

# DETECTION OF ARSINE IN SATURN

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## ABSTRACT

We report the detection of arsine ( $\text{AsH}_3$ ) in the atmosphere of Saturn. High-resolution spectra near  $4.7\ \mu\text{m}$  show a strong broad absorption at the position of the  $\nu_3$   $Q$ -branch of  $\text{AsH}_3$  and weaker features where the  $R(1)$  lines of the  $\nu_1$  and  $\nu_3$  bands occur. Comparison with synthetic spectra derived from a model atmosphere shows that (a) both the thermal emission and the reflected solar radiation contribute to Saturn's  $5\ \mu\text{m}$  flux; (b) the mole fraction of arsine is  $2.4^{+1.4}_{-1.2} \times 10^{-9}$  in the  $\sim 4$  bar region ( $T \sim 200$  K) from which the thermal emission originates; (c)  $\text{AsH}_3$  is 2.5–10 times less abundant in the upper troposphere (0.2–0.4 bar), a possible consequence of UV photolysis. The present observation of arsine implies upward transport from the  $\sim 360$  K region that is sufficiently rapid to inhibit conversion reactions. From a reanalysis of  $5\ \mu\text{m}$  spectroscopic observations of Jupiter by Bjoraker, Larson, and Kunde in 1986, we conclude that arsine is much less abundant on Jupiter ( $\text{AsH}_3/\text{H}_2 \lesssim 3 \times 10^{-10}$ ) than on Saturn.

*Subject headings:* infrared: spectra — line identifications — planets: abundances — planets: atmospheres — planets: Saturn — planets: spectra

## I. INTRODUCTION

Among the various gases detected in the atmospheres of Jupiter and Saturn, some—such as phosphine ( $\text{PH}_3$ ) and germane ( $\text{GeH}_4$ )—are not in local chemical equilibrium but originate from deeper hot atmospheric levels where they are stable. Their presence is attributed to upward vertical transport which is faster than the chemical reactions destroying them. These nonequilibrium species can be regarded as probes of the deep atmosphere and provide information on the vertical mixing rates in the convective interior. (Prinn and Barshay 1977; Lewis and Fegley 1984; Fegley and Prinn 1985). From extensive calculations of the thermochemistry of Jupiter and Saturn, Fegley and Lewis (1979) and Fegley and Prinn (1985) proposed a list of disequilibrium species with potentially observable abundances, on which figures arsine ( $\text{AsH}_3$ ). This diagnostic molecule is particularly attractive because it possesses a strong fundamental mode ( $\nu_3$ ) optimally placed in the so-called  $5\ \mu\text{m}$  window, as outlined by Treffers *et al.* (1978). The low gaseous opacity prevailing at  $5\ \mu\text{m}$  offers the opportunity of probing pressure levels of several bars, traversing long path lengths and thus permitting the detection of trace constituents in the atmospheres of the giant planets. In this paper we report the detection of  $\text{AsH}_3$  in Saturn's atmosphere from high-resolution observations near  $4.7\ \mu\text{m}$ .

## II. OBSERVATIONS

The observations of Saturn were obtained on 1987 April 9–12 at the Canada-France-Hawaii 3.6 m telescope on Mauna Kea using the Fourier transform spectrometer. Spectra cover the  $2090\text{--}2170\ \text{cm}^{-1}$  ( $4.6\text{--}4.8\ \mu\text{m}$ ) range at an unapodized resolution of  $0.10\ \text{cm}^{-1}$ . Ten separate scans were recorded with a  $5''$  aperture centered on Saturn's disk for a total integration time of  $\sim 3$  hr. Saturn's sub-Earth latitude was then  $32^\circ\text{N}$ , and

the field of view encompassed  $\sim 15\text{--}50^\circ\text{N}$  latitude. Individual spectra were first divided by spectra of  $\alpha$  Lyr recorded during the same night at a similar zenith angle, and then co-added. The  $\alpha$  Lyr spectra also provided an absolute intensity calibration accurate to  $\pm 20\%$  (Drossart *et al.* 1987). The final spectrum shown in Figure 1a has a peak signal-to-noise ratio of  $\sim 12$ .

