The Astrophysical Journal, 338:L71–L74, 1989 March 15

ARSINE IN SATURN AND JUPITER

Keith S. Noll
Lunar and Planetary Laboratory, University of Arizona
T. R. Geballe
Joint Astronomy Center
and
R. F. Knacke
Astronomy Program, State University of New York at Stony Brook
Received 1988 November 16; accepted 1988 December 14

ABSTRACT

We have found a prominent absorption feature in Saturn and Jupiter near 4.7 μm that is coincident with the ν_3 Q-branch of AsH_3. A smaller absorption at the location of the ν_1 Q-branch of AsH_3 is also observed in Saturn. Based on the two spectral coincidences and agreement of the band structure, we conclude that AsH_3 is present in both atmospheres. The mole fractions of AsH_3 are determined to be $q\mathrm{AsH_3} = 1.8^{+1.8}_{-0.9}$ ppb in Saturn and $q\mathrm{AsH_3} = 0.7^{+0.7}_{-0.4}$ ppb in Jupiter, and are probably representative of the As/H ratio in the gaseous envelopes of these planets. Arsenic is significantly enriched over the solar abundance in both planets. Mass-dependent compositional gradients in the atmospheres are ruled out. The ratio of the abundances in the planets, which can be computed without making absolute abundance determinations, suggests that AsH_3 is almost a factor of 2 higher in Saturn than in Jupiter. The observed enrichments are consistent with the core instability model for the formation of the giant planets. Models of arsenic chemistry that predict strong depletions of AsH_3 at temperatures below 370 K are not consistent with the observations, suggesting that vertical convection or perhaps some other mechanism inhibits depletion.

Subject headings: abundances — planets: Jupiter — planets: Saturn

Arsine, AsH_3, is the fully hydrogenated form of arsenic analogous to ammonia, NH_3, and phosphine, PH_3. The ν_1 and ν_3 Q-branches of AsH_3 are located in the 5 μm spectral window at 2115.2 cm^{-1} and 2126.4 cm^{-1} (Yin 1966; Olson, Maki, and Sams 1975). Treffers *et al.* (1978) conducted a search near 5 μm for minor constituents in Jupiter using 0.6 cm^{-1} resolution spectra and reported an upper limit of $q\mathrm{AsH_3} < 4.5$ ppb. In Noll *et al.* (1988*a*) we reported evidence for the ν_1 Q-branch of AsH_3 near 2115 cm^{-1} in a spectrum of Saturn and estimated the abundance to be within an order of magnitude of solar. In this *Letter* we report new spectra of Saturn and Jupiter that show a much stronger, heretofore unidentified absorption near 2126 cm^{-1} in both Jupiter and Saturn that we interpret as unambiguous evidence for the presence of AsH_3. Arsenic is the first new element identified in a planetary atmosphere since germanium was found in Jupiter (as GeH_4) a decade ago.

I. OBSERVATIONS

Spectra of Saturn covering the region of the AsH_3 ν_1 and ν_3 Q-branches were obtained at the United Kingdom Infrared Telescope, UKIRT, on 1987 March 15 and 1988 April 5. We used the UKIRT Cooled Grating Spectrometer (CGS II) with a 0.25 cm^{-1} nominal resolution Fabry-Perot interferometer. Spectra were sampled every 0.10 cm^{-1}. The telescope was pointed at the center of Saturn's visible disk, and IR/visible pointing was checked as needed on a bright star.

Spectra of Jupiter were obtained at UKIRT on 1986 June 21 and 1984 September 9 at a resolution of 0.07 cm^{-1}. All scans were centered on Jupiter's North Equatorial Belt (NEB) and peaked up on the position of maximum intensity. Four scans of Saturn covering different spectral intervals and three of Jupiter have been pieced together and are shown in Figure 1.

Frequency calibration was achieved by observing CO lines from a gas cell. Stellar standards were used for intensity calibration which is accurate to $\pm 20\%$. Signal-to-noise ratios per point of ~ 10 or more for Saturn and ~ 30 for Jupiter were obtained over most portions of the final ratioed spectra.

II. ANALYSIS

The computer models used to produce the synthetic spectra shown in Figure 1 are discussed in detail in previous papers (Noll *et al.* 1988*a*, *b*). The molecular abundances used in our model spectra are summarized in Table 1. One notable change from previous models is the replacement of estimated PH_3 line parameters with new, fully determined line parameters from Tarrago *et al.* (1987). Models with the new PH_3 line list reduce the size of the feature at 2115 cm^{-1} that we identified as the AsH_3 ν_1 Q-branch in Noll *et al.* (1988*a*). Nevertheless, an obvious discrepancy between the model spectrum and the data remains. Most importantly, the accuracy of the new PH_3 line list allows us to exclude with certainty the possibility that a feature as large as the one at 2126 cm^{-1} could be due to PH_3.

