POLYCYCLIC AROMATIC HYDROCARBONS IN THE ATMOSPHERES OF TITAN AND JUPITER

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are important components of the interstellar medium and carbonaceous chondrites, but have never been identified in the reducing atmospheres of the outer solar system. Incompletely characterized complex organic solids (tholins) produced by irradiating simulated Titan atmospheres reproduce well the observed UV/visible/IR optical constants of the Titan stratospheric haze. Titan tholin and a tholin generated in a crude simulation of the atmosphere of Jupiter are examined by two-step laser desorption/multiphoton ionization mass spectrometry. A range of two- to four-ring PAHs, some with one to four alkylation sites are identified, with net abundance $\sim 10^{-4}$ g g^{-1} (grams per gram) of tholins produced. Synchronous fluorescence techniques confirm this detection. Titan tholins have proportionately more one- and two-ring PAHs than do Jupiter tholins, which in turn have more four-ring and larger PAHs. The four-ringed PAH chrysene, prominent in some discussions of interstellar grains, is found in Jupiter tholins. Solid state ^{13}C NMR spectroscopy suggests $\simeq 25\%$ of the total C in both tholins is tied up in aromatic and/or aliphatic alkenes. IR spectra indicate an upper limit in both tholins of $\simeq 6\%$ by mass in benzenes, heterocyclics, and PAHs with more than four rings. Condensed PAHs may contribute at most $\sim 10\%$ to the observed detached limb haze layers on Titan. As with interstellar PAHs, the synthesis route of planetary PAHs is likely to be via acetylene addition reactions.

Subject headings: molecular processes — planets and satellites: individual (Titan, Jupiter)

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are increasingly recognized as astrophysically important molecules. In an attempt to explain the diffuse interstellar bands at optical frequencies, Platt (1956)—from a straightforward integration of the one-dimensional Schrödinger's equation with infinite potential walls—argued that similar absorption features should be expected from molecules of dimensions 10–20 Å. Donn (1968) proposed that PAHs might be the Platt particles, a suggestion that today seems consistent with several astrophysical constraints (Léger & d'Hendcourt 1985). However, the diffuse interstellar bands have resisted precise identification. PAHs were suggested as components of the interstellar medium from chemical arguments (Sagan & Khare 1970) and from their stability in hard radiation environments (Sagan 1972; Sagan & Khare 1974). Compelling evidence for the presence of PAHs was first provided by comparison of laboratory and interstellar infrared emission spectra (Léger & Puget 1984; Allamandola, Tielens, & Barker 1985, 1989; Léger, d'Hendcourt, & Boccara, 1987).

In the solar system, several percent by weight of the carbonaceous chondrites is organic material, most of which is aromatic polymer; two-, three-, and four-ring PAHs such as naphthalene ($\mu = 128$ daltons), phenanthrene ($\mu = 178$), pyrene ($\mu = 202$), and chrysene ($\mu = 228$) and their alkyl derivatives are also abundant (e.g., Oró et al. 1971; Pering & Ponnamperuma 1971; Hayatsu et al. 1977, 1980; Cronin, Pizzarello, & Cruikshank 1988; Hahn et al. 1988). PAHs have also been detected in the H4 ordinary chondrite, Forest Vale (Zenobi et al. 1992). While there is no claim for these particular PAHs to the exclusion of others in the interstellar medium, simple PAHs such as the four-ringed chrysene have been prominently employed (e.g., Allamandola et al. 1989) in discussion of interstellar spectra. (Chrysene's spectroscopic and photophysical properties were better known than other PAHs of comparable mass.) Interplanetary dust particles (IDPs) display substantial variability among themselves, but a case has been made that at least some IDPs contain significant amounts of PAHs (Allamandola, Sanford, & Wopenka 1987), possibly of interstellar origin. Some IDPs also show infrared spectral similarities to carbonaceous chondrites (Sanford & Walker 1985). The dust impact mass spectrometers on the *Vega* and *Giotto* missions were unable to identify individual molecules in the dust grains in the coma of comet Halley, although broad categories of organic molecules were identified (Krueger & Kissel 1987; Kissel & Krueger 1991); PAHs are conspicuous by their absence.

Neither have PAHs been identified in remote observations of planets, satellites, asteroids, comets, or rings in the solar system. But they are certainly anticipated on the asteroidal parent bodies of the carbonaceous chondrites, and may be present on the surface of bodies with high-radiation doses and

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low-albedo markings, such as Iapetus, Triton, and the Uranian satellites and rings. We here discuss the possible presence of PAHs in the atmospheres of Jupiter and Titan. Both of these worlds are distinctly colored at visible frequencies, but the chemical composition of the cloud chromophore(s) involved is unknown (e.g., West, Strobel, & Tomasko, 1986). Aliphatic or aromatic conjugated polyenes have long been suspected to at least play a role (Sagan et al. 1967; Khare & Sagan 1973; Sagan & Salpeter 1976). Indeed, many synthetic dyes employ the anthracene ring system.