## III. ANALYSIS

Absorption features due to  $\text{PH}_3$ ,  $\text{CH}_3\text{D}$ , CO, and  $\text{GeH}_4$  are clearly identified in the spectrum of Saturn and are marked in Figure 1b. A preliminary analysis of these data (Bézar *et al.* 1987) has shown that both the thermal emission and the reflected solar radiation contribute to Saturn's  $5\ \mu\text{m}$  spectrum as illustrated in Figure 1. Synthetic spectra for the two components were generated from a line-by-line radiative transfer program which includes the hydrogen collision-induced absorption and molecular lines from the  $2\nu_2$ ,  $\nu_2 + \nu_4$ ,  $2\nu_4$  bands of  $\text{PH}_3$ , the  $\nu_2$  of  $\text{CH}_3\text{D}$ , the 1–0 of CO, and the  $\nu_3$  of  $\text{GeH}_4$ . CO line parameters were obtained from the GEISA spectral line compilation (Husson *et al.* 1986). Line information for  $\text{CH}_3\text{D}$  was taken from Chackerian and Guelachvili (1983). Spectroscopic data for  $\text{PH}_3$  come from the recent analysis of Tarrago *et al.* (1987). P. Lepage (private communication) provided the line positions, energy levels, and relative intensities for the five isotopes of  $\text{GeH}_4$ . We obtained absolute line strengths using the determination of the  $\nu_3$  band intensity for  $^{74}\text{GeH}_4$  by Schaeffer and Lovejoy (1985). The temperature profile employed here is the one derived from *Voyager* ingress radio-occultation data recorded at northern mid-latitudes (Lindal, Sweetnam, and Eshleman 1985). The profile was extrapolated downward of the 1.3 bar level following an adiabatic lapse rate.

