PHOSPHINE IN JUPITER'S ATMOSPHERE: THE EVIDENCE FROM HIGH-ALTITUDE OBSERVATIONS AT 5 MICROMETERS

HAROLD P. LARSON, RICHARD R. TREFFERS, AND UWE FINK
Lunar and Planetary Laboratory, University of Arizona
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ABSTRACT

The presence of PH_3 in Jupiter's atmosphere is confirmed with new spectroscopic observations at 5 μm recorded from the Kuiper Airborne Observatory. The mixing ratio $[P]/[H_2]$ estimated from these observations is consistent with the solar value of 6×10^{-7}. The availability of abundant phosphorus throughout the spectroscopically accessible regions of Jupiter's atmosphere has important implications for the production of chromophores in the cloud layers and the observed low abundance of water vapor.

Subject headings: planets: abundances — planets: Jupiter — planets: spectra

I. INTRODUCTION

We have been engaged in a program of spectroscopic observations of Jupiter at 5 μm from the Kuiper Airborne Observatory since late 1974. Our first spectrum at moderate resolution led to the detection of H_2O vapor on Jupiter (Larson *et al.* 1975). This spectrum contained additional absorptions that because of the limited spectral resolution could not be convincingly assigned to other trace atmospheric constituents. We therefore observed Jupiter again from the Kuiper Airborne Observatory in 1975 December, achieving nearly 5 times the spectral resolution of our previous results. This new spectrum revealed much more clearly the spectroscopic character of the unknown Jovian absorbers. This paper reports the first results of the analysis of these latest observations: the identification of phosphine (PH_3). Phosphine has absorption bands in the observable regions of Jupiter's spectrum at 5 μm and also at 10 μm. Ridgway (1974) first reported evidence for phosphine from his ground-based observations at 10 μm. Subsequent analysis (Ridgway, Wallace, and Smith 1976) continued to support this identification, but the authors emphasized the need for independent experimental verification of the presence of PH_3. Their detection of PH_3 on Jupiter was quite surprising; and if its presence could be established beyond all reasonable doubt, there follow several important implications for Jupiter's atmospheric chemistry. In this paper we confirm the presence of PH_3 on Jupiter, and in addition we contribute new information on its abundance and distribution as a consequence of the deeper spectroscopic probing of the Jovian atmosphere at 5 μm.

II. OBSERVATIONS

Figure 1 illustrates a severe problem encountered in ground-based spectroscopic observations at 5 μm: obscuration by the terrestrial atmosphere. The terrestrial 5 μm window (Fig. 1, *lower curve*) is defined at long wavelengths by lines of the 6.3 μm H_2O vapor band, and at short wavelengths by the ν_3 fundamental band of CO_2 at 4.3 μm. No portion of this telluric window is free of strong absorptions, and beyond about 5.0 μm this window is practically useless for searching for trace atmospheric constituents on another planet. By contrast, the telluric 5 μm window at aircraft altitudes (Fig. 1, *upper curve*) is dramatically opened, primarily as a consequence of flying above most of the H_2O vapor in our atmosphere. Other telluric absorptions (CO_2, CO, N_2O) are also significantly reduced in strength and may be removed from observational data by the ratio spectrum technique. Our detection of many weak lines in Jupiter's high altitude spectrum and their assignment to PH_3 is a direct consequence of the freedom of our spectra from telluric interference.

