Jovian Atmosphere: Near-Ultraviolet Absorption Features

Greenspan and Owen (*1*), in a stimulating discussion of the Jovian atmosphere, have reconsidered Stecher's (*2*) rocket ultraviolet spectroscopy of Jupiter. They conclude that, while the general reflectivity between 2000 and 3000 Å can be matched by some 12 km-atm of H_2 and a small surface reflectivity, there still exist two significant absorption features in this wavelength range. This residual absorption, shown by the dashed line connecting the error bars in Fig. 1, includes a feature centered at 2600 Å and a general reflectivity decline shortward of 2400 Å, with the possibility of very high absorption below 2100 Å.

The existence of the 2600-Å absorption feature had in fact been suspected earlier. From near-infrared spectra, Zabriskie (*3*) had estimated the abundance of molecular hydrogen above the Jovian cloudtops as several km-atm, and the expected near-ultraviolet spectrum determined by Rayleigh scattering from this amount of hydrogen was calculated by Brandt (*4*). When this spectrum was compared with rocket observations of Jupiter at 2700 Å performed by Boggess and Dunkelman (*5*), Brandt noticed a significant deficit in the observed flux below the calculated values. I then attempted (*6*) to determine whether any likely constituents of the Jovian atmosphere might be responsible for this absorption. The observed or suspected major atmospheric constitutents—hydrogen, helium, neon, methane, ammonia, and water—can all be excluded. Of the most abundant interaction products of these gases, expected both on the basis of laboratory simulation experiments (*7*) and on the basis of quenched thermodynamic equilibrium calculations (*8*), none have appropriate absorption features in this region. Other simple molecules capable of absorption at these wavelengths—such as aldehydes and ketones—require water vapor as a precursor. But the water will be condensed out at lower levels and will be unavailable. For these reasons I concluded that the absorption does not occur in the gas phase above the clouds, but rather occurs within the clouds. Since the Jovian clouds are not likely to have a very sharp upper boundary, cloud particles may be present at altitudes considerably above what is usually called the cloud "tops."

Greenspan and Owen have suggested that absorption by gas-phase benzene may explain the absorptions, although they state that "a detailed fit of the absorption profile to the observations does not provide a very convincing match. The amount of gas needed (0.04 cm-atm) is also rather high, considering the low vapor pressure of benzene at the relevant temperatures." The chemistry of organic molecules in condensed ammonia is very complex (*9*), and it is certainly by no means obvious what the preferred molecular species present as minor constituents in the Jovian clouds might be.

However, almost all common organic molecules with the desired absorption properties are derivatives either of benzene or of purine. The character of the spectrum as indicated in Fig. 1 immediately suggests the possibility that purines and pyrimidines may be important. These molecules characteristically exhibit strong absorption features near 2600 Å, which are commonly used as an analytic tool in their detection. They also show absorption features shortward of 2300 Å with the absorptivity becoming very large near 2100 Å. In Fig. 1 are shown absorptance measurements on dilute aqueous solutions of the purine adenine performed with a Beckman DB-G double-beam ultraviolet spectrophotometer. While there are minor absorption shifts, both auxochromic and bathochromic, were we to use other purines or pyrimidines, or other solvent systems, these spectra would still be typical of all the nucleotide bases. Considering the differences between absorption in a homogeneous medium and absorption during multiple anisotropic scattering in a cloud layer (*10*), we see that a rather good fit to the Jovian residual absorption is obtained with ~ 1 μg of adenine per square centimeter column.