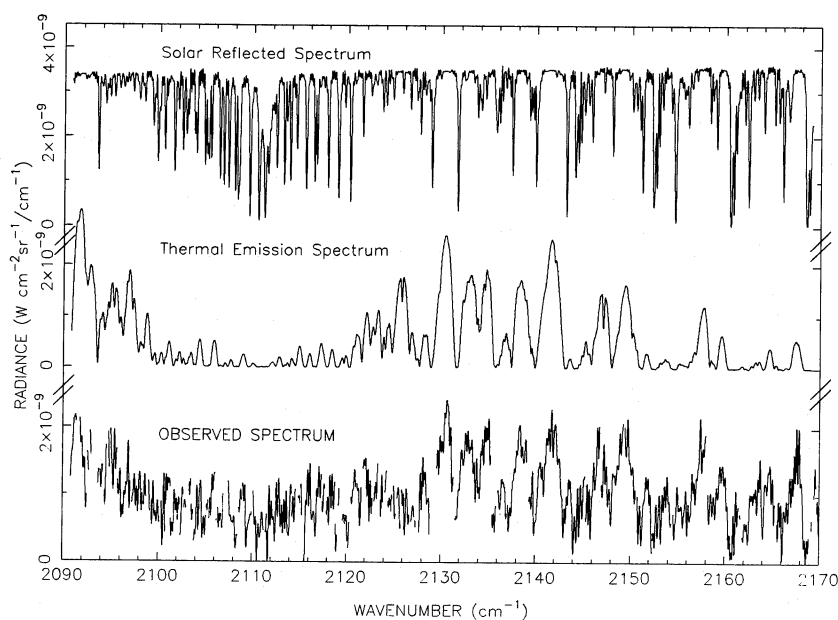


FIG. 1a

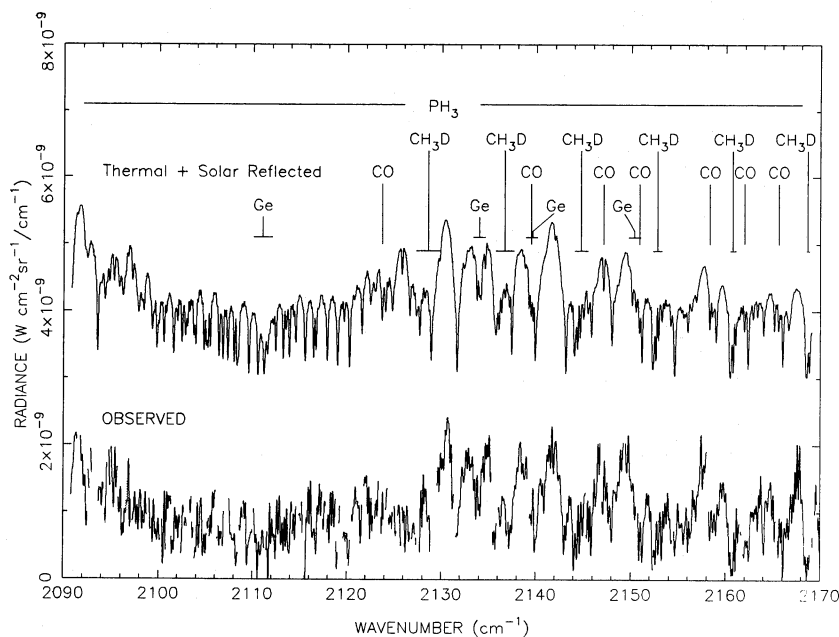


FIG. 1b

FIG. 1.—(a)  $5\ \mu\text{m}$  spectrum of Saturn observed at a resolution of  $0.10\ \text{cm}^{-1}$  (bottom). Only data points corresponding to a relative telluric transmission higher than 0.55 are plotted. A synthetic thermal emission spectrum and a solar reflected spectrum (calculated for a Lambertian reflecting layer located at 0.3 bar) are shown for comparison. The thermal spectrum is generated with  $\text{CH}_3\text{D}/\text{H}_2 = 3.2 \times 10^{-7}$ ,  $\text{CO}/\text{H}_2 = 1.6 \times 10^{-9}$ ,  $\text{GeH}_4/\text{H}_2 = 5 \times 10^{-10}$ , and  $\text{PH}_3/\text{H}_2 = 4.5 \times 10^{-6}$ .  $\text{GeH}_4$  and  $\text{PH}_3$  mixing ratios, respectively, 2 and 4 times lower are used in the computation of the reflected spectrum. (b) Observations are compared with a synthetic spectrum mixing the two components. For clarity, the latter has been shifted by  $3 \times 10^{-9}\ \text{W cm}^{-2}\ \text{sr}^{-1}\ \text{cm}^{-1}$ . The reflecting layer has a I/F reflectivity of 0.30 and a transmittance  $T_H = 0.50$ . Absorption features resulting from  $\text{CH}_3\text{D}$ , CO, and  $\text{GeH}_4$  lines are marked. The other ones are predominantly due to  $\text{PH}_3$  absorption.

The reflection of sunlight by “haze” particles located in the upper troposphere is treated through a reflecting layer model parameterized by its I/F reflectivity and pressure level  $p_H$ . This haze structure is further likely to partly scatter and absorb the thermal emission originating from deeper levels. This effect is simply accounted for by multiplying the computed thermal radiation by an “effective” haze transmittance  $T_H$ . The atmospheric model finally includes an opaque cloud at the expected

position of the  $\text{NH}_4\text{SH}$  cloud deck:  $p = 4.5\ \text{bar}$ ,  $T = 215\ \text{K}$  (Prinn et al. 1984).

The presence of a reflected component in Saturn’s  $5\ \mu\text{m}$  spectrum is particularly evident in the  $2100\text{--}2120\ \text{cm}^{-1}$  region where the Q-branch of the  $\nu_2 + \nu_4$  band of  $\text{PH}_3$  occurs, greatly reducing the thermal flux whereas the observed flux is much less attenuated (Fig. 1a). Matching the observed continuum level between absorption lines yields  $I/F = 0.30 \pm 0.06$  for the

reflecting layer, while fitting the shape of the  $\text{CH}_3\text{D}$  multiplets forces the haze layer to be located between the 0.2 and 0.4 bar pressure levels (Bézard *et al.* 1987). A combination of the thermal emission and solar reflected components permits us to reproduce fairly well the overall shape of the observed spectrum, as shown in Figure 1b. The gaseous abundances used to generate the best-fit spectrum exhibited here are given in the figure caption. A more detailed description of the atmospheric model will be given in a forthcoming paper.