Our high-resolution airborne spectroscopic observations of Jupiter were made during flights on 1975 December 10, 12, and 13 UT. The manner in which the experiment was conducted was identical to the previous flight program, briefly described in Larson *et al.* (1975). Our airborne Fourier spectrometer is described in detail in Larson and Fink (1975). The performance of the airborne telescope was particularly impressive during our flights. A new digital tracking system kept the planet centered on the spectrometer's aperture even in moderately severe turbulence when the spectrometer itself no longer functioned properly. At the time of our observations the diameter of Jupiter was 41″.4; the spectrometer accepted the central 25″ of this disk. Observations of the Moon at the same air mass as Jupiter provided a record of residual telluric absorptions. These were removed from Jupiter's observed spectrum by the ratio technique. Most of the high-resolution 5 μm spectrum of Jupiter is contained in Figure 2. This spectrum represents the weighted average of all flight data, yielding a signal-to-noise (rms) ratio of about 120. The spectral resolution is 0.5 cm^{-1}; no apodization was applied to the interferograms.
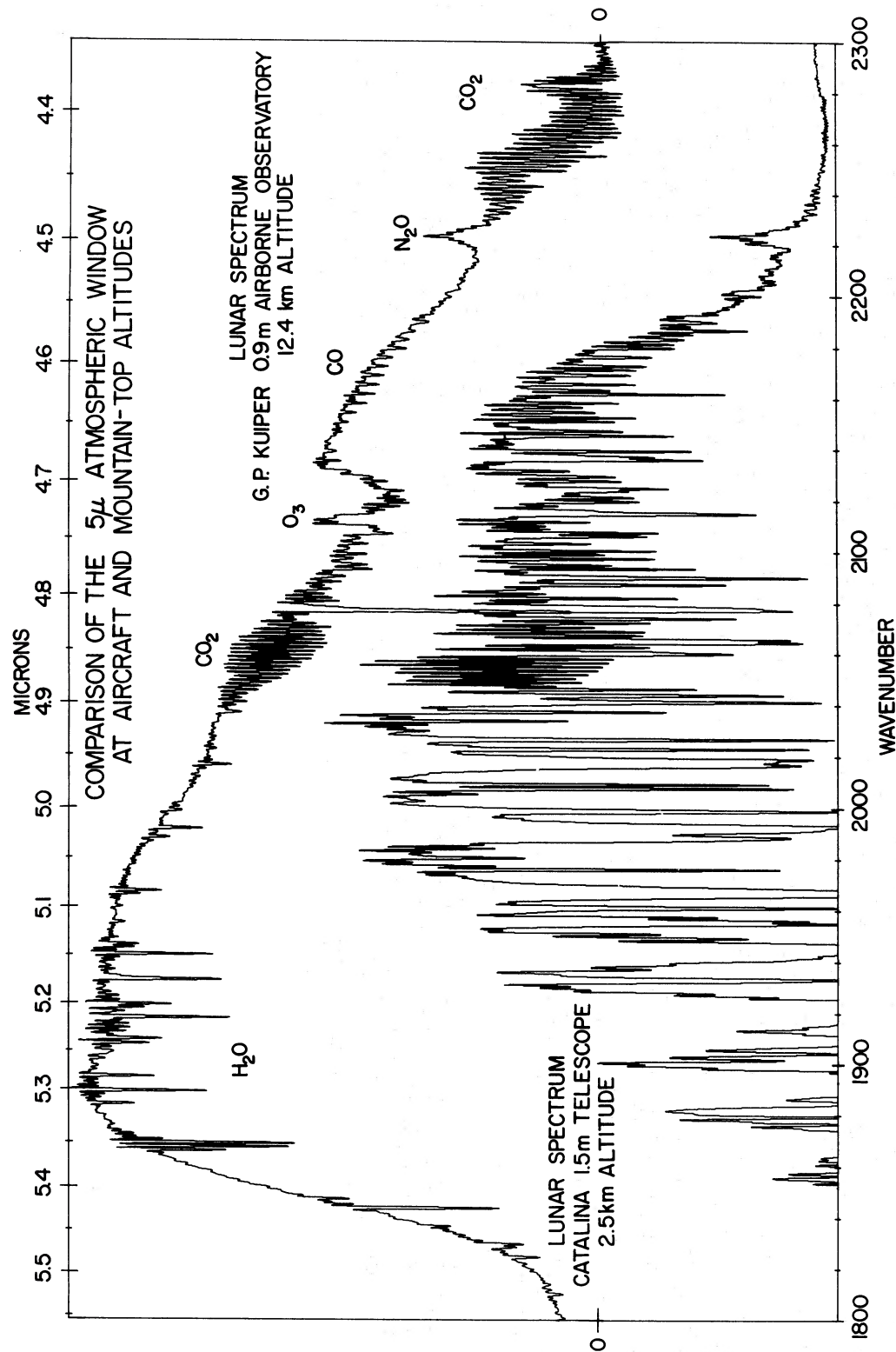
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FIG. 1.—The transmission of the Earth's atmosphere in the 5 μm region is compared at two sites, a mountaintop observatory and an aircraft. The ground-based window is defined at both extremes by telluric absorptions, while the long-wavelength edge of the high-altitude window is limited by the response of InSb detectors. The Jovian 5-μm spectrum is wholly contained within the high-altitude telluric window.

