_2O; the second is to remove photolysis products necessary for particle formation. For convenience of observation, the 500-cm^3 cell used in the quantitative measurements was constructed of brass with walls coated with soot. The UV beam from the Xe discharge lamp and the infrared-filtered W lamp beam entered through windows at opposite ends of the cell. Photometric and visual observations were made at 90°.

Reproducible quantitative measurements of the particle formation process were difficult to obtain because the measurable quantity, ϕ, depends on the position of the particle cloud in the cell. The photometric measurements of the time dependence of ϕ provided three semiquantitative parameters that characterize the particle formation process: (i) the photolysis time, t_0, required to produce detectable scattering; (ii) the rate of increase in ϕ after the onset of detectable scattering ($\phi > 3 \times 10^{-7}$ cm^{-1}); and (iii) the magnitude of $\phi_{\max}$, the aggregate steady-state scattering coefficient. Values of t_0 ranged from 20 seconds for favorable initial conditions to over 10^3 seconds. The measurements of t_0 were usually reproducible to within a factor of 2, although on rare occasions long photolysis times (up to an hour) were required to produce a measurable scattering even under nominally favorable reactant conditions. In many experiments ϕ remained roughly constant near $\phi \sim \phi_{\max}$ for long time periods. This constancy appears to be the result of steady-state competition between the rate of particle growth and the rate of gravitational sedimentation.

When we connected the He-filled cell to a mass spectrometer, we found that the only impurity present in the cell with a partial pressure P greater than the detection limit of 10^{-4} torr was H_2O vapor. When the cell was connected to a fast pumping system which produced $P_{H_2O} \leq 10^{-4}$ torr, particle production could not be observed for any pressure of added He up to 1 atm. When $P_{H_2O} > 3 \times 10^{-3}$ torr, particles could almost always be produced if enough nonabsorbing buffer gas (He or N_2) was added. The minimum pressure required for particle production decreased with increasing P_{H_2O}. For He, the approximate minimum pressure necessary for the formation of visible particles was 150 torr at $P_{H_2O} = 10^{-2}$ torr, 50 torr at $P_{H_2O} = 10^{-1}$ torr, 30 torr at $P_{H_2O} = 1$ torr, and 0 torr at $P_{H_2O} = 8$ torr. The minimum N_2 pressure for any P_{H_2O} was roughly one-half that for He. Since molecular diffusion coefficients in N_2 are about one-half those in He, this result supports our hypothesis that the role of the buffer gas is the containment of reactive species.

For $P_{H_2O} \sim 10^{-2}$ torr the minimum He pressure required for particle formation was reduced about 50 percent by the addition of O_2 at a pressure of 0.1 torr or by CO_2 at a pressure of 2 torr. Under these conditions metastable $O(^1D)$ formed in the photolysis of O_2 and CO_2 produced OH according to the reaction

$$O(^1D) + H_2O \rightarrow 2OH$$

at a rate faster than the rate of OH production from direct H_2O photolysis

$$H_2O + h\nu \rightarrow OH + H$$

This result suggests that OH might be important in the process of particle production. Similar inferences about the ability of $O(^1D)$ to stimulate particle production can be made from the observation that for $P_{H_2O} = 10^{-2}$ torr and $P_{CO_2} = 50$ torr, the addition of N_2 reduced the growth rate of ϕ by a factor consistent with the efficiency of N_2 in quenching $O(^1D)$ relative to that for CO_2. For $P_{H_2O} = 10^{-2}$ torr and $P_{He} = 300$ torr, the particle formation rate was markedly reduced by the addition of CO at a pressure of 1 torr or NO at a pressure of 0.05 torr.

The wavelength dependence of the rate of particle production in pure H_2O or in H_2O/He systems appears to be consistent with that for H_2O absorption. When the partial pressures of added O_2 or CO_2 are higher than that of H_2O, the shorter wavelengths required for CO_2 or O_2 absorption are more important than those at the peak of the H_2O absorption continuum. These conclusions are based on observations of a reduction in particle production when H_2O, CO_2, or O_2 filters were placed between the Xe lamp and the photolysis cell; they apply only to the wavelengths below 1700 Å where the lamp has a significant output.

The physical properties of the particles—size, shape, charge, and density—were inferred from observations of the particle polarization and of particle motion in the presence or absence of electric fields. The degree of polarization of the light scattered at 90° was very high (> 95 percent) when the particles first became visible and decreased toward zero as time went on. We interpret this result to be a consequence of particle growth since light scattered at 90° by spherical particles is highly polarized when the radius r is $< \lambda/2\pi$ (where λ is the wavelength) and then becomes largely unpolarized when r is $\gg \lambda/2\pi$. Similar results were obtained when individual particles were examined visually through a polarizing film. The dim (that is, small) particles were highly polarized; the bright ones were unpolarized. Since only quasi-spherical objects can produce strongly polarized 90° scattering, the observation of > 95 percent polarization of the small particles indicates that they are roughly spheroidal (*5*).