The synthetic spectrum however disagrees with the data around  $2126\text{ cm}^{-1}$ . The discrepancy exceeds 5 times the rms noise level at this wavenumber and remains significant over the  $2122\text{--}2128\text{ cm}^{-1}$  interval (Fig. 2). It cannot be removed by increasing the absorber concentrations without strongly disturbing the fit elsewhere, suggesting the presence of an additional absorber. None of the species already detected in Saturn's atmosphere (including their minor isotopic varieties) possesses a rovibrational  $Q$ -branch able to produce a broad absorption feature in the relevant region. On the other hand, arsine has a fundamental mode ( $\nu_3$ ) at  $2126.4\text{ cm}^{-1}$  close to its  $\nu_1$  mode located at  $2115.2\text{ cm}^{-1}$  (Olson, Maki, and Sams 1975). In order to investigate its possible influence on Saturn's spectrum, we have as a first step computed the transitions involving the two fundamentals  $\nu_1$  and  $\nu_3$  of arsine, from the formulation previously developed by Tarrago and Delaveau (1986) for analyzing interacting bands of  $\text{C}_{3v}$  molecules. The required spectroscopic constants were taken from Olson, Maki, and Sams (1975). Band strengths of  $160$  and  $600\text{ cm}^{-2}\text{ atm}^{-1}$  at  $296\text{ K}$  for the  $\nu_1$  and  $\nu_3$ , respectively, were used to obtain absolute intensities for the individual lines. These values were estimated by comparing a  $0.28\text{ cm}^{-1}$  resolution laboratory spectrum of arsine provided by K.S. Noll and H. P. Larson (private communication) with simulated transmittance spectra (a self-broadening coefficient of  $0.10\text{ cm}^{-1}\text{ atm}^{-1}$  was assumed in the computations). More recently and for a few low- $J$  lines, we checked that the so-estimated intensities lie within 30% of

experimental values determined from a very high resolution laboratory spectrum (W. B. Olson, private communication).

As a second step, we generated spectra for Saturn with various mixing ratios of arsine set independently in the thermal emission and in the solar reflected components. After comparison with the observations, we retained the concentrations which yield minimum variance in the post-fit residuals. The so-inferred  $\text{AsH}_3/\text{H}_2$  ratio is  $2.4^{+1.4}_{-1.2} \times 10^{-9}$  for the thermal component, whereas a lower value,  $3.9^{+2.1}_{-1.3} \times 10^{-10}$ , is derived for the solar reflected spectrum, relevant to higher atmospheric levels. The error bars account for instrumental noise and include a  $\pm 30\%$  uncertainty in the  $\text{AsH}_3$  band strength determinations.

The best-fitting spectrum, shown at the bottom of Figure 2, reproduces fairly well the shape of the observed absorption feature around  $2126\text{ cm}^{-1}$ . The additional opacity brought by  $\text{AsH}_3$  also greatly improves the fit in the vicinity of the  $R(1)$  lines of the  $\nu_1$  and  $\nu_3$  bands, which gives further support to the presence of arsine in Saturn. On the other hand, the  $Q$ -branch of the  $\nu_1$  band has negligible influence on the spectrum because it falls in a region of strong absorption by  $\text{PH}_3$  where the thermal flux is extremely low (see Fig. 1).

#### IV. ARSINE IN JUPITER

The presence of arsine in Saturn being established, it comes natural to wonder whether this molecule can also be found in Jupiter's atmosphere. We then turned to the  $5\text{ }\mu\text{m}$  airborne observations of Jupiter performed by Bjoraker, Larson, and Kunde (1986) at a spectral resolution of  $0.5\text{ cm}^{-1}$ . At first glance, their spectrum does not show direct evidence of absorption by arsine, and a careful analysis of these data including radiative transfer calculations is required.

We have generated synthetic spectra for Jupiter using the same atmospheric model as in Bjoraker, Larson, and Kunde (1986), except for the mole fractions of  $\text{CO}$  ( $1.6 \times 10^{-9}$ ) and  $\text{GeH}_4$  ( $5 \times 10^{-10}$ ) which were taken from recent analyses of

