HCN fluorescence on Titan

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Abstract

The HCN emission features near 3 µm recently detected by Geballe et al. (2003, Astrophys. J. 583, L39) are analyzed with a model for fluorescence of sunlight in the ν3 band of HCN. The emission spectrum is consistent with current knowledge of the atmospheric temperature profile and the HCN distribution inferred from millimeter-wave observations. The spectrum is insensitive to the abundance of HCN in the thermosphere and the thousand-fold enhancement relative to photochemical models suggested by Geballe et al. (2003, Astrophys. J. 583, L39) is not required to explain the observations. We find that the spectrum can be matched with temperatures from 130 to 200 K, with slightly better fits at high temperature, contrary to the temperature determination of 130 ± 10 K of Geballe et al. (2003, Astrophys. J. 583, L39). The HCN emission spectrum is sensitive to the collisional de-excitation probability, $P_{10}$, for the ν3 state and we determine a value of $10^{-5}$ with an accuracy of about a factor of two. Analysis of absorption lines in the C2H2 ν3 band near 3 µm, detected in the same spectrum, indicate a C2H2 mole fraction near 0.01 µbar of $10^{-5}$ for $P_{10} = 10^{-4}$. The derived mole fraction, however, is dependent upon the value adopted for $P_{10}$ and lower values are required if $P_{10}$ at Titan temperatures is less than its room temperature value.

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Keywords: Titan; Atmosphere; Composition; Temperature

1. Introduction

Recently, Geballe et al. (2003) discovered HCN emissions from Titan along with C2H2 absorption lines in a high resolution spectrum of the region near 3 µm. Geballe et al. (2003) show that the emissions are due to fluorescence of sunlight in the C–H stretch, ν3 band of HCN. Previously, fluorescence in the ν3 band of CH4, which is also a C–H stretch mode, has been detected on Titan and Jupiter (Kim et al., 1996, 2000; Dinelli et al., 1997; Drossart et al., 1998) and in cometary comae (Weaver et al., 1989). Geballe et al. (2003) show that the emission features can be used to probe atmospheric structure and derived a rotational temperature of 130 ± 10 K and an HCN mole fraction of 0.3–1.0% near Titan’s mesopause from analysis of the spectrum. The temperature is close to the predicted values (Yelle, 1991) but Geballe et al. (2003) claim that the HCN mole fraction is roughly three orders of magnitude larger than predicted by chemical models of the atmosphere. The temperature and HCN abundance in Titan’s upper atmosphere are closely coupled and a large increase in the HCN mole fraction should be accompanied by a decrease in temperature (Yelle, 1991). In addition, the C2H2 spectral lines are seen in absorption, which is surprising considering that the strengths of the C2H2 and HCN bands are nearly identical (Geballe et al., 2003). We therefore present below a more comprehensive analysis of these spectral features.

Fluorescent emissions from planetary atmospheres occur when excited molecular energy levels undergo radiative transitions to a lower level. Strong emission lines can be formed if the radiative de-excitation rate, $A_{10}$, is larger than the collisional de-excitation, $C_{10}$. Collisional de-excitation rates are proportional to atmospheric density and the ratio $A_{10}/C_{10}$ determines the formation region for emission lines. An important aspect of fluorescence in vibrational bands is that collisional de-excitation of vibrational states is slow (typically $10^{4}$–$10^{5}$ collisions are required to cause a downward transition (Lambert, 1977) and radiative de-excitation tends to dominate in the upper atmosphere. If the collisional de-excitation rates are known, this circumstance can be exploited to interpret the intensity of emission lines in terms of the density of the fluorescent species above the altitude where $A_{10} \sim C_{10}$. On the other hand, collisional redistribution of rotational states is rapid and tends to dominate at all altitudes. Collisions force an equilibration between rota-

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tional and translational modes so the rotational populations of each vibrational state follow a Boltzmann distribution at the local atmospheric temperature, even if the vibrational populations themselves do not. This implies that relative rotational line intensities are sensitive to the atmospheric temperature, though proper account must be taken of radiative transfer in the band to interpret the spectrum in terms of temperature.