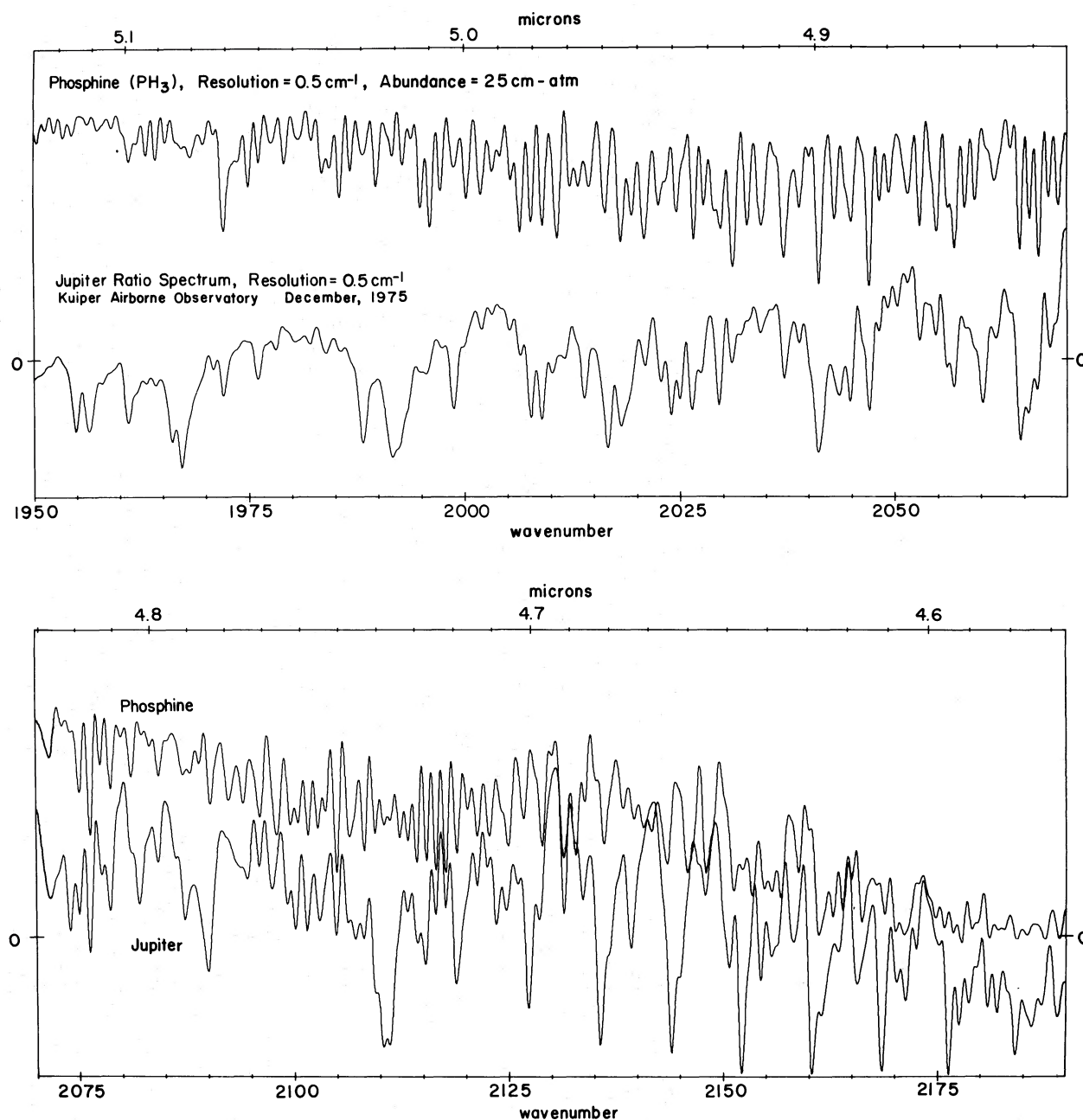COMPARISON OF THE 5μ ATMOSPHERIC WINDOW
AT AIRCRAFT AND MOUNTAIN-TOP ALTITUDES

MICRONS

LUNAR SPECTRUM
G.P. KUIPER 0.9m AIRBORNE OBSERVATORY
12.4 km ALTITUDE

LUNAR SPECTRUM
CATALINA 1.5m TELESCOPE
2.5km ALTITUDE

WAVENUMBER

FIG. 2.—The high-altitude ratio spectrum of Jupiter is compared with a laboratory comparison spectrum of PH_3. Many of the prominent absorptions in the top segment of Jupiter's spectrum are H_2O, while CH_3D dominates the spectrum between 2120 and 2180 cm^{-1}. The prominent Jovian absorption at 2111 cm^{-1} has been tentatively assigned to GeH_4. Phosphine absorptions on Jupiter are most clearly seen near 2075 cm^{-1}.