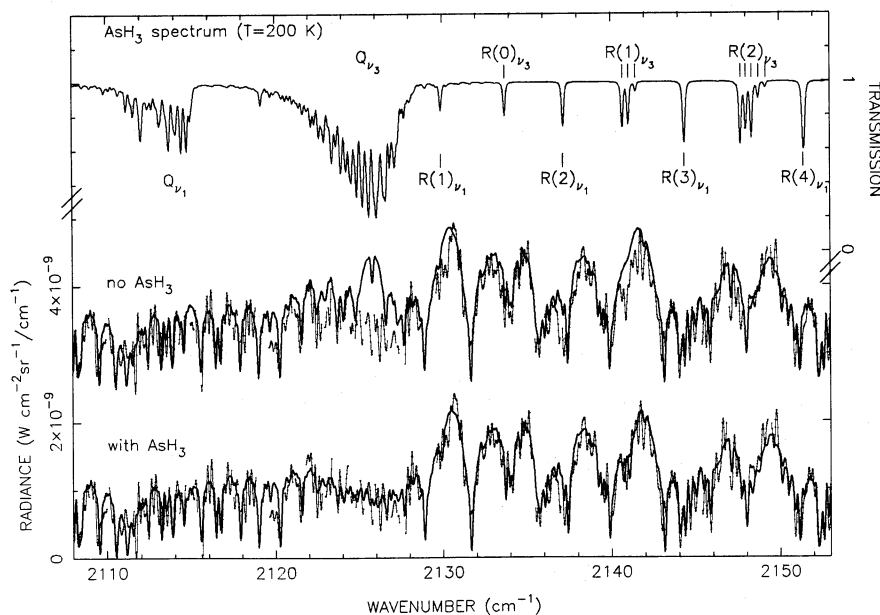


FIG. 2.—Computed absorption spectrum of  $\text{AsH}_3$  (0.02 cm amat at 200 K) at a resolution of  $0.10\text{ cm}^{-1}$  (top). The observed spectrum of Saturn (dotted line) is successively superposed on the synthetic spectrum of Fig. 1b, and on a spectrum in which the  $\text{AsH}_3$  opacity is added.

high-resolution  $5\ \mu\text{m}$  observations by Noll *et al.* (1986, 1988). We have incorporated the improved  $\text{PH}_3$  spectroscopic data from Tarrago *et al.* (1987) that already served in the analysis of Saturn's spectra reported here. In contrast with Saturn, solar flux has a negligible contribution to the  $5\ \mu\text{m}$  flux of Jupiter (Bjoraker *et al.* 1982) and thermal-only spectra were accordingly calculated.

The influence of arsine on Jupiter's spectrum is illustrated in Figure 3, where the planetary data are compared with calculations including three arsine mixing ratios (assumed to be constant with altitude). A mole fraction of  $2.4 \times 10^{-9}$ , which is our preferred value for Saturn's atmosphere, is clearly at odds with Jupiter's spectrum. On the other hand, the addition of a small amount of arsine ( $3 \times 10^{-10}$ ) significantly improves the fit in the vicinity of the  $\nu_3$  Q-branch at  $2126\ \text{cm}^{-1}$ . We believe that these calculations are strongly suggestive of the presence of arsine in Jupiter. However, discrepancies still remain between the calculated and observed spectra (e.g., at  $2142\ \text{cm}^{-1}$ ), the amplitude of which compare with that of the  $\nu_3$  Q-branch absorption feature produced by an  $\text{AsH}_3$  mixing ratio of  $3 \times 10^{-10}$ . Consequently we think that no firm conclusion concerning the identification of  $\text{AsH}_3$  in Jupiter should be drawn until a better reproduction of the  $5\ \mu\text{m}$  spectrum of the planet is achieved. Adopting this philosophy, the reported value of  $3 \times 10^{-10}$  would still represent a reasonable upper limit of the arsine abundance of Jupiter.

#### V. DISCUSSION

The arsine mixing ratio  $2.4^{+1.4}_{-1.2} \times 10^{-9}$  derived for Saturn's atmosphere is far in excess of its equilibrium abundance at the cool atmospheric regions ( $T \sim 200\ \text{K}$ ) probed by the  $5\ \mu\text{m}$  thermal emission. Chemical equilibrium models of the giant planets (Fegley and Lewis 1979; Lewis and Fegley 1984; Fegley and Prinn 1985) predict that arsine, which is the stable As-bearing compound below the  $\sim 360\ \text{K}$  level, is replaced by the trifluoride  $\text{AsF}_3$  at lower temperatures. This conversion inhibits the arsenic precipitation which would otherwise take place at about the same temperature level. The observation of arsine can, however, be interpreted by vertical transport from atmospheric layers where  $T \gtrsim 360\ \text{K}$ , provided that convective

mixing is more rapid than the rates of the interconversion reactions. Quenching from hot levels is similarly invoked to explain the detections of  $\text{PH}_3$  and  $\text{GeH}_4$  in Jupiter and Saturn.