Acetylene (ethyne) is known to be produced from CH_4 by short UV or charged particle irradiation of simulated Jovian (Ferris & Morimoto 1981; McDonald, Thompson, & Sagan 1992) and Titanian (Thompson et al. 1991) atmospheres and is observed spectroscopically on both worlds (Noll et al. 1986; Coustenis, Bezard, & Gautier 1989). High-temperature pyrolysis of any of a range of hydrocarbons, from C_1 to C_4, yields one- and two-ring aromatics, including naphthalene, as the principal reaction products; acetylene polymerization is indicated as the reaction pathway (Friedman, Bovee, & Miller 1970; see also Allamandola et al. 1989, Fig. 23), because of the high local thermodynamic temperatures of these energy sources.

In quenched thermodynamic equilibrium numerical experiments (Eck et al. 1966), relevant to lightning and to high-temperature impact shocks in planetary atmospheres, polycyclics are generated at 1 bar and 1000 K in appreciable abundances when the C:H ratio approaches unity. At 10^{-6} bar and 1000 K the PAH abundance is high (10^{-2}–10^{-3}) for C:H:O ratios of 30:50:20, 4:94:2, and 12:86:2, but not for 10:70:20 (at which the abundance at thermodynamic equilibrium is negligible). $T \sim 1000$ K and $p \sim 10^{-6}$ bar are in the parameter range of maximum PAH yield later found by Frenklach & Feigelson (1989) in their kinetic study of C-rich circumstellar envelopes. Apparently PAH synthesis is poisoned at low C:H ratios in experiments where there are also low C:O ratios. In gas phase laboratory plasma discharge experiments with C:H < 1:4, PAHs tend to form; pyrene, coronene, and chrysene are specifically identified, and fluoranthene is suspected (Eck et al. 1966). Quenched thermodynamic equilibrium calculations at 1 μbar pressures suggest $\sim 10^{-8}$ PAH production on Jupiter (Sagan et al; 1967; Lippincott et al. 1967). Kim et al. (1985) propose acetylene polymerization to benzene on Jupiter, which seems consistent with the results of low-pressure continuous-flow plasma-discharge simulations of the Jovian stratosphere by McDonald et al. (1992). Since PAHs are known to be generated from methane-containing atmospheres by photochemical, shock, or plasma-charge particle processes, they might well be expected in the Jovian planets and Titan.

2. ORGANIC SOLIDS IN THE ATMOSPHERES OF JUPITER AND TITAN

Tholins are complex, usually brownish, organic solids produced by irradiating reducing atmospheres. We here discuss Jupiter tholin I, made from an equimolar mixture of CH_4 and NH_3 with 2.5% H_2O (Khare et al. 1981), intended as a (very) crude simulation of the deep accessible atmosphere of Jupiter; and Titan tholin, made from a 90% N_2/10% CH_4 gas mixture (Khare et al. 1984). Jupiter tholin I was made by sparking the gases at standard temperature and pressure (STP). After 35 days of discharge, the pressure increased by 0.3 bar, owing to production of H_2, N_2, and CO. Titan tholin was prepared by

continuous DC discharge through a gas mixture flowing at $\simeq 0.05$ cm^3 s^{-1} at 0.2 mbar. Further details on the experimental protocol can be found in the references cited. The measured optical constants of Titan tholin show a remarkable agreement with the observed properties of the Titan haze (Khare et al. 1984; McKay, Pollack, & Courtin 1989; Samuelson & Mayo 1991; Sagan, Thompson, & Khare 1992). Both tholins are composed of a rich array of organic molecules, including, on acid hydrolysis, amino acids (for Jupiter tholin I: Khare et al. 1981, 1986; Stoker et al. 1990; McDonald et al. 1991; for Titan tholin: Khare et al. 1985, 1986; McDonald et al. 1993).

Among the techniques used in these analyses were sequential and nonsequential pyrolytic gas chromatography/mass spectrometry (GC/MS), which provided evidence for one- and two-ring aromatic nitriles in Jupiter tholin I and alkylated one- and two-ring aromatic hydrocarbons in Titan tholin. While aliphatic hydrocarbons are well-known to be aromaticized on heating, the extent and duration of heating in the pyrolytic stage is not expected to have generated the aromatics identified (Khare et al. 1981; Thompson et al. 1991). A yield of about 1% benzene derivatives has been found in Jupiter tholin I on acid hydrolysis (McDonald et al. 1991), but no evidence for PAHs in these materials has been provided hitherto by soft analytic techniques.
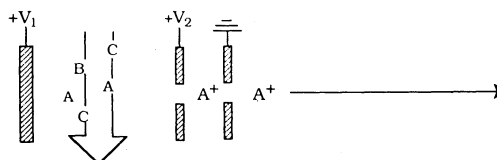
3. TWO-STEP LASER MASS SPECTROMETRY