III. IDENTIFICATION

The PH_3 absorptions contained within Jupiter's 5 μm window belong to two overlapping fundamental bands: ν_1 at 2323 cm^{-1}, and ν_3 at 2328 cm^{-1} (McKean and Schutz 1956). The Q-branches themselves cannot be seen on Jupiter's spectrum as they lie in regions of totally saturated Jovian CH_4 absorptions. Lines of

the P-branches of each of these two bands do, however, extend into the Jovian 5 μm atmospheric window. These bands have not yet been analyzed so we could not numerically synthesize the spectrum of PH_3 for comparison with the observational data. Rather, we adopted an empirical approach in which laboratory absorption spectra of PH_3 were recorded with the same spectrometer that was used in the astronomical

observations. This provided an exact match of instrumental line shape and ensured that all lines of PH_3 were reproduced without error. A disadvantage of this approach is that laboratory comparison spectra of PH_3 represent simple absorption at ambient laboratory temperatures and pressures. These conditions may not closely simulate the pressure and temperature of the Jovian atmosphere, nor do these spectra represent the radiative transfer process characterizing the spectral line-forming region of Jupiter's atmosphere at 5 μm. With these laboratory comparison spectra we can estimate the column density and distribution of PH_3 on Jupiter, but a more precise analysis will first require understanding the spectrum of PH_3 itself as input to more complex modeling of the PH_3 in Jupiter's atmosphere.

Figure 2 compares Jupiter's high-resolution ratio spectrum with a laboratory spectrum of PH_3. More than 100 PH_3 lines are evident in this comparison spectrum, many of which are themselves blended. The spacing and relative intensities of the PH_3 lines do not provide any particularly obvious groupings of lines to aid the eye. The Jovian spectrum is also quite complex. Between 2120 and 2190 cm^{-1} strong CH_3D lines dominate the spectrum, while from 1950 to 2050 cm^{-1} many strong Jovian H_2O lines are evident. Only in the rather narrow region 2050–2120 cm^{-1} is the Jovian spectrum reasonably free of such strong absorptions, permitting weaker absorptions of other atmospheric constituents to become more obvious.

It is in this region that the agreement between the spectra of PH_3 and Jupiter is rather obvious. In particular, unassigned lines between 2075 and 2080 cm^{-1} in the Jovian spectrum very closely match those in the PH_3 spectrum. Other suggestive coincidences of Jovian lines with PH_3 lines, such as in the 2100–2125 cm^{-1} region, can also be seen. We have examined the laboratory comparison spectra of numerous other gases (hydrides, simple hydrocarbons), but none of these provided a match with any of these unassigned Jovian absorptions.

While the eye can scan effectively for local groups of lines common to both spectra in Figure 2, visual comparison alone cannot provide a totally convincing identification of PH_3 on Jupiter. We have employed correlation analysis to provide an independent and objective measure of the degree to which PH_3 fits the Jovian spectrum. This method makes use of all of the positional information contained in the comparison spectrum. The technique was applied to our spectra in the following manner. The phosphine spectrum was first shifted by some amount σ_s, usually 10–25 cm^{-1}, relative to the Jovian spectrum. The data sets were multiplied together point by point and the products integrated, returning a single output point for the displacement σ_s. The shift of the phosphine spectrum was then decremented by $\Delta\sigma$ to generate a second output point. This process was repeated until the comparison spectrum had been shifted a total of $2\sigma_s$. The resulting collection of output points is called
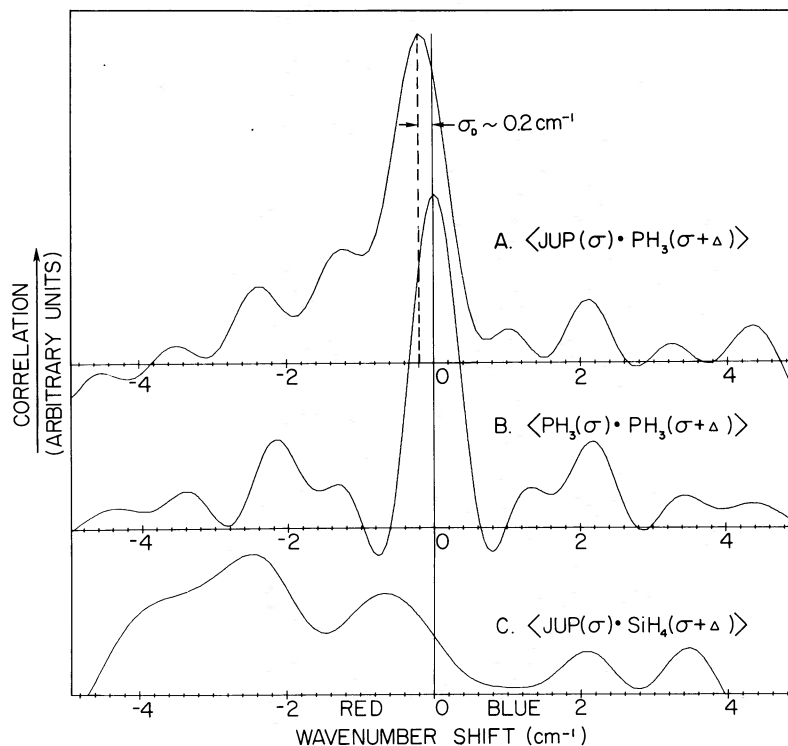