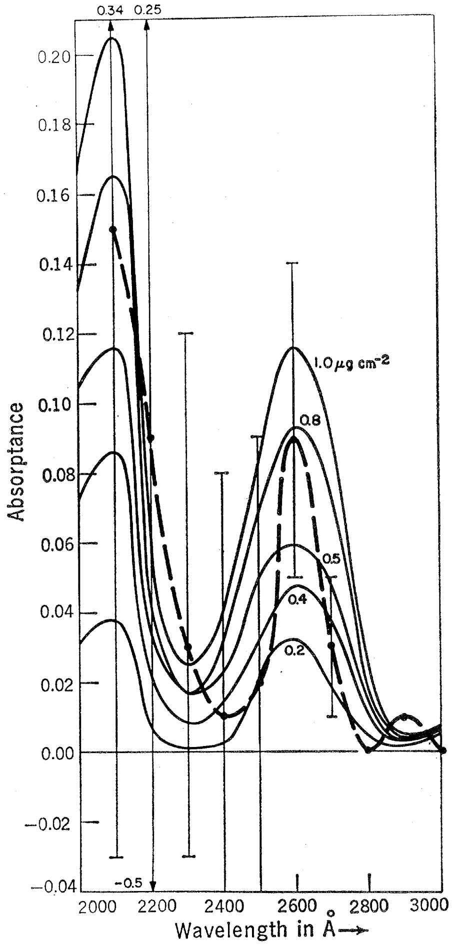

Fig. 1. Residual absorption on Jupiter in the rocket ultraviolet is shown by the dashed line and the associated error bars. The solid curves are the ultraviolet absorptances of various quantities of adenine, measured in dilute aqueous solution in the laboratory. The residual absorption is based on curves (*1*) normalized at 3000 Å.

At the lower temperatures of the Jovian clouds, and with the adenine not in aqueous solution, rotational and vibrational fine structure to these electronic transition features will be further suppressed, and the fit with the Jovian spectra improved (*11*). Thus, extremely small quantities of purines or pyrimidines appear adequate to explain the observations. By contrast, ~ 100 times more benzene is required, and even apart from the fine structure we find that the fit of aqueous solutions of benzene to the rocket spectra is poor. This is of course far from a unique spectral identification of adenine. But it is of interest that a fit can be achieved with very small quantities of an abundant condensed-phase organic molecule.

The synthesis of adenine under conditions not too dissimilar from those expected in the Jovian environment has been performed in experiments relevant to the origin of life on earth. Adenine and/or its precursor, 4-amino-imidazole-5-carboxamide, have been produced directly from hydrogen cyanide and aqueous ammonia solutions; by 5-Mev electron irradiation of methane, ammonia, and water mixtures in the gas phase; and by ultraviolet irradiation of hydrogen cyanide solutions (*12*). Hydrocyanic acid is expected as a minor constituent of the Jovian atmosphere and clouds (*7, 8*). More recently, adenine and other bases have been produced by heating NH_3, H_2, and CO and gradually cooling from about 800°K (*13*).

High-resolution ultraviolet spectra of Jupiter, preferably with some resolution of the disk, as well as laboratory spectra of more refined simulations of the Jovian clouds, can be very useful in checking the conclusions reached here. For example, there is a characteristic fine structure in the B bands of gas-phase benzene and many of its derivatives (*14*); aqueous solutions of benzene show such fine structure, particularly between 2400 and 2700 Å. No such fine structure is generally observed with purines and pyrimidines. High-spectral-resolution infrared spectroscopy of Jupiter—for example, with interferometric techniques—would also be of great interest.

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15. The research reported here was supported in part by NASA grant NGR-09-015-023 and by funds from a PHS institutional grant to Harvard University. I thank Dr. Tobias Owen for an informative conversation and Mrs. Elinore Green for laboratory assistance.

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In our original interpretation of certain features in the ultraviolet spectrum of Jupiter (*1*), we stated that the observed absorption at 2600 Å and the sharp intensity decrease below 2100 Å were most probably due to one or more kinds of large organic molecules. Sagan suggests that adenine would provide a better fit to the observations than benzene, the specific example that we investigated. While we agree that the purines and pyrimidines represent a good additional source of organic absorbers, we feel that a specific identification is premature, particularly in the face of the many interpretational problems that remain to be solved.

In fact, there are a large number of organic substances that would match the data within the associated errors. A very abbreviated list of several of these compounds is presented in Table 1 (*2*). In order to decide which of these (if any) are actually present in the Jovian atmosphere, it is necessary to satisfy the following conditions: (i) the ultraviolet reflectivity of Jupiter must be specified with great precision, (ii) the distribution and amount of absorber in the Jovian atmosphere must be known, and (iii) the distribution and amount of atmospheric scatterers (molecular and particulate) must be specified. At the present time, only two sets of low-resolution observations are available, so the permitted variations of (ii) and (iii) have a rather wide range.