Two-step laser mass spectrometry (L^{2}MS) has been described by Hahn et al. (1987) and Engelke et al. (1987). A pulse of laser energy thermally desorbs intact neutral molecules from a substrate, and a second laser causes "soft" (i.e., without fragmentation) ionization of PAHs, exclusive of any aliphatic compounds that may be present (Fig. 1). The absence of molecular fragmentation allows direct analysis of a mixture of unknown compounds, something that "hard" thermal ionization mass spectrometry cannot provide. In the first step of this desorption/multiphoton ionization technique, a small quantity of solid sample is deposited onto glass-fiber filter paper. The sample and holder are mounted on the end of a

2- Step laser mass spectrometry

1. IR laser pulse desorbs molecules from surface
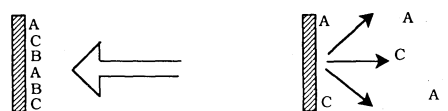
2. UV laser pulse selectively ionizes polycyclic aromatics.

3. Ions are separated by Time-of-Flight MS.

FIG. 1.—Two-step laser mass spectrometry. In the first step, intact neutral molecules are desorbed from a surface by the pulsed output of a CO_2 laser. An ultraviolet laser pulse then selectively ionizes the polycyclic aromatic hydrocarbons, represented here by A's. The ions are separated by time of flight.

Teflon rod and inserted into the evacuated chamber of the spectrometer. As the rod rotates, the pulsed output of a CO_2 laser (10.6 μm; 30 mJy per pulse; 19 ms pulse width; 0.5 Hz repetition rate) is focused onto a small (~ 1 mm diameter) spot on the sample. The IR radiation passes through the film of organics adsorbed on the surface of the sample and is absorbed by the underlying material, causing neutral molecules to escape in a rapid thermal desorption process. It is believed (Zare & Levine 1987) that the rapid heating rate of 10^8 K s^{-1} causes internally lukewarm intact molecules to be desorbed, even though slower heating rates cause molecular decomposition on the surface. The surface cools within a few tens of microseconds, and rotation of the sample rod exposes the fresh sample to the next pulse. After an appropriate time delay (~ 40 ms), the fourth harmonic of a Nd:YAG laser (266 nm, 1.0 mJy per pulse, 10 ns pulse width, 0.5 Hz repetition rate) causes 1 + 1 resonance-enhanced multiphoton ionization (REMPI) of the desorbed molecules in an interaction region about 5 mm from the surface. In this process, one photon excites an aromatic π electron into a high-energy molecular orbital, and a second photon ejects it. Photons at 266 nm are not energetic enough to break σ bonds between carbon atoms. Thus, compounds not containing π electrons or not absorbing strongly at 266 nm are not ionized.

The two-, three-, and four-ring PAHs naphthalene, phenanthrene/anthracene, and pyrene/fluoranthene and their alkylated homologs are the compounds most easily detected by this technique (Zenobi et al. 1989). The M$^+$ ions are accelerated down a linear time-of-flight mass spectrometer, at the end of which their signal is recorded by a microchannel plate array. The signal is amplified and fed into a digital oscilloscope which displays and records the spectra. Because 1 + 1 resonance-enhanced multiphoton ionization is a soft ionization tech-

nique, the spectra are dominated by the parent ion masses. Sensitivities in the subfemtomole (10^{-15} mole) range have been reported, corresponding to an ionization efficiency 100–1000 times greater than conventional surface ionization processes (Hahn et al. 1987). Usually, data from multiple laser shots are averaged, although a complete mass spectrum can be obtained from a single shot. The entire process takes only a few minutes, and the potential for contamination is low since sample handling is minimal.

4. RESULTS OF L²MS

Figure 2 shows L²MS spectra for milligram quantities of Jupiter tholin I and Titan tholin. Most of the major peaks belong to the alkylated phenanthrene/anthracene series. Representative structures are shown in Figure 3. L²MS has consistently been shown to be specific for PAHs, but it does not resolve PAH isomers. Thus, the placement of the alkyl groups around the fused ring structures in Figure 3 is arbitrary. Each spectral peak actually reflects a group of aromatic isomers. Titan tholin principal peaks are for phenanthrene with two and three alkylation sites; Jupiter tholin I shows as additional principal peaks phenanthrene with four alkylation sites, and chrysene—the four-ringed PAH prominent in some discussions (e.g. Allamandola et al. 1989) of interstellar grains. Conceivably the difference is dose-related, Titan tholin being generated in a continuous flow system, while Jupiter tholin I was reprocessed by the radiation source long after initial formation. Several other tholin samples—including the irradiation products of simulated Uranian and Neptunian atmospheres (Khare et al. 1987), and of C_2H_6/H_2O mixed ices (Khare et al. 1993)—yielded no detectable PAHs.