FIG. 3.—The presence of PH_3 on Jupiter is confirmed with the Doppler-shifted extremum (*top curve*) produced in the cross-correlation of Jupiter's spectrum with a laboratory comparison spectrum of PH_3.

the correlogram. If a pattern is common to both data sets, the correlogram will exhibit an extremum at the relative displacement where the coincidence was found. If PH_3 exists on Jupiter, the cross-correlation of the data in Figure 2 should produce an extremum at σ_D, where σ_D is the Doppler shift of the planetary lines. Jupiter was receding from the Earth at the time of our observations; therefore, absorption lines formed in its atmosphere should be shifted by 0.18 cm^{-1} to longer wavelengths compared to laboratory data.

The results are contained in Figure 3. The correlation of PH_3 with itself (Fig. 3, *center curve*) defines the general character of the correlograms produced in this application. The extremum at zero wavenumber shift is, of course, expected in the autocorrelogram, while the secondary maxima represent lesser degrees of correlation as a consequence of semiperiodic structure in the PH_3 spectrum. These secondary features are actually additional signatures of the PH_3 molecule. The correlogram at the top of Figure 3 is the cross-correlation of the spectra of Jupiter and PH_3 contained in Figure 2. It is important to note that this correlogram actually peaks at a wavenumber shift of about 0.2 cm^{-1}, the red Doppler shift expected for PH_3 lines formed in the Jovian atmosphere. This demonstrates quite convincingly the presence of PH_3 on Jupiter. There is even good agreement between the secondary structure in these two correlograms, further strengthening the identification of PH_3 on Jupiter. The differences that do exist are due to the presence of

other strong Jovian absorptions such as CH_3D and H_2O which add other structure to the cross-correlation.

As an additional illustration of the spectrum correlation technique we have included in Figure 3 the correlation of Jupiter's spectrum with another gas, silane (SiH_4), that has frequently been sought in Jupiter's atmosphere. The spectrum of SiH_4 is very similar to that of PH_3 in terms of complexity and density of lines, and it occurs in the same region of Jupiter's spectrum. Visual comparison of the spectra shows no indication of this gas on Jupiter, and the absence of any positive correlation in Figure 3 (*lower curve*) confirms the absence of this gas in Jupiter's atmosphere. From these data we find that the mixing ratio $[Si]/[H_2]$ is less than 10^{-5} of its solar value of 6.3×10^{-5} (Cameron 1973). This is consistent with thermochemical calculations (Greenspan and Owen 1967, Lewis 1969) that predict no volatile silicon compounds in Jupiter's atmosphere. A complete description of upper limits to numerous other gases based upon the observational data in Figure 2 is in preparation as a separate publication.