In fitting the absorbance of adenine to a replotted version of our "best fit" to the Jupiter data, Sagan favors the location of the absorber in the cloud layer, presumably frozen out with the ammonia in the crystals that form the visible clouds. However, our "best fit" model matches the observations with only 12 km-atm of H_2, a layer of gas that is well above the cloud tops as evidenced by the low temperature (110°K) corresponding to the lower boundary of the gas. Within the error limits of the original data, we have shown that the observations could be matched by 16 km-atm of H_2. In this case, the temperature is increased only to 120°K as compared with the ~165°K commonly associated with the cloud tops (*3*). Furthermore, this latter model does not permit any "surface" reflectivity. Hence any absorption at the base of the layer of gas or below will have no effect on the emerging radiation. In fact, it appears that more than 30 km-atm of H_2 will lie above the 165°K level in the Jovian atmosphere (*1*).

The reason Sagan (*4*) originally postulated that the absorber at 2600 Å had to be in the cloud layer was that the amount of hydrogen above the clouds was thought to be very small (4.6 km-atm) and the Rayleigh scattering coefficient used by Brandt (*5*) with this amount of gas led to an opacity at 2600 Å of only 0.2. Using the revised formulation of the scattering coefficient given by Dalgarno and Williams (*6*) and 30 km-atm of H_2, we find an opacity of 1.8, an increase that is consistent with our conclusion that absorption in the clouds will not have a noticeable influence on the ultraviolet spectrum.

Table 1. A partial listing of some suitable organic absorbers.

Adenine
Adenosine
Benzene
Benzenesulfonamide
Benzyl alcohol
Benzylamine
1-Benzyl-β-D-arabopyranoside
Caffeine
Cresol
3-Cyanopyridine
Cytosine
Mephenesine
2-(*N*-Methylaminoethyl) benzyl alcohol
4-Methylbenzenesulfonamide
N-Methyl-tetrahydroisoquinoline
Neostigmine methylsulfate
Phenol
3-Phenylpropionic acid
N-(4-Sulfamylphenyl)-β-D-glucosylamine
Sulfanilamide
Toluene

We are thus constrained to models in which the absorber lies above the scattering gas or is mixed in with the scatterer in some manner. If the absorber is uniformly mixed with the scatterer, the albedo can be expressed as

$$\bar{p}^{\lambda} = \frac{\pi \tau_s}{3(\tau_s + \tau_a)} + \left[2A - \frac{\pi \tau_s}{\tau_s + \tau_a} \right] E_4 (\tau_s + \tau_a)$$

where A is the constant reflectivity of the reference level, τ_s and τ_a are the scatterer and absorber optical thicknesses, respectively, and E_4 ( ) is a fourth-order exponential integral. Retaining our original "best fit" of 12 km-atm of H_2 and 7 percent reflectivity we have calculated the absorber optical thickness required at each wavelength to provide exact agreement with the observations. For comparison, we have performed the cor responding calculation for 16 km-atm of H_2 with zero surface reflectivity. These results are presented in Fig. 1 which is a plot of $\log_{10}$ (τ_a) versus

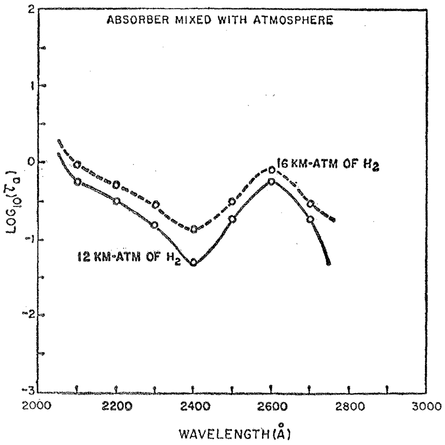

Fig. 1. Optical thickness τ_a of absorber required to match the Jovian brightness observations when the absorber is uniformly mixed with 12 or 16 km-atm of molecular hydrogen.

λ, a presentation that can be compared with published absorption curves (*2*) without regard for abundance (abundance differences correspond to a vertical displacement of the absorption profiles). It should be noted that the shape of the absorption profile is different in the two cases presented in Fig. 1 and one-third more absorber is required to match the 16 km-atm curve at 2600 Å (*7*).