The PAH concentrations in these solids lie in the range tens to hundreds of parts per million (ppm). Although more quanti-
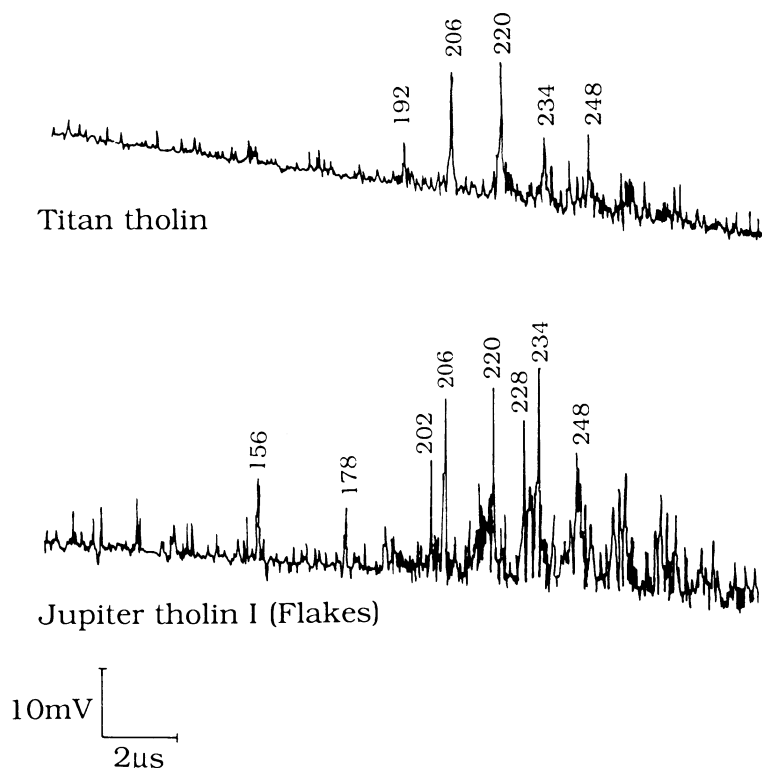

FIG. 2.—Tholin mass spectra. Oscilloscope traces show voltage vs. time. Mass assignments are given in Fig. 3.

Polycyclic Aromatic Hydrocarbons identified in Tholins
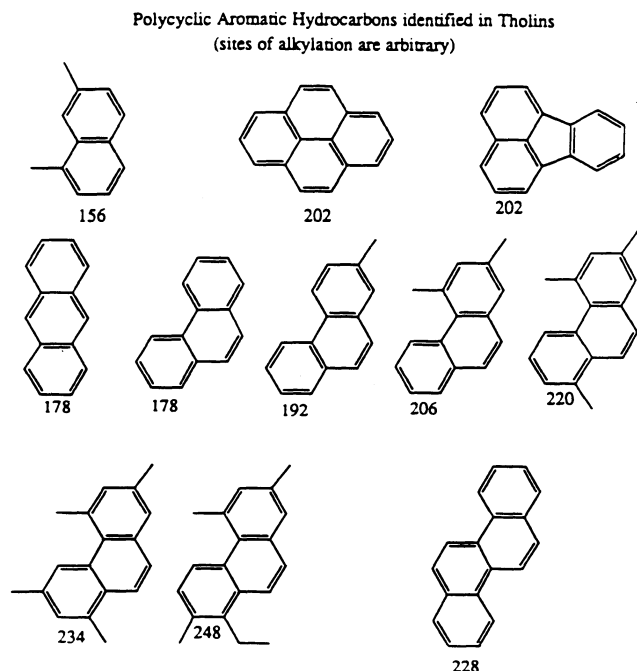(sites of alkylation are arbitrary)

FIG. 3.—Interpretation of major peaks shown in Fig. 2. The exact isomers shown here are arbitrary.

tative results could be obtained by spiking samples with internal standards (Hahn et al. 1988), this was not attempted for two reasons. First, sample material was limited. More importantly, the samples were subjected to various procedures such as dessication prior to analysis, which might be expected to alter the original concentration of these labile compounds in the polymer. Other concerns which limit the precision of this technique include the following: (a) only generic alkyl-substituted rings, not individual isomers, are determined, and specific isomers within each mass category can be expected to have different ionization efficiencies; (b) different sample materials have different desorption efficiencies; (c) some lighter compounds (notably naphthalene) can be partially lost to the high vacuum of the instrument before analysis; and (d) the overall sensitivity of the instrument depends partly on factors such as the cleanliness of the microchannel plates, base pressure, etc., that are sometimes varied between samples. The strength of L²MS lies in its semiquantitative applications, and the technique is envisioned as complementary to currently more exact techniques such as GC/MS. However, in many cases a PAH "fingerprint" can have utility even when the exact structures and concentrations of a sample remain unknown.