2. Model description

The HCN emission lines are produced by emission from the ν3 level excited from the ground state by the absorption of a solar photon (Geballe et al., 2003). Thermal excitation due to collisions with ambient molecules is ~ 5 orders of magnitude smaller than solar excitation. In principle ν3 excitation may also be caused by absorption of solar photons into higher energy ν3 overtone states, which then cascade downward to the ν3 level. However, this process would produce 2ν3 → ν3 spectral features, which are not observed. Calculation of the solar energy deposition rate in the 2ν3 band reveals that, because it is roughly two orders of magnitude weaker than the ν3 band, photons are absorbed primarily in the lower stratosphere, where large collisional de-excitation rates prevent any significant fluorescence. We can therefore rule out observationally and theoretically the possibility of a significant cascade contribution.

The HCN fluorescence spectrum depends upon the relative radiative and collisional decay rates, the atmospheric temperature profile, and the altitude distribution of HCN. Listed in Table 1 are radiative decay rates for the ν3 bands of HCN and C2H2 along with the collisional de-excitation rate constant as measured at room temperature. The collisional de-excitation rate is equal to the product of the rate constant and atmospheric density C10 = k10N∞. Setting C10 = A10 and assuming a temperature of 175 K, we find that the collisional and radiative de-excitation rates are equal at ~ 0.1 mbar. However, collisional de-excitation rates are expected to decrease with decreasing temperature and the values of k10 measured in the laboratory should be larger than the values that apply to Titan. Thus the HCN emissions should probe Titan’s atmosphere to at least the 0.1 mbar level and possibly deeper.

The collisional de-excitation rates C10 can be written as

\[ C_{10} = P_{10} \sigma^2 N_{\infty} \sqrt{8kT/\pi m}, \]

where \( \sigma \) is the diameter for collisions, assumed to be 4 Å, \( \sqrt{8kT/\pi m} \) is the mean velocity of collisions, and \( P_{10} \) is the probability that a collision induces a transition out of the vibrationally excited state. The primary uncertainty in \( C_{10} \) is due to \( P_{10} \). Hastings et al. (1983) have measured \( P_{10} = 9.7 \times 10^{-5} \) for HCN-N2 collisions at room temperature. They argue that de-excitation occurs through a V–V transition to the ν1 + ν2 state, rather than directly to the ground state even though the reaction is endothermic by \( \Delta E \sim 200 \text{ cm}^{-1} \). This is reasonable because the energy difference is roughly equal to thermal energy (kT) at 296 K, but it suggests that the rate could be highly temperature sensitive. In fact, low temperature de-excitation probabilities are usually significantly lower than their room temperature values (Yelle, 1991). We show later that a value of \( P_{10} = 10^{-5} \), a factor of 10 lower than the room temperature measurements, provides a good fit to the HCN emission lines in the observed spectrum. We note that the rate constant adopted by Geballe et al. (2003) is equivalent to \( P_{10} = 0.04 \), and is much higher than the experimental value.

The collision de-excitation probability for the ν3 band of C2H2 has been measured by Hager et al. (1980). These authors find \( P_{10} = 9 \times 10^{-5} \) for collisions with N2 at room temperature, approximately equal to the value for HCN. As with HCN, de-excitation is believed to occur through V–V transfer to a complex combination band that is easily de-excited. For C2H2, however, the nearby vibrational complex is at approximately the same energy as the ν3 band so the rate should be less temperature sensitive than it is for HCN. We adopt \( P_{10} = 10^{-4} \) for C2H2 for our baseline model.

The altitude profile of HCN in Titan’s stratosphere is well established from millimeter wave observations (Marten et al., 2002). The disc-averaged mole fraction increases slowly with altitude from a value of \( 4 \times 10^{-8} \) at 10 mbar to \( 8 \times 10^{-7} \) at 4 mbar. At altitudes below 10 mbar HCN condenses and its mole fraction drops rapidly to zero. At altitudes above 4 mbar, photochemical models predict a mole fraction in the thermosphere, \( X_{\infty}(\text{HCN}) \), of ~ 3 \times 10^{-3} (Yung et al., 1984). According to Yung et al. (1984) the large values of HCN are reached at a pressure of ~ 10^{-3} mbar. We interpolate between the Marten et al. (2002) results at 4 mbar and \( X_{\infty} = 3 \times 10^{-3} \) at 10^{-3} mbar by assuming that the mole fraction varies linearly with log pressure. This procedure yields an HCN mole fraction of 2.5 \times 10^{-4} at 600 km, a factor of ~ 30 smaller than the value suggested by Geballe et al. (2003). We also consider models with \( X_{\infty} \) equal to \( 10^{-4} \) and \( 10^{-6} \).