Line parameters for AsH_3 are not available on either the GEISA or AFGL molecular line compilations so detailed models cannot be made. Laboratory spectra of AsH_3 were provided by H. P. Larson (1988, private communication) including an unpublished, higher resolution, version of the spectrum presented in Treffers *et al.* (1978), and several new laboratory spectra at lower abundances, which we have used in our analysis.

III. RESULTS

Even without detailed models several useful conclusions can be drawn. First, the locations of the 2126 cm^{-1} features in the

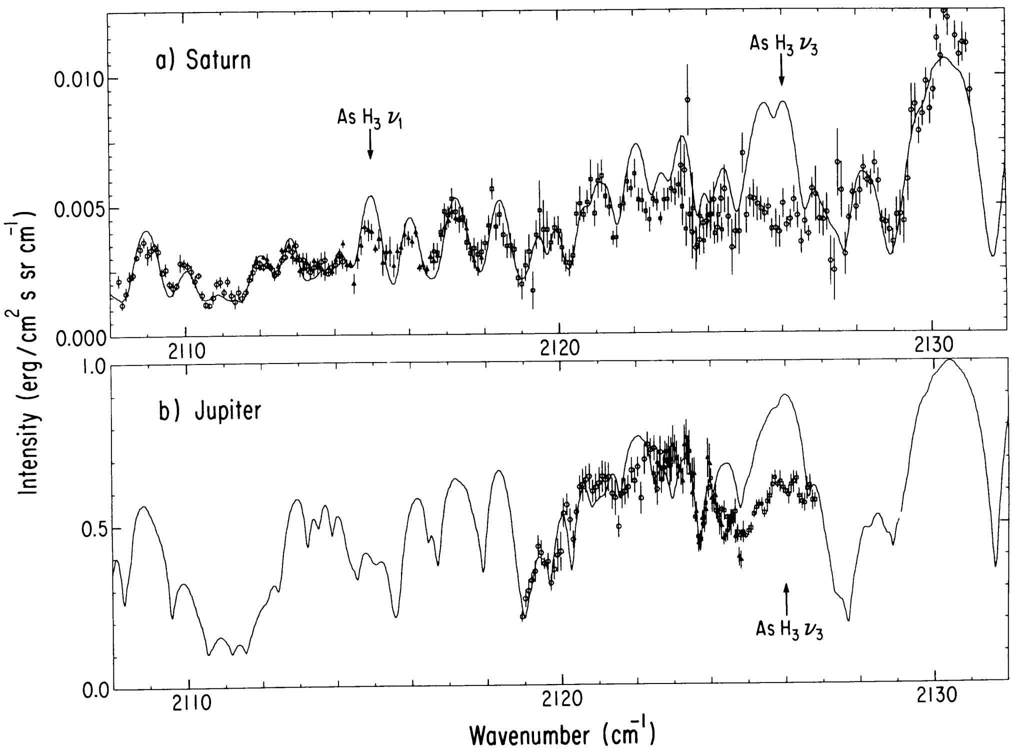

FIG. 1.—Observed and calculated spectra of (*a*) Saturn and (*b*) Jupiter. Observations are denoted by symbols with error bars. There is some overlap between adjacent scans. The calculated model spectra shown by the smooth curves are based on abundances given in Table 1. Note the large discrepancies between the observed and model spectra from 2122 to 2126.6 cm^{-1} and the smaller one near 2115 cm^{-1}, the positions of the AsH_3 *Q*-branches.

spectra of both Saturn and Jupiter and the 2115 cm^{-1} feature in Saturn coincide with the locations of the ν_3 and ν_1 *Q*-branches of AsH_3 ($\nu_1 = 2115.2$ cm^{-1}, $\nu_3 = 2126.4$ cm^{-1}; Yin 1966; Olson, Maki, and Sams 1975). Second, the 2126 cm^{-1} absorption drops off rapidly at higher frequencies, but more gradually at low frequencies. This is a characteristic signature of a molecular *Q*-branch and is apparent in Larson's AsH_3 spectrum. Finally, the FWHM of the 2126 cm^{-1} absorption feature is at least 1.5 cm^{-1} in both objects, with evidence for absorption extending as low as 2122 cm^{-1}. Again, this is characteristic of a group of absorption lines rather than a single line and is further evidence that the absorption is a molecular *Q*-branch.

a) Abundance in Saturn

We estimate the column abundance of AsH_3 in Saturn by comparing the optical depth, τ_S, of the planetary absorption feature to τ_l of the laboratory spectrum over the interval where the data points and model spectrum are clearly separated. After removing the contribution of reflected sunlight, we determine that the average optical depth of the Saturn feature in the interval 2125.1–2126.6 cm^{-1} is $\tau_S \sim 0.69 \pm 0.1$.