No major peaks representing large amounts of nitrogen-containing heterocyclic compounds are observed, even though Jupiter tholin I was synthesized from a mixture containing equal amounts of nitrogen and carbon and Titan tholin from a mixture made mainly of nitrogen. This might be expected, as heterocyclics appear to have a lower ionization efficiency at 266 nm than do aromatic hydrocarbons. For example, in a calibration experiment, we find that a mixture containing equimolar amounts of phenanthrene ($\mu = 178$) and 1,10-phenanthroline ($\mu = 180$) will yield a signal at $\mu = 178$ that is 50 times stronger than that at $\mu = 180$, even though the latter compound is simply phenanthrene with two of the ring carbons replaced by nitrogens. Interestingly, Jupiter tholin I shows

many more minor peaks at odd mass numbers than does Titan tholin, which might be attributed to the presence of nitrogen-containing heterocyclic compounds.

The predominance of alkylated PAHs over their purely aromatic homologs in these samples is consistent with an equivalent thermodynamic temperature of formation of 150° C or less (Blumer 1976). This is in sharp contrast to the PAHs detected by the same technique in C1 and C2 carbonaceous chondrites (Hahn et al. 1988), in which unalkylated naphthalene, phenanthrene, and pyrene are the most abundant PAHs. These latter PAHs are possibly formed in the carbon-rich envelopes of red giant stars (Allamandola et al. 1987; Frenklach & Feigelson 1989; Cherchnoff, Barker, & Tielens 1992) and thus bear no genetic relationship to PAHs formed in comparatively cold planetary atmospheres, although both are thought to be processed through acetylene addition and hydrogen abstraction.

Several percent of available interstellar carbon seems to be tied up in PAHs with four or more rings (Allamandola et al. 1989), and it is these which dominate the interstellar IR spectra. In contrast, if PAHs constitute only $\sim 10^{-4}$ of the organic aerosols of Jupiter and Titan, they would not be expected to dominate the IR spectrum, and the characteristic interstellar emission features attributed to PAHs (e.g., at 3.3, 6.2, 7.7, and 11.3 μm) should be absent, as they are (Sagan, Khare, & Lewis 1985; McDonald et al. 1993).

5. SYNCHRONOUS FLUORESCENCE (SF)

Fluorescence emission of tholins may be due, in part, to the superposition of the fluorescence of many PAHs of different sizes and structures. The methodology used here for enhanced selectivity in luminescence analysis is based on the technique of synchronous excitation. The SF methodology provides a simple way to measure the luminescence signal and spectral fingerprints for rapidly screening complex chemical samples. The principle of SF has been described in detail previously (Vo-Dinh 1978, 1982); only the basic features are summarized here.

Conventional fluorescence spectroscopy uses either a fixed-wavelength excitation (λ_{ex}) to produce an emission spectrum or a fixed wavelength emission (λ_{em}) to record an excitation spectrum. With synchronous spectroscopy, the fluorescence signal is recorded while both λ_{em} and λ_{ex} are simultaneously scanned. A constant wavelength interval ($\Delta\lambda$) is maintained between the excitation and the emission monochromators throughout the spectrum. As a result, the intensity of the synchronous signal, I, can be written as a product of two functions as follows:

$$I_s(\lambda_{ex}, \lambda_{em}) = kcE_x(\lambda_{ex})E_M(\lambda_{em}) ,$$

where k is a constant, c is the concentration of the analysate, E_x is the excitation function, and E_M is the emission function.

The basic principle of the SF methodology is illustrated in Figure 4. For a single molecular species the observed intensity I_s is simplified (often to a single peak associated with the 0–0 band), and the bandwidth is narrower than for the conventional emission spectrum. Figure 4a shows the fluorescence excitation and emission spectra of a PAH compound, perylene. In Figure 4b, the synchronous signal of the same sample is given; in this example a 3 nm interval ($\Delta\lambda$) between λ_{em} and λ_{ex} was used. The fluorescence emission spectrum exhibits several bands and remains unchanged when other excitation wavelengths are employed. However, if the synchronous technique is used, only a single emission peak is obtained (Fig. 4b). This band-narrowing effect can significantly reduce spectral overlap
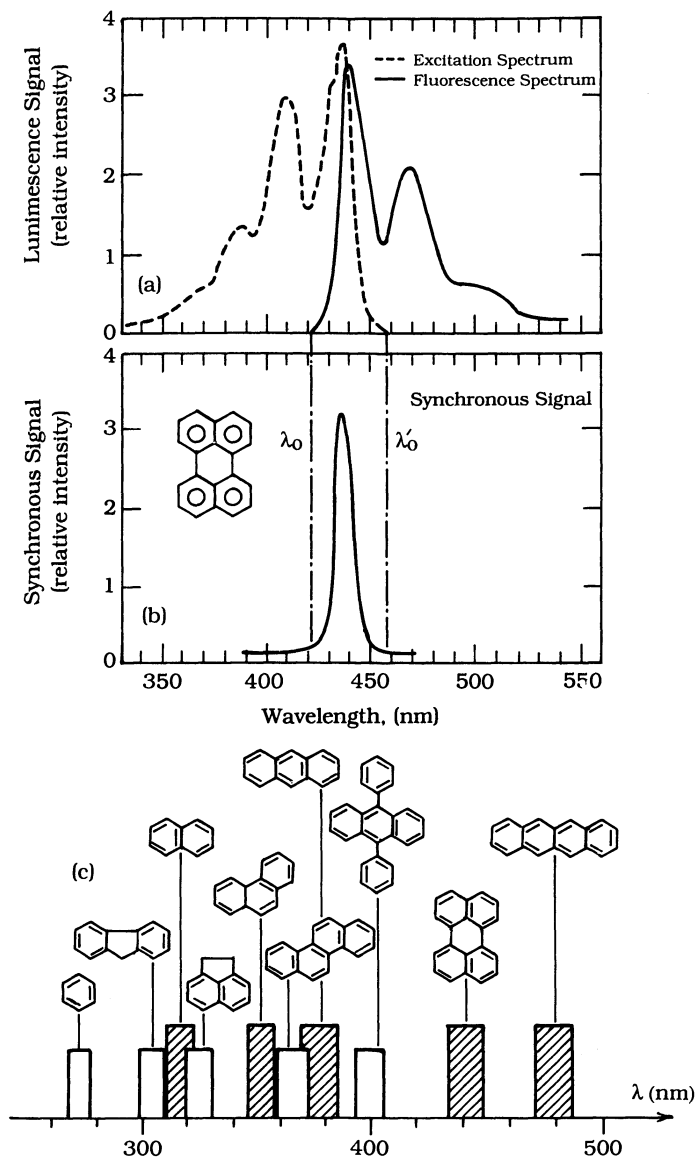
FIG. 4.—Principle of synchronous fluorescence (SF) method: (a) Conventional emission and excitation spectrum, (b) Synchronous fluorescence spectrum, and (c) Wavelength of SF bands for several polyaromatic hydrocarbons.