There is less information on the altitude profile of C2H2. Analysis of Voyager IRIS observations yields mole fraction of 3.0 \pm 0.3 \times 10^{-6} in the equatorial stratosphere (Coustenis et al., 1995), increasing to 6.6 \pm 2.1 \times 10^{-6} at 70° N, whereas analysis of disc averaged observations by ISO (Coustenis et al., 2003) determines a mole fraction of 4.5 \times 10^{-6} near 1 mbar. Photochemical models predict that the C2H2 mole fraction increases to values of ~ 10^{-3} in the thermosphere (Yung et al., 1984; Toublanc et al., 1995; Lara

<table>
<thead>
<tr>
<th>Band parameters</th>
<th>HCN</th>
<th>C2H2</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν10 (cm⁻¹)</td>
<td>3314</td>
<td>3300</td>
</tr>
<tr>
<td>A10 (Hz)</td>
<td>86</td>
<td>85</td>
</tr>
<tr>
<td>k10 (cm² s⁻¹)</td>
<td>2.6 \times 10^{-14}</td>
<td>3.1 \times 10^{-14}</td>
</tr>
<tr>
<td>P10 (mbar)</td>
<td>9.7 \times 10^{-5}</td>
<td>9 \times 10^{-5}</td>
</tr>
</tbody>
</table>

a Values at 296 K.
Our baseline model has a C2H2 mole fraction in the ther-
etent with Voyager UVS occultation results (Vervack, 1997).
however, an abundance this large is inconsis-
tent with Voyager UVS occultation results (Vervack, 1997).
Our baseline model has a C2H2 mole fraction in the ther-
mosphere of $X_{\infty} = 10^{-5}$. We connect the stratospheric mole 
frations to that adopted for the thermosphere by assuming that
the thermospheric abundance applies to 0.01 µbar and 
that the mole fraction varies linearly as log pressure between
10 mbar and 0.01 µbar. Condensation of C2H2 is included at
deeper levels. The baseline model atmosphere is shown in
Fig. 1.

We use the temperature profile of Yelle et al. (1997) in
our analysis, which is constructed to satisfy a variety of
constraints from observations and models. Temperatures at
pressures greater than 1 mbar have been determined through
a combination of radio occultation measurements (Lindal et
al., 1983) and measurements of the CH4 band at 7.8 µm
(Coustennis et al., 1995, 2003). Temperatures in the ther-
mosphere have been determined through UV occultation
(Smith et al., 1983). The region near 1 µbar is expected
both theoretically and observationally to have a negative
temperature gradient. Observational evidence comes from
comparison of densities at higher and lower altitudes which,
through hydrostatic equilibrium, determine a mean temper-
ature less than the values at higher and lower altitudes (Lel-
louch et al., 1990). Theoretical evidence comes from thermal
structure models that predict a well developed mesopause
near 0.1 µbar (Yelle, 1991). Yelle et al. (1997) also presents
maximum and minimum temperature models, but these are
designed for spacecraft engineering use and are extremely
conservative. Examination of the uncertainties in the observ-
ations and models suggest that 5 K is a more reasonable
value for the temperature uncertainty near 1 mbar at the time
of the observations (Coustennis et al., 2003).