Our identification of PH_3 in Jupiter's 5 μm spectrum explains an unidentified feature reported in all previous studies of Jupiter in this spectral region. This feature is most pronounced at reduced spectral resolution. Figure 4 compares the spectrum of PH_3 with our spectrum of Jupiter recorded from the Kuiper Airborne Observatory in 1974 October, at a spectral resolution of 2.5 cm^{-1}. Of particular interest in this comparison
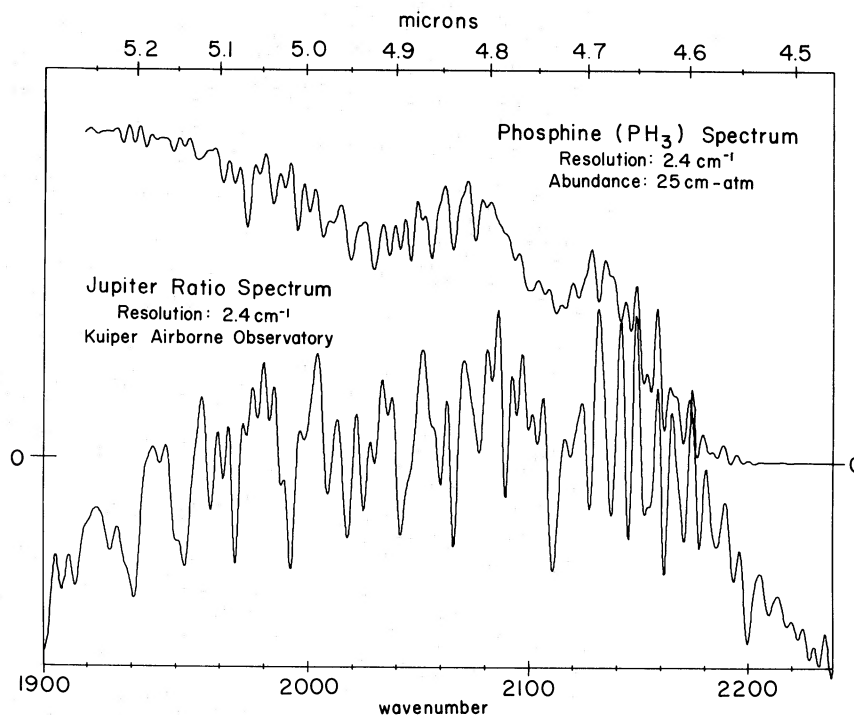

FIG. 4.—These spectra are similar to those in Fig. 2, but presented at lower spectral resolution to demonstrate that the superposition of many unresolved PH_3 lines accounts for the broad absorption in Jupiter's spectrum at 4.73 μm. As discussed in the text, the relative intensities of the PH_3 lines become progressively too strong on either side of the 4.73 μm feature, producing other features such as the shallow depression at 4.9 μm that should not be present in Jupiter's spectrum.

is the broad depression common to both spectra between 2080 and 2130 cm^{-1}. This broad absorption, centered at 4.73 μm, was first seen in the low-resolution spectroscopic observations of Jupiter at 5 μm by Münch and Neugebauer (1971). They proposed a variety of gases and solids to explain this feature, but at their limited resolution they could not distinguish between the various possibilities. Beer and Taylor (1973) also noted this same feature in their high-resolution observations. They proposed various solid species, especially those containing the CN group, but they could not provide a unique identification either. Phosphine apparently was never seriously considered, probably because the most obvious features of its spectrum, the Q-branches, are not contained within the Jovian 5 μm atmospheric window. It is now evident, however, that this broad Jovian absorption at 4.73 μm is the result of the superposition of many weak unresolved lines in the P-branches of the ν_1 and ν_3 PH$_3$ bands. This explanation of the 4.73 μm absorption constitutes an important new observational constraint on the presence of certain other compounds on Jupiter, such as those proposed by Beer and Taylor containing CN, that can be linked to organic processes in Jupiter's atmosphere.

IV. ABUNDANCE AND DISTRIBUTION

The spectrum of PH$_3$ in Figures 2 and 4 represents an abundance of 25 cm-atm (1 atm PH$_3$ in a 25 cm tube). This abundance was chosen to match the relative intensities of the PH$_3$ lines in the 2080 cm^{-1} region of Jupiter's spectrum (see Fig. 2). Also, only abundances near this value, or higher, produced the broad 4.73 μm feature when the spectra are presented at lower resolution (see Fig. 4). While this abundance seems appropriate for the central region of the Jovian 5 μm window, for wavelengths above and below about 4.7 μm the PH$_3$ lines in the laboratory comparison spectrum become progressively stronger than those in Jupiter's spectrum. This is not unexpected behavior since a single abundance of PH$_3$ in a laboratory absorption tube cannot provide an intensity match to Jupiter's spectrum except over a relatively narrow spectral interval. Reasons include unexplored effects of temperature, and, to a lesser degree, pressure, which can alter the intensity distribution for a given abundance of PH$_3$. Also, the opacities of those Jovian atmospheric constituents (CH$_4$, NH$_3$, H$_2$O) defining the 5 μm window are rapidly varying with wavelength, an effect that cannot be simulated experimentally. Finally, the transfer of radiation in a real planetary atmosphere is far more complex than in a laboratory absorption tube. While a model calculation employing spectrum synthesis can simulate these effects, this will not be possible until these particular PH$_3$ bands are analyzed in the laboratory. Since 25 cm-atm of PH$_3$ provided a reasonable intensity match to part of Jupiter's spectrum, we adopt this abundance for a preliminary estimate of the mixing ratio [P]/[H$_2$] on Jupiter. This ratio is approximately 1×10^{-6}, slightly higher than the solar value of 0.6×10^{-6} (Cameron

