

Comments on the Infrared Absorption Line Formation in Cloudy Planetary Atmospheres

NORHIKO FUKUTA

Denver Research Institute, University of Denver, Colo.

10 March 1971 and 26 July 1971

ABSTRACT

It is proposed, for the interpretation of infrared absorption spectra carrying information of a planetary atmosphere and the condensing clouds, that the following three conditions must be considered: 1) the exchange of the cloud constituents with overlying clear gas due to convective mixing; 2) the partition of constituent gases between the gaseous and the condensed phases, and that with respect to the cloud phase change; and 3) the loss of signal-giving molecules in the condensed phase due to dissociation.

¶ In the Venus atmosphere, the presently available data suggest that the line formations of HCl and HF occur in the overlying clear layer if the condensate phase is liquid, and in the light-scattering cloud if the condensate is ice.

1. Introduction

Infrared absorption spectroscopy which relies on rotation or vibration-rotation bands has been a useful method for the study of constituent molecules in distant planetary atmospheres through our atmospheric windows. In order to interpret the data in terms of rotational temperatures and pressure broadening, a proper model of the planetary atmosphere is required which describes the process of the absorption line formation.

There are two models currently dealing with cloudy planetary atmospheres. One is the reflecting-layer model in which the absorption lines are assumed to form in the clear atmosphere lying above the cloud. The other is a model in which line formation takes place mainly during the scattering in the cloud because the light penetrates the cloud to a considerable depth. Multiple scattering, together with the higher concentration of the light absorbing molecules, suggests that line formation occurs preferentially in the cloud (see Chamberlain, 1965; Belton, 1968). This model has often been considered to be more realistic. During our recent study, however, we found that the condensing cloud system needs to be explained in terms of the physicochemical and cloud-physical behavior of the constituent gases. It is the purpose of this note to discuss such points by considering the Venusian atmosphere as an example

where various observations and their analyses are available.

2. Atmospheric conditions for infrared absorption

If condensing clouds exist in a planetary atmosphere, the abundance of soluble gaseous molecules changes depending upon the cloud conditions. The IR line formation of the molecules in the clouds, therefore, must be considered in terms of these conditions. Three principal conditions proposed for the clouds are as follows:

First, a condensing cloud convects and exchanges all the constituents with the overlying clear gas layer. As a result, the composition of the layer becomes the same as that of the cloud. Possible exceptions are the constituents of the condensed phase, such as water or humidity in our atmosphere which varies to some extent.

The second condition is related to the partition of a particular gas constituent between the gaseous and the condensed phases of the cloud. This partition strongly depends on the solubility of the gas in the condensed phase, assuming this phase to be in a liquid state. When the condensed phase is solid, the gas constituent would be found entirely in the gaseous phase unless a multi-component solid forms.

The third point pertains to the abundance of the

gas constituent in the condensed phase. The gas molecules of a strong electrolyte dissociate in a condensed phase such as water. The dissociation becomes complete at low concentrations. If so, the IR absorptions, representing particular kinds of rotational-vibrational or vibrational modes of motion which existed in the gaseous molecules, disappear. The IR absorptions, therefore, no longer become available for the identification of the particular molecular species in the condensed phase.

3. The Venus atmosphere

In the atmosphere of Venus, in which no type of cloud appears entirely satisfactory as the cloud model (Gierasch and Goody, 1970), water vapor is known to exist in a sufficient quantity so that condensation is possible under the existing lapse rate (Avduevsky *et al.*, 1970), and the resultant water can help the dissociation of electrolytic solutes. Therefore, the strong electrolyte gases, HCl and HF, found in the atmosphere (Connes *et al.*, 1967) come under the conditions stated in the previous section.

Let us look into this problem semi-quantitatively employing the following data:

Water vapor: 4–11 mg liter⁻¹ (at $P=0.6$ atm)
(Avduevsky *et al.*, 1970)

Level of the line formation in scattering model:

$P=0.2$ atm (Belton, 1968)

Total HCl in the absorbing path: 1.9 mm-atm
(Connes *et al.*, 1967)

HCl mixing ratio is assumed to be constant (the first requirement).

In this model, the cloud formation is illustrated in Fig. 1 in terms of an undiluted parcel ascent.¹ When the gas parcels having mixing ratios corresponding to the observed limits (solid lines) ascend, they exceed the saturated vapor contents over water or ice (broken lines), thereby forming a condensed phase (the curve with a maximum). The average amount of the condensed phase reaches a maximum of 1.25 gm m⁻³ at about the 257K level with an average cloud base of 272K and 0.34 atm, and with an average cloud top level of 230K and 0.0081 atm. If entrainment of dry gas is allowed into the parcel, the level of the base becomes higher and that of the top becomes lower than the values appropriate to undiluted parcel ascent. Therefore, a cloud top of 238K and 0.04 atm is chosen for the present model. By the same token, the amount of the condensed phase may be considerably lower than 1.25 gm m⁻³, and a conservative figure of 0.1 gm m⁻³ is assumed (Fukuta *et al.*, 1969, 1970).

¹ The cloud base temperatures referred to by Avduevsky *et al.* (1970) are lower than the present values by about 15K since they used 0.5–1% for the possible range of water vapor content instead of using the observed values. For simplicity, temperature equilibrium is assumed at each level in the present model.