3. Spectral calculation

We synthesize the near IR spectrum of Titan by solving
the radiative transfer equation for overlapping vibrational
bands in rotational LTE. To implement the radiative trans-
fer equations we use a vertical grid that extends from $10^3$
to $10^{-4}$ µbar and is sampled at a rate of 10 levels per decade
of pressure. Both HCN and C2H2 lines are included in the
calculation and are treated in an identical manner. Line para-
eters are obtained from the GEISA database (Jacquin-
Husson et al., 1999). The spectrum is calculated in vacuum
wavenumbers at a resolution of 0.003 cm$^{-1}$ then converted
to air wavelengths and smoothed to a resolving power of
20,000 for comparison with the observations. The coupled
radiative transfer equations for the two bands are solved
with a modified Rybicki technique using six angular streams.
The formulation of the radiative transfer equation and the
numerical technique used in its solution are described in
Appendix A. The solar incidence and emission angles are set
to 60 degrees to simulate a disc-averaged spectrum. The con-
tinuum level seen in the observations is established by scat-
tering of sunlight by aerosols and absorption by the far wings
of pressure-broadened CH4 lines in the lower stratosphere
and troposphere (Griffith et al., 1998). Because the contin-
uum is established at pressures greater than those of interest
here, we do not treat it rigorously but instead model the ef-
effect of aerosol scattering and CH4 absorption by specifying
a Lambertian reflecting surface at the lower boundary whose
frequency dependent albedo is adjusted to reproduce the ob-
served continuum levels.

Results for the baseline model are compared with the ob-
servations in Fig. 2, where we show only the P branch. There
are significant differences between the line intensities in the
R and P branches which Geballe et al. (2003) suggest are
due to difference in pointing because the R and P branches
were measured in different exposures. We follow Geballe
et al. (2003) and analyze only the P branch. The spectrum
also has gaps due to difficulty in correcting for telluric ab-
sorption features (Geballe et al., 2003) and, in particular, the
P(1), P(9), and P(15) lines are missing, presumably because
of this problem. Aside from these spectral gaps, the emission
spectrum is well matched by the model. Most absorption
and emission lines are fit to within $\pm 2 \times 10^{-15}$ W m$^{-2}$ µm$^{-1}$
and the C2H2 absorption features are about as well matched as
the HCN emission lines.

Examination of the radiative transfer source function re-
veals several characteristics of HCN line formation. Figure 3
shows the direct solar source function, the multiply scattered
source function and the net source function for the HCN and
C2H2 bands. These quantities are precisely defined in Ap-
pendix A. At high altitudes the direct solar contribution to
the source functions, $S^o$, dominates, but the scattering con-
tribution, $J$, is everywhere significant and for HCN becomes
larger than $S^o$ at pressures greater than $\sim 50$ µbar. Scattering
is less important for C2H2, but even for this band $J$ is $\sim 40%$
of $S^o$. The decrease of $S^o$ with increasing pressure for HCN
indicates that the lines are optically thick, contrary to asser-
tions in Geballe et al. (2003). The optically thin approxima-
tion does appear adequate for C2H2 for our baseline model.
The strength of the scattering term and the importance of op-

Fig. 1. The altitude distributions of HCN, C2H2 and temperature used in the baseline model atmosphere.
Fig. 2. Observations and baseline model for the spectral region containing the HCN P branch. Note that the P(1), P(9), and P(15) line are not observed as a result of telluric absorption. The data are from Geballe et al. (2003).

Fig. 3. The direct solar source function $S^0$, the multiply scattered source function $J$, and the net source function, $S$ for the HCN and C$_2$H$_2$ bands. The HCN and C$_2$H$_2$ source functions are similar, yet the HCN lines appear in emission and the C$_2$H$_2$ lines in absorption. The solution to this puzzle becomes apparent when the spectrum is examined at high resolution. Figure 4 shows a synthetic spectrum for a small region containing both an

Fig. 4. A high resolution synthetic spectrum showing details of the HCN and C$_2$H$_2$ line profiles.