The laboratory spectra did not use a broadening gas and do not resolve the many individual lines of the *Q*-branch. Estimates of line strengths indicate that many of the unresolved line cores will be saturated. This will tend to lead to an overestimate of the planetary abundance. Using several laboratory spectra with the greatest weight on the lowest column abundance ($N_l = 0.027$ cm-amagat) to minimize the effects of line saturation, we estimate $N_S = 0.04$ cm-amagat for the ν_3 *Q*-branch, with an uncertainty of a factor of 2.

Following the same procedure for the ν_1 *Q*-branch at 2115 cm^{-1} we find an average optical depth of $\tau_S = 0.31 \pm 0.1$ from 2114.7 to 2115.2 cm^{-1}. From comparison with the laboratory spectra we estimate $N_S = 0.06$ cm-amagat. This is in good agreement with the abundance found from the stronger ν_3 *Q*-branch. Combining the results of the two we arrive at a best estimate of $N_S = 0.05^{+0.05}_{-0.03}$ cm-amagat.

The primary source of error is the uncertainty of assuming $\tau_l \propto N_l$ in the laboratory data. Larson's series of laboratory spectra at different abundances indicate that the underestimate of τ_l is probably less than 20% for the lowest column-abundance sample; however, we have assigned a more conservative, factor-of-2 uncertainty. Ultimately, better estimates will require detailed modeling of the spectrum using line-by-line laboratory data. Other sources of error include uncertainties in the modeling of the reflected solar contribution, the effect of analyzing only a portion of the *Q*-branch where the feature is cleanly separated from the model curve, and the lower temperature of the Saturn atmosphere compared to the laboratory

TABLE 1

MODEL ATMOSPHERE MOLECULAR ABUNDANCES

Molecule	Jupiter	Saturn
H_2	0.89	0.932
He	0.11	0.068
CO	1.6 ppb	0.3 ppm ($P \leq 68$ mbar)
PH_3	0.6 ppm	3.0 ppm
CH_3D	0.20 ppm	0.26 ppm
NH_3	0.0002 ($T > 147$ K)	0.0003 ($T > 147$ K)
H_2O	63 ppm ($T > 270$ K)	Saturated
GeH_4	0.5 ppb	0.4 ppb

AsH_3. These sources of error are less than the uncertainty in the laboratory data.

The conversion of a column abundance to mole fraction depends on the location of the line-forming region. In our Saturn atmosphere models, this region is above an opaque cloud at $P = 2.9$ bars and $T = 193$ K (see Larson *et al.* 1980; Fink *et al.* 1983; Noll *et al.* 1988*a*). To first order, the mole fraction, q, can be found using $N = qP/\bar{m}g$, where $\bar{m}$ is the mean molecular weight of the atmosphere, and g is the gravitational acceleration. A somewhat more refined number can be obtained by using the multilayer model atmosphere to convert from column abundance to mole fraction. Following this method we find the mole fraction is $q_S = 1.8^{+1.8}_{-0.9}$ ppb.

b) Abundance in Jupiter

The abundance of AsH_3 in Jupiter is estimated in the same way as for Saturn. The average optical depth of the 2126 cm^{-1} feature in the Jupiter spectrum is $\tau_J = 0.34 \pm 0.1$. The uncertainty in the optical depth is reduced for Jupiter because reflected solar radiation is negligible compared to the thermal emission. However, the smaller range of the data and the intrinsic variability of the NEB radiance increases the uncertainty in scaling the models to the data.