in multicomponent mixtures. Correlation of the single wavelength position with the structure of the compounds becomes easier. The main relationship between the size of a PAH and its fluorescence spectrum is reflected in the dependence of its 0–0 band energy upon its number of benzenoid rings (Birks 1970). With conventional spectroscopy, this basic rule often cannot be utilized to advantage because of severe spectral overlap from other components in the mixture. By confining each individual spectrum to a narrow and definite spectral band, the synchronous method offers the possibility of identifying specific compounds or a group of compounds in a mixture. Figure 4c schematically shows the approximate SF wavelength positions of several PAHs. We note in passing a rough correlation of the band for perylene with the diffuse interstellar band at 443 nm.

All tholin samples (~ 10 mg) were extracted in cyclohexane in an ultrasonic bath for 1 hr. The samples were then centrifuged and the supernatant analyzed by synchronous fluores-

cence. The instrument used for SF measurement was a Perkin-Elmer (model LS-50B) spectrometer. Standard microcells were used for SF measurement of the liquid sample.

6. RESULTS OF SF ANALYSIS

Figure 5 depicts the SF spectra ($\Delta \lambda = 10$ nm) of Titan and Jupiter I tholins. Fluorescence measurements of tholins provide important confirmation of the presence of PAHs, which are known to be strongly fluorescent (Birks 1970; Vo-Dinh 1989). Examination of the intensity distribution of the SF profiles provides several conclusions. As a general rule, the larger the number of rings an aromatic compound contains, the longer the wavelength at which its fluorescence emission occurs (see Fig. 4c). Synchronous fluorescence bands below the 300 nm region (in Fig. 5) indicate the presence of monocyclic PAHs. SF bands in the 300–340 nm region indicate the presence of PAH compounds containing two benzene rings. Except for anthracene which exhibits an SF band at $\simeq 840$ nm, most three- and four-ring PAHs have SF bands at 340–380 nm. SF bands occurring above 380 nm reflect the presence of PAHs having four or more aromatic rings. The SF peak of the Jupiter I tholin spectrum (Fig. 5, *dashed curve*) occurs at wavelengths longer than that for Titan tholin. Figure 5 indicates that the Titan sample (*solid curve*) has a relatively higher content of one- and two-ring PAHs than does the Jupiter sample. It is noteworthy that the Titan tholin investigated in this study has a strong peak at 320–340 nm, indicative of naphthalene and related alkyl derivatives. Although it is possible to identify certain methylated naphthalenes based on their SF characteristic peaks, the broad freatures of the peaks at 320–340 nm indicate that the tholins contain a mixture of many alkylated naphthalenes. The strong peaks at 330–380 nm confirm the general character of our L^{2}MS results. The SF spectrum of the Jupiter I tholin (Fig. 5, *dashed curve*) shows relatively strong bands in the spectral region above 380 nm,
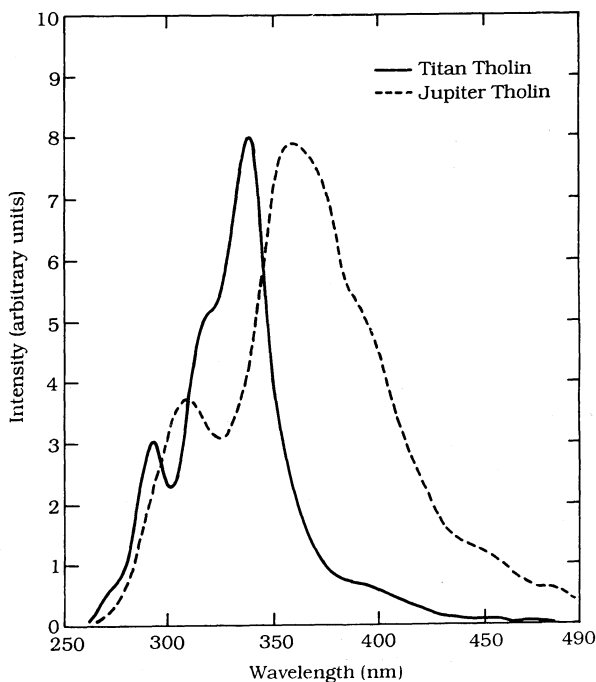