If the absorber lies *above* the scattering layer, the albedo can be expressed as

$$\bar{p}^{\lambda} = \pi E_4(\tau_a) - (\pi - 2A) E_4 (\tau_s + \tau_a)$$

where the terms have been previously defined. Solving for the absorption required for the same two models considered above, we obtain two new profiles depicted in Fig. 2. The shapes of the curves are similar to those for the corresponding "mixed" cases, but now one-fourth less absorber is required.

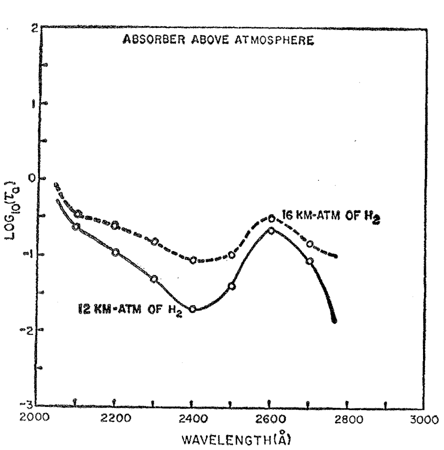

Fig. 2. Optical thickness τ_a of absorber required to match the Jovian brightness observations when the absorber lies above 12 or 16 km-atm of molecular hydrogen.

For the sake of illustration only, we have reproduced (in Fig. 3) absorption curves of six substances taken from the list in Table 1 (*8*). A comparison with Figs. 1 and 2 indicates that none of these substances fits any of the representations of the data very well. On the other hand, the uncertainties associated with each of the calculated values represented in Figs. 1 and 2 are such that all three substances (as well as many others—see Table 1) *might* be present.

Because of the rich variety of ultraviolet absorbers and the possibility that more than one contributes to the observed absorption, the identification problem may never be settled unambiguously until the atmosphere of Jupiter is explored directly. Nevertheless, this indication that complex organic molecules may indeed be present in the Jovian atmosphere is sufficiently exciting to justify considerable additional effort. It would be significant even if we could simply restrict the observed spectral features to a particular group of organic molecules, and we feel confident that this goal can be achieved. The process of formation and the vapor pressure of the various possible organic absorbers may serve as additional constraints. For example, aldehydes and ketones require water vapor as a precursor (*4*), while benzene and several of the substituted aromatic hydrocarbons as well as some purines and pyrimidines can form above the clouds where water vapor will not be available because of the low ambient temperatures.

Observations of the planet's ultraviolet spectrum at higher resolution or even low-resolution observations made with very high precision will greatly aid attempts to limit the number of alternatives. The infrared spectrum should also receive more attention, particularly the region from 8 to 14 μ where some of these substances and their derivatives exhibit absorptions. Since we have established that the ultraviolet absorber lies above the level from which the emission observed in this spectral region originates ($T_{IR} = 128°K$), the substance will also act as an absorber in the infrared, as it will be considerably colder than the underlying ammonia. A preliminary spectrum published by Low (*9*) already indicates the presence of absorption near 13.5 μ. Both C_2H_2 and HCN, gases expected to occur in photochemical reactions involving the substances in Table 1, absorb in this region. It is apparent that many surprises await future investigators of the Jovian spectrum.

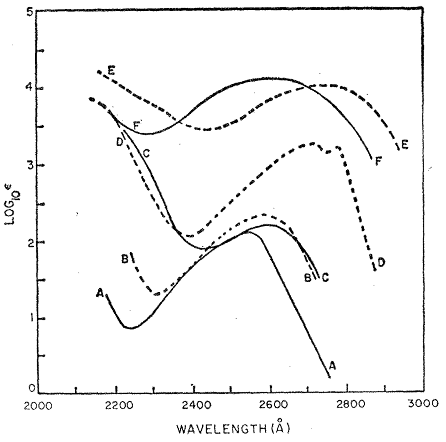

Fig. 3. Molecular extinction coefficient ϵ of several organic substances which may be responsible for the observed Jovian absorption features: (*A*) benzene, (*B*) toluene, (*C*) benzylamine, (*D*) *o*-cresol, (*E*) caffeine, and (*F*) adenine.

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2 November 1967