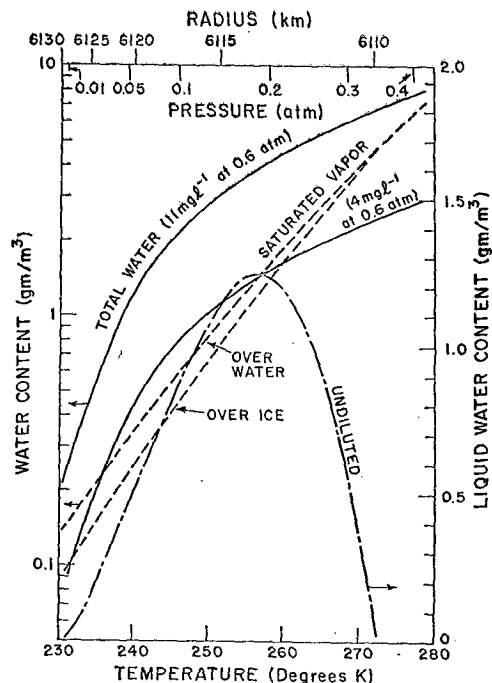


FIG. 1. Condition for cloud formation in the Venus atmosphere. The data for the temperature pressure and radius are taken from Avduevsky *et al.* (1970). The curve for the cloud liquid water content is for the average undiluted plume ascent.

If a constant mixing ratio is assumed as discussed above, the efficiencies of the line formation for a minute constituent, such as HCl, in both the reflecting-layer model and the scattering-layer model, are approximately proportional to the abundance in the absorbing path. Under such a condition, the scattering-layer model with the mean free path length of 1.4 km and an average scattering of 24 times at the 0.2-atm level (Belton, 1968) is about 17 times more efficient in line formation² than the reflecting-layer model which represents the layer above the 0.04-atm altitude. Regarding CO₂ line formation, there is little doubt that it takes place in the cloud. However, as we shall see below, HCl line formation occurs in the overlying clear layer if the phase of the condensate is liquid. Since the reported relative abundance, $p_{\text{HCl}}/p_{\text{CO}_2}=6 \times 10^{-7}$ (Connes *et al.*, 1967), is merely the ratio of the abundance of each species appearing in the signals, each species must be representing a different layer—HCl in the clear layer above the cloud and CO₂ in the cloud layer. In order to reduce this ratio to the abundance ratio in the overlying clear layer, the CO₂ value has to be reduced by the factor of 17, namely, $p_{\text{HCl}}/p_{\text{CO}_2}=1.0 \times 10^{-5}$.

If this proportion is maintained in the cloud with the liquid water content assumed above, then 99.99% of HCl goes into the liquid, resulting in a solution of (1.2 gm HCl)/(100 gm H₂O) at the level of 0.2 atm

² Phase effect and the relative inefficiency of pressure broadening at high altitudes are ignored in this discussion.

and 258K and only 10⁻⁵% of HCl remains in the gaseous phase of the cloud (0.04 atm, 238K) with a concentration of (0.24 gm HCl)/(100 gm H₂O) in the droplets. In such dilute solutions of strong electrolyte, almost 100% dissociation is duly anticipated. Thus, if the cloud consists of a dilute solution of HCl, line formation in the reflecting-layer model becomes reconcilable with other requirements.

There is at least another possible phase for the cloud condensate, i.e., ice, as we have discussed before. When the cloud condensate is ice, HCl cannot stay in it unless the concentration is so high that the HCl solution does coexist (Lewis, 1968). However, the existence of such a high concentration solution is not possible since it inevitably raises the amount of HCl in the overlying layer by evaporation far beyond the observed values. With ice in the condensed phase, the total amount of HCl in the cloud must be in gaseous phase, and this concurs with the condition used in Belton's scattering-cloud model.

The cloud level in the Venus atmosphere appears in the subfreezing temperature zone somewhere between 270 and 230K, and the maximum amount of the condensate per unit volume occurs around the 257K zone. In this temperature zone in our atmosphere, supercooled clouds are often observed. The light scattering in the cloud is a function of the diameter and abundance of the cloud droplets which, in turn, depends on the amount of the condensate and the cloud nuclei con-

centration. The 257K zone could, therefore, possibly be responsible for line formations of CO₂ and H₂O but the temperature zone appears unsuitable for line formation of HCl and HF since the liquid condensate is likely to exist there. Although the uncertainty is too great to continue this kind of speculation, there is a possibility of HCl or HF line formation occurring at higher altitudes because ice clouds are very common in our atmosphere at around 240K and Venus clouds are considered to behave in a similar manner.

REFERENCES

- Avduvsky, V. S., M. Ya. Marov and M. K. Rozhdestvensky, 1970: A tentative model of the Venus atmosphere based on the measurements of Veneras 5 and 6. *J. Atmos. Sci.*, **27**, 561-568.
- Belton, M. J. S., 1968: Theory of the curve of growth and phase effects in a cloudy atmosphere: Application to Venus. *J. Atmos. Sci.*, **25**, 596-609.
- Chamberlain, J. W., 1965: The atmosphere of Venus near her cloud tops. *Astrophys. J.*, **141**, 1184-1205.
- Connes, P., J. Connes, W. S. Benedict and L. D. Kaplan, 1967: Traces of HCl and HF in the atmosphere of Venus. *Astrophys. J.*, **147**, 1230-1237.
- Fukuta, N., T.-L. Wang and W. F. Libby, 1969: Ice nucleation in a Venus atmosphere. *J. Atmos. Sci.*, **26**, 1142-1145.
- , — and —, 1970: Reply. *J. Atmos. Sci.*, **27**, 334-335.
- Gierasch, P., and R. Goody, 1970: Models of the Venus clouds. *J. Atmos. Sci.*, **27**, 224-245.
- Lewis, J. S., 1968: Composition and structure of the clouds of Venus. *Astrophys. J.*, **152**, L79-83.