FIG. 5.—Synchronous fluorescence spectra of Titan (*solid curve*) and Jupiter I (*dashed curve*) tholins.

indicating more large PAHs (more than four rings) in the Jupiter I than in the Titan tholins. This result, again, might be expected because of the higher doses employed in synthesizing Jupiter I tholin (continuous irradiation, closed reaction vessel) than Titan tholin (brief radiation exposure in a continuous flow system).

We performed SL calibration measurements with several alkylated naphthalenes, notably 1-methyl and 2-methyl naphthalenes, and observed a slight spectral shift (5–10 nm) with respect to the SL peak of unsubstituted naphthalene at about 320 nm. Ethyl substitution provides similar results. Since there are a very large number of possible combinations for a higher number of alkylation sites, we did not attempt to measure them all. The broad-band nature of the SL peaks indicates that there are several alkylation sites, leading to several overlapping peaks which contribute to the broad peak at 320–340 nm. Our assignment of alkylated naphthalene is also consistent with the fact that, theoretically, alkylation is not expected to affect the electronic energies of PAHs significantly. Only the benzenoid-ring size of the PAH is an important factor in the first excited singlet level, which determines the position of the SL peak.

7. HIGHER MASS PAHs?

We have attempted to gain additional information on the nature of aromatic structures in tholins by analysis of solid-state ^{13}C nuclear magnetic resonance (NMR) spectra. Both Jupiter I and Titan tholins exhibit resonances consistent with aromatic and/or alkene carbons in ^{13}C NMR spectra (P. Hatcher, private communication). The unsaturated ^{13}C resonance accounts for approximately 25% of the total carbon signal in both cases. Due to the overlap in the chemical shifts of olefinic (double-bonded) and aromatic carbons, however, determining the true aromatic contribution to this resonance requires additional information, currently unavailable. The C:H ratios of Titan and Jupiter I tholins are, respectively, 0.62 and 0.78 (Sagan, Khare, & Lewis 1985), but this is consistent with conjugated alkenes as well as aromatic rings.

Aromatic molecules show strong infrared absorbances in the 690–860 cm^{-1} region, while molecules containing olefinic carbons show equally strong absorbances in the 1600–1650 cm^{-1} region (Pasto & Johnson 1969). The ratio of maximum absorbance in the 690–860 cm^{-1} region to that in the 1600–1650 cm^{-1} region is about 1:3 for both Titan (Khare et al. 1984) and Jupiter I tholins (see Sagan & Khare 1979; McDonald et al. 1991). This indicates that aromatic carbons are no more than 25% of the multiple-bonded carbons in both samples—i.e., 25% of the unsaturated ^{13}C NMR signal—giving an upper limit of around 6% for the total fraction of tholin carbons present in aromatic ring structures. Since two- to four-ring PAHs are present in both tholins in the 100 ppm range, the remainder of the aromatic carbons must be present in substituted benzene derivatives, in PAHs with more than four rings, in aromatic polymers, or in other molecules (including nitrogen heterocycles) that are not efficiently ionized by L^{2}MS or detected by SF. These IR and NMR data are consistent with results of the L^{2}MS and SF analyses, but do not directly confirm the presence of PAHs in tholins. We note that in modern absolute reaction rate kinetics experiments (Cherchnoff et al. 1992) the highest PAH yields for a "very favorable" stellar environment are less than 10^{-4}—more than two orders of magnitude below the abundances deduced for the interstellar grains. This is comparable to the two- to four-ring PAH yields of the present experiments and is possibly much less than the total PAH yield. (Of course, our experiments were not performed under simulated circumstellar conditions.) The fraction of PAHs in a given interstellar grain may increase with time, owing to a natural selection for radiation tolerance (Sagan 1972; Sagan & Khare 1979).