Each particle was found to be positively charged and to move downward in the absence of convective currents. The mass-to-charge ratio m/q could thus be estimated from a Millikan oil-drop type of experiment with two parallel conducting plates placed inside the cell. The electrostatic field E was adjusted to bring the particle to rest; for stationary particles,

$$Eq = mg$$

where g is the gravitational acceleration. Brighter, less polarized particles invariably had higher m/q ratios than dimmer, more polarized particles. For the brightest particles

$$m \text{ (in grams)} = 5 \times 10^{-12} q/e$$

where e is the electronic charge. The mass of these particles is therefore at least 5×10^{-12} g.

After the stopping potential was measured, the electric field was removed and the terminal velocity, v_T, was measured. At high pressures of buffer gas, where the molecular mean free path is much shorter than the particle dimensions, v_T is proportional to ρr^2, and the Stokes relation (*6*) was used to calculate the density ρ from m and v_T. At lower pressures, where the gas viscosity is pressure-dependent, the Stokes-Cunningham (*7*) expression was employed. For all the particles observed the product of the density and the charge was approximately constant with

$$\rho \frac{q}{e} \sim 0.2 \text{ g/cm}^3$$

We assume approximate sphericity in view of the polarization measurements mentioned above. It seems logical to assume that all particles have the same density. It follows that they all have the same charge. The most likely value for the number of charges per particle is therefore one so that $\rho \sim 0.2$ g/cm^3. The largest particles in both the high- and low-pressure cases thus had radii of about 2 μm.

The calculated low density of the particles shows that they are not simply ordinary H_2O droplets; moreover, H_2O vapor cannot ordinarily condense to the liquid phase under unsaturated conditions. However, if liquid H_2O (somehow formed at the surface during UV exposure) comprised much of the particle's weight, then the m/q ratio should decrease rapidly with time when the UV light was turned off. Thermodynamic expressions for droplet evaporation (*6*) show that a particle with $r = 2$ μm at $P_{H_2O} = 10$ torr (approximately one-half the saturation vapor pressure) should completely evaporate in about 0.3 second, whereas at $P_{H_2O} = 10^{-2}$ torr the evaporation time is about 0.15 second. When the UV lamp was turned off, the particles were observed to change their m/q ratio by less than the minimum detectable 20 percent in a period of 5 minutes. It is therefore certain that very little of the particle mass is composed of ordinary liquid H_2O. We conclude that the particles are spherical, are composed of a material other than liquid H_2O, have a unit positive charge, have a density of about 0.2 g/cm^3, and have radii ranging up to 2 μm.

It is possible to use the derived particle properties and the observed aggregate steady-state scattering coefficient, ϕ_{max}, to provide estimates of particle growth characteristics. To accomplish this, size distributions of the particles must be derived. We have developed a particle growth model (*8*) whose basic hypothesis is that the rate of addition of mass to the particles is proportional to the particle's surface area. We shall summarize here the conclusions of the analysis for two reaction mixtures at steady-state: for $P_{H_2O} = 10$ torr with no buffer gas and for $P_{H_2O} = 10^{-2}$ torr in 300-torr He.

For $P_{H_2O} = 10$ torr the rate of mass addition calculated in this way had a cumulative uncertainty of about a factor of 3. Within this degree of uncertainty, the calculated rate at which mass was added to the particles was just equal to the (mass) rate at which H_2O vapor absorbs the UV light. The observed behavior of the aggregate scattering coefficient is just what would be expected if every molecular fragment resulting from H_2O absorption were able to "stick" to the first particle it collided with. The formation rate of particles is about 10^3 cm^{-3} sec^{-1}, and the mean particle lifetime (the time required for the particles to grow large enough to fall 1 cm) is about 30 seconds. For $P_{H_2O} = 10^{-2}$ torr in 300-torr He the rate of mass addition to the particles is about an order of magnitude greater than the rate of H_2O absorption. The production rate is about 30 cm^{-3} sec^{-1}, and the lifetime is about 300 seconds.

The implications for particle composition of the rates of growth, the observed particle charge, and the upper limits for impurity species will be discussed elsewhere (*8*). We list here some of the conclusions. The maximum amounts of gaseous or particulate impurities contained initially in the added gases are not sufficient to provide a significant fraction of the total mass of the particles. Any particulate species originating from the walls during the gas-filling operation would, through coagulation and sedimentation, be reduced to a concentration too low to contribute significantly to the total particle mass. A gaseous impurity supplied continuously from the walls is unable to supply a significant mass to the particles by direct addition, even if such a species were to stick to the particles at every collision. If such an undetected impurity is important, it must be activated at almost every collision with a newly formed H_2O photolysis product and then stick at nearly every collision with a particle.