1973). While this result is provisional, based upon our experience with fitting the intensities of the H$_2$O lines to the Jovian 5 μm spectrum, we do not anticipate any drastic revision of abundances estimated by simpler methods. Thus, a phosphorus mixing ratio on Jupiter close to the solar value of 6×10^{-7} seems reasonable on the basis of available evidence.

Without a model calculation no conclusions can be reached concerning the vertical distribution of PH$_3$ on Jupiter. Since there are no compelling independent arguments that the PH$_3$ should be concentrated in a relatively narrow layer of the Jovian atmosphere, we adopt the simplest picture of a constituent uniformly mixed throughout the spectroscopically observable regions of Jupiter's atmosphere. These conclusions are in agreement with those of Ridgway, Wallace, and Smith (1976) who also found PH$_3$ at about its solar abundance in the upper regions of Jupiter's atmosphere accessible at 10 μm. It is significant that they did not see PH$_3$ in emission which would have indicated a nonuniform distribution.

V. DISCUSSION

These new observations of PH$_3$ on Jupiter bear directly on several important questions concerning the physics and chemistry of Jupiter's atmosphere:

1) What chemical or dynamical mechanism permits spectroscopically detectable amounts of PH$_3$ in Jupiter's atmosphere when thermochemical calculations predict that it not be there?

2) Is the observation of abundant PH$_3$ related to the observed depletion of H$_2$O vapor on Jupiter?

3) Is PH$_3$ involved in the production of chromophores in the Jovian clouds? We expand briefly on each of these points below.

Lewis (1969) made the most comprehensive predictions of the stability and spectroscopic detectability of numerous compounds in Jupiter's atmosphere. He finds PH$_3$ stable deep in Jupiter's atmosphere where the temperatures are above 1000 K, but by 800 K, well below the spectroscopically accessible regions of Jupiter's atmosphere, P$_4$O$_6$ becomes the dominant phosphorus compound. At still lower temperatures other phosphorus oxides are formed, but PH$_3$ itself should not be present above the 500 K level, a depth that is probably just beyond the reach of spectroscopic observations. Thus, to find PH$_3$ in Jupiter's troposphere and stratosphere in amounts consistent with the solar abundance of phosphorus is a significant departure from Lewis's equilibrium model. This suggests that there is some previously unrecognized property of Jupiter's atmosphere having profound influence on its chemical composition.

Two possible explanations have recently been mentioned by Prinn and Lewis (1975). The first assumes rapid vertical convection extending to deep atmospheric levels where PH$_3$ is stable. The time scale is such that little oxidation of the PH$_3$ occurs while it is being transported up to the spectroscopically accessible regions of Jupiter's atmosphere. This mechanism may permit the spectroscopic detection

of other constituents expected only in deeper, hotter atmospheric levels. The presence of CO on Jupiter (Beer 1975) can be interpreted in this way, but the stability of oxides under equilibrium conditions in Jupiter's reducing atmosphere must first be critically reexamined before the CO molecule can be used to explain the presence of other unexpected species.