8. PAHs IN TITAN'S DETACHED LIMB HAZE?

In the laboratory, as intermediate-sized molecules such as PAHs are produced simultaneously with tholin, some fraction of them is adsorbed into the tholin matrix. Although they are insufficiently abundant and/or volatile to be detected as gas-phase products in simulation experiments (e.g., Thompson et al. 1991), the presence of PAHs in Titan tholin indicates that such molecules are produced in the gas phase and, at the very low pressures found in Titan's upper stratosphere, will remain in the gas phase. Nearly all gas-phase species will eventually condense at lower altitudes, eventually exceeding their saturation vapor pressures. Sagan & Thompson (1984) investigated the altitudes of condensation for several groups of candidate species, including those found upon pyrolysis of tholin—PAHs and others. Could PAHs, if present in the same mass fraction in Titan's atmosphere as found in Titan tholin, contribute to the thin, high-altitude hazes observed by Voyager (Smith et al. 1981)? If these are condensation hazes, organic molecules with roughly 9–12 C and N atoms seem to be indicated.

The radiative transfer models of Thompson & Sagan (1984) indicated a total stratospheric column density of haze of about 4×10^{-6} g cm^{-2}. This result has been substantiated in more recent work (McKay et al. 1989; Courtin et al. 1991; Samuelson & Mayo 1991). It is about 10% the column density of gas-phase nitriles (Sagan & Thompson 1984, Table V). Since some (probably most) of the small (two- to four-ring) PAHs formed in the experiment must be deposited on the walls of the laboratory system, the expected mass function of PAHs in Titan's atmosphere must equal or exceed the 10^{-4} g g^{-1} incorporated into Titan tholin. We would then expect the mass fraction of PAHs in Titan's atmosphere to exceed 10^{-5} of the HCN mass fraction, which is $\sim 2 \times 10^{-7}$ (Sagan & Thompson 1987): that is, greater than 2×10^{-12}, or a mole fraction greater than 1×10^{-14} (for a typical molecular mass ~ 200). Sagan & Thompson (1984) considered the condensation of PAH species such as naphthalene, phenanthrene, anthracene, etc., in Titan's atmosphere. The minimal estimate of 10^{-14} lies between the $\alpha = 0.5$ and $\alpha = 1.0$ cases in their condensation models (see their Figs. 9c, 9d). Their Figure 9c shows that for mole fractions of $\sim 10^{-12}$—possible if our estimates of total aromatic carbon hold—molecules of the same volatility as phenanthrene and anthracene can condense at and above the level of the detached haze. Thus, PAHs could contribute to the detached and higher altitude (EUV-detected) hazes. But is their extinction sufficient to dominate light scattering at these altitudes?

For a mole fraction of 6×10^{-12}, an optimistic estimate of the vertical optical depth τ_v of condensate, using the formula of Sagan & Thompson (1984, p. 147 with $r = 0.01$ μm, $f_c = 1$, $\mu = 178$, $g = 110$ cm s^{-2}, and $\rho = 1$ g cm^{-3}), is $\sim 10^{-4}$, while two- to four-ring PAHs alone would give $\tau_v \sim 10^{-7}$. Rages & Pollack (1983) derive an extinction of about 3×10^{-5} km^{-1} in the region of the detached haze and a thickness of about 30 km (see their Fig. 10b), so the observed τ_v must be $\simeq 10^{-3}$. To produce the required optical thickness at these high altitudes, aromatic species would have to be a major component of the stratosphere, comparable in mass abundance to the tholin

itself. This is not the case for PAHs, which are, in addition, almost certainly excluded in this abundance by the absence of a strong 240–270 nm absorption feature in *IUE* spectra of Titan. Other molecules of volatility similar to PAHs, but present in higher abundance, may better account for the detached haze. The 6% of other aromatics could provide part of this mass, but other possibly abundant species may be important: for example, the nitrogen analogs of the carboxylic acids and their derivatives found in other tholins (McDonald et al. 1991), as well as nitrogen containing rings such as imidazole or the 1-*H*-tetraazole tentatively identified in the gas phase in simulation experiments (Thompson et al. 1991). Alternatively, the detached limb hazes of Titan may have a dynamical explanation (Toon et al. 1992) and may be unrelated to the condensation of high molecular weight organics.

9. CONCLUSION

Small polycyclic aromatic hydrocarbons are anticipated in the atmospheres of Titan, Jupiter, and other Jovian planets, generated by C_2H_2 polymerization, and related to processes thought to account for interstellar PAHs. The net PAH yield seems to be greater, perhaps significantly greater, than the most favorable cases known in C-rich circumstellar envelopes. Benzene and PAHs might profitably be looked for with *Galileo*, *Huygens*, and other entry probes into the atmospheres of bodies in the outer solar system. PAHs in Uranus and Neptune may be produced not only from direct atmospheric irradiation, but also from photochemical and radiochemical processes in acetylene ice. Whether larger abundances of PAHs with 5–20 rings, as proposed for the interstellar medium, exist in Titan and the Jovian planets is unknown; the issue may be dose-dependent.

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