By comparing the Jovian and laboratory spectra we estimate $N_J = 0.02^{+0.02}_{-0.01}$ cm-amagat where the greatest source of uncertainty is again the laboratory spectra followed by the determination of τ_J. Converting this to a mole fraction requires an estimate of the line-formation pressure. The peak of the contribution function occurs at 7 ± 2 bars and using this we derive $q_J = 0.7^{+0.7}_{-0.4}$ ppb.

c) Saturn/Jupiter Abundance Ratio

A striking result of this analysis is the relatively greater abundance of AsH_3 in Saturn compared to Jupiter. Because of the uncertainties inherent in estimating absolute abundances, it is useful to compare the abundances in the two planets directly. This bypasses the uncertainties of comparison with laboratory data. The planetary lines are resolved in both planets, therefore, we can use $N_S/N_J = \tau_S/\tau_J$ and substituting for N arrive at

$$\frac{q_S}{q_J} = \frac{P_J \bar{m}_S q_S \tau_S}{P_S \bar{m}_J g_J \tau_J}.$$

Using appropriate values we find $q_S/q_J = 1.8 \pm 1.3$. The main sources of uncertainty in this equation are first, the measured optical depths, and second, the assumed pressures of line formation. The optical depths are derived above and $P_J = 7 \pm 2$ bars. The main remaining model-dependent uncertainty is the depth of formation of lines in Saturn's atmosphere. P_S may be greater than 2.9 bars which would result in a reduction of q_S/q_J. At the present, however, we can conclude that the best estimate suggests the mole fraction of AsH_3 on Saturn is 1.8 times greater than on Jupiter although the uncertainties allow for values from 0.5 to 3.1.

IV. DISCUSSION

Models of arsenic chemistry in the atmospheres of Jupiter and Saturn predict a depletion of AsH_3 at $T < 370$ K (Barshay and Lewis 1978; Fegley and Lewis 1979). Barshay and Lewis (1978) predicted that vertical mixing can bring AsH_3 into the observable part of the atmosphere. Indeed, their estimated mixing ratio of 0.4 ppb in Jupiter is within the observed range. We can conclude that the observed quantities of AsH_3 are then representative of the global abundance of As in the gaseous envelopes of Jupiter and Saturn. Arsenic is the second rock-forming element (after P) that has this property. Ge has also been detected in Jupiter and Saturn as GeH_4 (Fink, Larson, and Treffers 1978; Noll *et al.* 1988*a*) but GeH_4 is estimated to hold only about one-tenth of the atmospheric Ge at $T < 400$ K, and uncertainties in the chemistry are large (Barshay and Lewis 1978; Fegley and Lewis 1979; Fegley and Prinn 1985).

The solar abundance of As relative to H is 0.23 ppb (Cameron 1982). The ratio of As to H in Jupiter and Saturn relative to that in a solar mixture of elements, $\rho = (\mathrm{As/H})_{\mathrm{planet}}/(\mathrm{As/H})_\odot$ is $\rho_J = 1.5^{+1.5}_{-0.8}$ and $\rho_S = 4^{+4}_{-2}$. *In both cases the most probable value is a significant enhancement over the solar value.*

Enrichment of heavy elements is one of the key tests of the core-instability model for the formation of the giant planets (see review by Pollack 1985). The expected enrichment can be computed from

$$\rho_g = \frac{q_g^* M_{\mathrm{core}} f/m_g}{M_{\mathrm{H\text{-}He}}/m_{\mathrm{H\text{-}He}}} \cdot \frac{1}{(g/H)_\odot},$$

where q_g^* is the mass fraction of element g in the solid component, and M and m are the total mass and mean molecular mass of the core and hydrogen-helium components of the planet. The fraction, f, mixed into the surrounding H-He envelope is constrained to be less than 1. If this fraction does not vary much from planet to planet, the enrichments will then be proportional to the ratio of $M_{\mathrm{core}}/M_{\mathrm{H\text{-}He}}$. Using values of core and envelope masses from Hubbard and Marley (1989) we obtain $\rho = 6.2f$ for Jupiter and $\rho = 31f$ for Saturn with uncertainties difficult to estimate, but proportional to the uncertainties of these model results.

The enrichments of arsenic we find are qualitatively in accord with the predictions of this model. As one would expect a higher abundance of arsenic is observed in Saturn. In addition, the fractions, f, required to obtain the observed enrichments of As are 0.18 and 0.13, satisfying the requirement that $f < 1$. Also, the observed enrichments of As agree well with observed enrichments of P (as PH_3) and C (as CH_4). Recent observations near 5 μm suggest that the mole fraction of PH_3 in Saturn is 3–5 ppm (Noll 1987; Bézard *et al.* 1987), higher than previously thought. The enrichment of P in Jupiter is 1.1 ± 0.2 (Bjoraker 1985) and in Saturn is now 6.7 ± 2. For C, Gautier and Owen (1989) find enrichments of 2.5 ± 1 and 5 ± 2 in Jupiter and Saturn, respectively.