Very recently, the detection of arsine simultaneously reported by us (Bézar *et al.* 1988) and by Noll, Knacke, and Geballe (1988) has motivated a re-examination of the chemistry of As-bearing compounds in the atmospheres of Jupiter and Saturn (Fegley 1988). Preliminary calculations suggest that  $\text{AsH}_3$  destruction is actually kinetically inhibited in both planets. Chemical-dynamical models for Saturn lead to quench temperatures of 1420 and 680 K for the conversion to  $\text{AsF}_3$  and the precipitation into solid  $\text{As}_4$ , respectively, for an eddy diffusion coefficient  $K$  of  $2 \times 10^8\ \text{cm}^2\ \text{s}^{-1}$  estimated from theories for free convection. Slightly higher temperatures are predicted for Jupiter. The relevant atmospheric levels lie well below the 360 K region where  $\text{AsH}_3$  destruction would occur under thermochemical equilibrium conditions. This conclusion remains valid even if much lower values are assumed for  $K$  ( $\sim 10^4\ \text{cm}^2\ \text{s}^{-1}$ ). Gas parcels can then be transported upward to the cooler observable regions while undergoing negligible depletion in arsine, so that the measured mixing ratio should represent the actual arsine abundance at Saturn's deep levels.

Our result corresponds to an elemental ratio  $\text{As}/\text{H} = 1.2^{+0.7}_{-0.6} \times 10^{-9}$ , equal to  $5^{+3.5}_{-2.5}$  times the solar-system abundance based on C1 chondrites (Anders and Grevesse 1989). The enhancement is similar to the one in phosphorus (Bézar *et al.* 1987) and in carbon (Courtin *et al.* 1984) and thus supports previous deductions that Saturn is enriched in "heavy" elements relative to solar abundances (Gautier and Owen 1989). On the other hand, the lower arsine abundance ( $3.9^{+2.1}_{-1.3} \times 10^{-10}$ ) found in the upper troposphere (0.2–0.4 bar) may result from photochemical destruction, as is the case for  $\text{PH}_3$  in Jupiter and Saturn (e.g., Strobel 1977; Kaye and Strobel 1984). We finally found that arsine is definitely less abundant on Jupiter than on Saturn, by at least a factor of  $8^{+5}_{-4}$ . According to thermochemical kinetic calculations, this compositional difference should reflect a real deficiency of the Jovian atmosphere in arsenic, compared to the Saturnian. It is worth noting that the Jupiter/Saturn atmospheric abundance ratio of arsenic seems to be similar to the one in phosphorus ( $\sim 1:7$ )

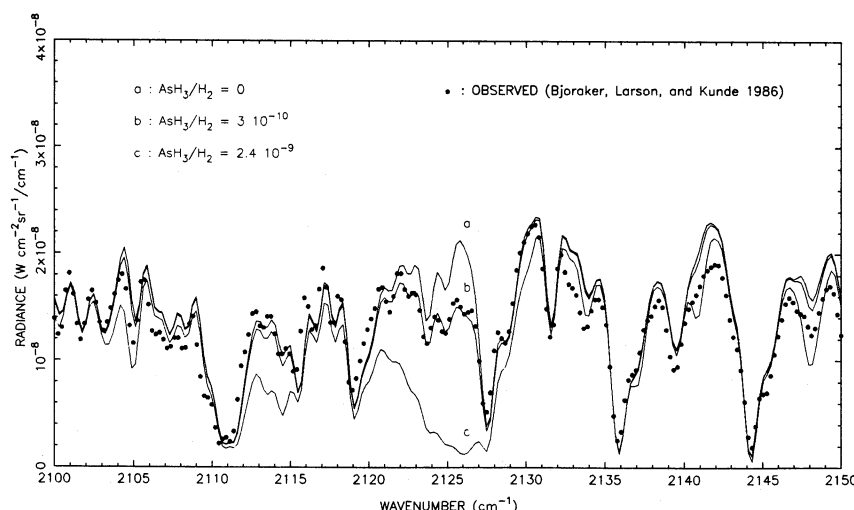


FIG. 3.—Jovian spectrum between 2100 and  $2150\ \text{cm}^{-1}$  at a resolution of  $0.5\ \text{cm}^{-1}$ . Observations (dots) are compared with three synthetic spectra (solid lines) calculated with arsine mixing ratios of 0 (a),  $3 \times 10^{-10}$  (b), and  $2.4 \times 10^{-9}$  (c).



but smaller than that in carbon ( $\sim 1:2$ ), although the large uncertainties involved probably preclude any firm conclusion. If confirmed, this behavior is probably linked to the origin and/or evolution of these atmospheres. Further progress on the topic could be achieved with the detection of new equilibrium or disequilibrium species involving "heavy" elements.

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