In conclusion, our results show that necessary conditions for the formation of the particles are the presence of H_2O vapor, UV light, and enough buffer gas to overcome wall effects. We do not yet have enough information to conclusively prove that these are sufficient conditions for particle formation. Explanations for our observations that involve superreactive undetected impurities seem to be unlikely—but then so does the logical alternative. This alternative, the simplest interpretation of our observations, is that the absorption of UV light by H_2O vapor leads to the formation of a low-density nongaseous substance that resembles neither the liquid nor the solid phase of ordinary H_2O.

If such a process does occur, it has, in addition to its obvious chemical interest, possible implications for planetary atmospheres where H_2O vapor is exposed to the sun's UV radiation. One might conjecture that the particulate substance we have described could be a constituent of Venusian clouds. On Mars the presence of particulate fragments with more than four or five atoms each could provide intermediates that circumvent the three-body rate limitations which currently plague explanations for the stability of the Martian atmosphere (*9*). In Earth's atmosphere direct production of particles by H_2O absorption would be limited to altitudes above 80 km. If the presence of $O(^1D)$ and H_2O constitute a sufficient condition for particle production, it could occur in the stratosphere where $O(^1D)$ is produced in O_3 photolysis. When such particles fall to lower altitudes, they could conceivably act as nucleation sites for raindrop formation.

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Mars: Has Nitrogen Escaped?

Abstract. *If eddy mixing is about as effective on Mars as it is on Earth, then there seems to be less nitrogen present on Mars than we would expect if terrestrial-type outgassing were the source. However, in this event a nonthermal escape mechanism involving the predissociation of exospheric nitrogen can be invoked to explain the low nitrogen concentration.*

One of the more interesting results from Mariner 6 and Mariner 7 was the apparent failure of the ultraviolet spectrometer to detect molecular nitrogen. Dalgarno and McElroy (*1*) concluded that the ultraviolet data "are consistent with a mixing ratio of N_2 in the martian atmosphere as large as 5 percent, if eddy mixing is extremely efficient." This is about the amount expected if outgassing is the source. However, they go on, "If the eddy mixing coefficient is similar to that for the earth, the limit is reduced by a factor of about 10." In this event there would be a serious conflict with our notions about the origin of the martian atmosphere. I suggest here that, in this latter case, nitrogen may well have been outgassed to the extent of the order of 5 percent but may subsequently have escaped from the planet, and thus that we need not abandon our ideas about its origin on this account.

Ordinary thermal escape is quite ineffective in removing N or N_2 from Mars. One possible nonthermal mechanism is the absorption of solar far-ultraviolet radiation by ground-state exospheric N_2 to give N_2^*, followed by predissociation of the excited molecules into atoms having sufficient kinetic energy and proper direction to escape from the planet (1.731 ev for N and upward). I consider here only the energy range of incident photons from about 12.5 ev (992 Å) to the first ionization limit, 15.58 ev (796 Å). Higher energy photons may be quite important but there is not as much information on the fraction predissociating (dissociative recombination may also contribute to the escape rate).

The photon's momentum can be disregarded, because the speed change for N_2 is considerably less than 1 m/sec.

Table 1. Calculated amount of nitrogen lost if outgassing occurred early in martian history.

Effective absorption cross section of N_2, 796 to 822 Å (15.07 to 15.58 ev) (*4*) (considering the path length dependence):	3×10^{-17} cm^2
Solar flux at 1 astronomical unit (*5*)*:	7×10^8 photon cm^{-2} sec^{-1}
Time-averaged flux at martian exobase:	$\frac{0.5}{(1.5237)^2} \times 7 \times 10^8 = 1.5 \times 10^8$ photon cm^{-2} sec^{-1}
Loss rate, *L*†:	$\frac{1}{2} \times 1.8 \times 10^6 \times 10\ \rho$ atom cm^{-2} sec^{-1}
Fractional loss rate‡:	$L/2 \times 2.5 \times 10^{23}\ \rho\ cm^{-2} = 0.18 \times 10^{-16}\ sec^{-1}$
Fraction lost in 1.4×10^{17} seconds:	$1 - e^{-2.52} \approx 92$ percent

* This value is lower by a factor of 3 than Hinteregger's earlier values. † Where ρ is the N_2 mixing ratio of the atmosphere as a whole. ‡ On the assumption that the surface pressure has always been 7 mbar $\approx 2.5 \times 10^{23}$ CO_2 molecules per square centimeter.