There are suggestive similarities in these numbers although the error bars are very large. However, it is worth noting that theoretical constraints for rock-forming elements such as As and P which are present in the pre–planetary nebula only as condensed material (at Jupiter and Saturn radii) are stronger than for C which may be present as condensed solids, volatile ices, or as gaseous CO and/or CH_4. This is a critical distinction in the core instability model because the condensed and gaseous material are incorporated into the growing planet by different physical paths. Therefore, the observed abundances of elements likely to be present as solids are a sensitive test of this model.

Finally, the high apparent abundance argues against the possibility of significant mass-dependent layering of the inner envelope of the giant planets. Arsenic is more than a factor of 2 higher in mass than phosphorous, but shows little difference in the derived values of ρ.

This work is supported by NASA grant NSG-7286 (K. S. N. and R. F. K.). Thanks go to Alan Tokunaga for participating in the early observations and for valuable discussions. We also thank the staff of UKIRT for their excellent support of our observations. Finally, we thank Hal Larson for providing laboratory spectra of AsH_3 prior to publication.

REFERENCES

Barshay, S. S., and Lewis, J. S. 1978, *Icarus*, **33**, 593.

Bézard, B., Drossart, P., Maillard, J. P., Tarrago, G., Lacome, N., Poussigue, G., Levy, A., and Guelachvilli, G. 1987, *Bull. AAS*, **19**, 849.

Bjoraker, G. L. 1985, Ph.D. thesis, University of Arizona.

Cameron, A. G. W. 1982, in *Essays in Nuclear Astrophysics*, ed. C. A. Barnes, D. D. Clayton, and D. N. Schramm (Cambridge: Cambridge University Press), p. 23.

Fegley, M. B., and Lewis, J. S. 1979, *Icarus*, **38**, 166.

Fegley, M. B., and Prinn, R. G. 1985, *Ap. J.*, **299**, 1067.

Fink, U., Larson, H. P., Bjoraker, G. L., and Johnson, J. R. 1983, *Ap. J.*, **268**, 880.

Fink, U., Larson, H. P., and Treffers, R. R. 1978, *Icarus*, **34**, 344.

Gautier, D., and Owen, T. 1989, in *Origin and Evolution of Planetary and Satellite Atmospheres*, ed. S. K. Atreya, J. B. Pollack, and M. S. Matthews (Tucson: University of Arizona Press), in press.

Hubbard, W. B., and Marley, M. S. 1989, *Icarus*, in press.

Larson, H. P., Fink, U., Smith, H. A., and Davis, D. S. 1980, *Ap. J.*, **240**, 327.

Noll, K. S. 1987, Ph.D. thesis, State University of New York at Stony Brook.

Noll, K. S., Knacke, R. F., Geballe, T. R., and Tokunaga, A. T. 1988*a*, *Icarus*, **75**, 409.

———. 1988*b*, *Ap. J.*, **324**, 1210.

Olson, W. B., Maki, A. G., and Sams, R. L. 1975, *J. Molec. Spectrosc.*, **55**, 252.

Pollack, J. B. 1985, in *Protostars and Planets II*, ed. D. C. Black and M. S. Matthews (Tucson: University of Arizona Press), p. 791.

Tarrago, G., Lacome, N., Poussigue, G., Levy, A., and Guelachvilli, G. 1987, Communications FB5 and FB6, 42nd Symposium on Molecular Spectroscopy, Columbus, Ohio.

Treffers, R. R., Larson, H. P., Fink, U., and Gautier, T. N. 1978, *Icarus*, **34**, 331.

Yin, P. K. 1966, Ph.D. thesis, Ohio State University.

Note added in proof.—Several interesting and helpful discussions were had with B. Bézard and E. Lellouch who presented their own work on AsH_3 at the 1988 November AAS Division of Planetary Sciences meeting in Austin, Texas (B. Bézard *et al.*, *Bull. AAS*, **20**, 879 [1988]). In particular, the problem of line saturation in the *Q*-branch and the differences in our models were discussed. The reader is referred to their work in *Ap. J.* (*Letters*) (*submitted*) for further details. We also note that B. Fegley (*Bull. AAS*, **20**, 879 [1988]) confirms that a small amount of vertical mixing is sufficient to transport AsH_3 to observable levels of the atmosphere.

THOMAS R. GEBALLE: Joint Astronomy Centre, 665 Komohana Street, Hilo, HI 96720

ROGER F. KNACKE: Astronomy Program, Department of Earth and Space Sciences, SUNY, Stony Brook, NY 11794

KEITH S. NOLL: Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721