The second explanation offered by Prinn and Lewis for the observed presence of PH_3 on Jupiter requires a depletion of the Jovian H_2O vapor abundance. This would remove the principal oxidizing agent in the conversion of PH_3 to other compounds, thus leaving PH_3 stable in the upper regions of Jupiter's atmosphere. There is some observational evidence in support of this mechanism. The detection of H_2O vapor in Jupiter's atmosphere by Larson *et al.* (1975) was combined with a surprisingly low abundance, about 10^{-3} the amount expected on the basis of the solar abundance of oxygen. The critical question raised by this result was whether it represented a true oxygen deficiency in Jupiter's interior, or just a localized depletion of H_2O vapor in the regions of the hot spots that are the sources of the $5 \mu m$ flux. Additional information on this question will be available when improved pressure and temperature measurements are derived from the Jovian H_2O vapor spectral line profiles in our most recent high-resolution observations. This physical modeling of Jupiter's atmosphere is not the only way to approach the H_2O vapor abundance problem, however. Sinks for the missing oxygen can be identified through chemical models based upon the observed abundances of Jupiter's atmospheric constituents and, often, through upper limits to some key molecules. In fact, our demonstration in Figure 3 of the absence of SiH_4 on Jupiter identifies just such a chemical sink of oxygen. Silicon has most likely been removed from the upper atmosphere through the formation of quartz (SiO_2). The high solar abundance of Si means that approximately 10% of the oxygen in Jupiter's upper atmosphere has been removed, assuming an initial solar abundance. This small reduction in the H_2O vapor abundance due to SiO_2 formation is probably not sufficient by itself to limit the oxidation of PH_3. Since the solar abundance of P is approximately 10^{-2} that of Si, there would still be a large excess of H_2O vapor compared to PH_3. If, on the other hand, there were a modest oxygen deficiency on Jupiter to begin with, say 0.1 times the solar value, then the silicon and oxygen abundances would be more nearly equal and the formation of SiO_2 would very effectively deplete the atmosphere of oxygen. This is, of course, only a speculative suggestion, but continuing analysis of Jupiter's $5 \mu m$ spectrum may reveal other constituents compatible only with this picture. The probable detection of germane (GeH_4) on Jupiter (Larson, Fink, and Treffers 1976), for example, provides another clue to Jupiter's atmospheric chemistry.

Since this rapid increase in observational material has not yet been fully evaluated, we will not pursue further the two mechanisms outlined above attempting to explain the presence of PH_3 on Jupiter. We do believe, however, that it would now be unrealistic to assume a solar H_2O vapor abundance in characterizing Jupiter's upper atmosphere.

One of the most intriguing problems in planetary science is the identification of the colored component of the Jovian clouds. Calculations assuming a solar composition and thermochemical equilibrium provide only white condensates (Lewis 1969). An explanation of the various shades of red, yellow, orange, blue, etc., that are visible in the Jovian clouds has long been sought both in inorganic species, particularly phosphorus and sulfur compounds, and in organic compounds. In the organic theories colored compounds are synthesized in the upper atmosphere from the abundant species H_2, CH_4, NH_3, H_2O, etc., in the presence of energy sources such as lightning or solar UV radiation. None of the expected compounds have ever been detected spectroscopically; and since we have just shown that the broad $4.73 \mu m$ absorption on Jupiter is due to PH_3 and not to solid CN-bearing materials, the role of organic constituents as chromophores in Jupiter's atmosphere seems somewhat weaker at the moment. Among theories of inorganic synthesis of colored compounds, the recent theory of Prinn and Lewis (1975) concerning a possible phosphorus cycle now appears especially relevant. Polymorphic forms of phosphorus, which are more numerous than for any other element, can appear white, yellow, red, violet, and even black depending upon the particular conditions under which they are prepared. Prinn and Lewis predict that if PH_3 is transported to stratospheric levels in the Jovian atmosphere, subsequent photochemical destruction by solar UV radiation will precipitate red phosphorus. Their model could not provide enough red coloration to impart an overall red color to the planet, but they did estimate that the presumed rapid vertical transport present in the Red Spot could deliver sufficiently large amounts of PH_3 to account for the characteristic red color of this feature. We therefore suggest that the new observational evidence for abundant PH_3 on Jupiter, combined with the Prinn and Lewis phosphorus cycle, now provides the most consistent explanation yet offered for the chemistry of the Red Spot. The role of phosphorus in the coloration of Jupiter's belts and zones may be negligible, as Prinn and Lewis suggest, but given the large amounts of PH_3 available and the possible production of differently colored polymorphic varieties of phosphorus, the question should still be considered open.

From the above discussion it is evident that PH_3 is an especially significant molecule for use as a tracer in furthering our understanding of many of Jupiter's physical and chemical properties. Its role in Jupiter's atmosphere deserves much additional study before any of the questions posed above can be considered fully answered. These investigations may now be pursued, however, without any uncertainty over the presence of PH_3 itself, and with new estimates of its abundance and distribution.

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U. FINK and H. P. LARSON: Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ   85721

R. R. TREFFERS, NASA–Ames Research Center, MS 235–6, Moffett Field, CA   94035