The HCN and C$_2$H$_2$ line, at a resolution approximately equal to the Doppler width of the lines. The C$_2$H$_2$ line consists of a strong emission feature near line center sitting in a deep absorption feature that extends to the wings of the line. These two aspects of the line profile are smoothed together at the resolution of the observations and the net effect is an absorption line that is less deep than it would be in the absence of fluorescence. The HCN line also has an emission feature near line center and absorption in the wings, but the absorption is significantly weaker than for C$_2$H$_2$ and the HCN lines appear in emission. The different strengths of absorption portions of the HCN and C$_2$H$_2$ lines are a consequence of the
different altitude distribution of these species. As shown in Fig. 1, C$_2$H$_2$ is more abundant than HCN in the stratosphere, where the absorptive wings of the line profile are formed. Partly this is a consequence of photochemistry and partly reflects the lower vapor pressure of HCN. As a result, absorption dominates for C$_2$H$_2$ and fluorescence for HCN.

4. Sensitivity tests

We have calculated a number of model HCN spectra to determine the effects of $X_{\infty}$, $P_{10}$, and the temperature profile. In Fig. 5 we show the difference between models with modified parameters and the baseline model. We vary parameters until the difference between the modified model and the baseline model is $\sim 2 \times 10^{-15}$ W m$^{-2}$ µm$^{-1}$, which is also approximately the accuracy of the fit between the baseline model and the observations. The effect of varying $X_{\infty}$ is surprisingly small. The differences only reach $2 \times 10^{-15}$ W m$^{-2}$ µm$^{-1}$ for $X_{\infty} = 10^{-6}$. The reason for this is presented in Fig. 6, which shows the solar flux absorbed in the HCN band as a function of pressure along with the single scattering albedo for the band, $\sigma$. Roughly speaking, HCN above the $\sigma = 0.5$ level scatters solar photons, forming the emission part of the line profile, while HCN below the $\sigma = 0.5$ level forms the absorption part of the line profile. Figure 6 shows that for $P_{10} = 10^{-5}$ the flux scattered in the band is essentially independent of $X_{\infty}$. This is because the scattering column extends to $\sim 1$ mbar for $P_{10} = 10^{-5}$ and the contribution from HCN above 10$^{-3}$ µbar is insignificant.

The HCN abundance from the lower stratosphere to 4 µbar has been determined from analysis of millimeter-wave observations (Marten et al., 2002). Assuming these values, we can determine $P_{10}$. The strength of the HCN emission lines is more sensitive to $P_{10}$. A value of $P_{10} = 2 \times 10^{-5}$, twice as large as that used in the baseline model, produces a poor fit to the observed spectrum. The explanation is again shown in Fig. 6. The absorbed flux increases rapidly with pressure in...
the $10^2$–$10^3$ µbar region and by varying $P_{10}$ we are altering significantly the solar flux absorbed in the scattering region of the atmosphere. Similarly a value of $P_{10} = 5 \times 10^{-6}$ produces emission lines that are too bright. We conclude that $P_{10} = 10^{-5}$ at Titan temperatures, with an uncertainty of a factor of two.

The HCN emission lines are weakly sensitive to temperature. To examine this aspect of the problem we specify in the calculations a constant temperature which is used only to calculate HCN line strengths and widths; the rest of the model atmosphere and the C$_2$H$_2$ emission lines remain unchanged. We show results in Figs. 7a and 7b. A temperature of 135 K produces weaker high J lines than the nominal temperature profile, by an amount that is marginally significant. The variation, however, is in a direction that degrades the fit to the observed spectrum. A temperature of 200 K also produces changes to the spectrum of marginal significance, although these are in the direction that would improve the fit to the observations. Based on the previous discussion, HCN line strengths should be determined primarily by the temperature near 1 mbar. This may indicate that temperatures in this region are higher than assumed in our baseline model. In fact, a recent analysis of ISO observations of Titan (Coustenis et al., 2003) retrieves temperatures near 1 mbar $\sim 5$ K warmer than we assume. This suggests that the HCN emissions may be a useful probe of temperature in Titan’s atmosphere, but higher quality observations are needed.

Geballe et al. (2003) argued that a rotational temperature of $130 \pm 10$ K could be inferred from the HCN spectrum. This led them to adopt a collisional de-excitation rate equivalent to $P_{10} = 0.04$ in order to place the emission altitude near the mesopause where the temperature is $\sim 135$ K. This is difficult to understand in light of the results shown in Fig. 7. and no details were presented by Geballe et al. (2003) to support their temperature determination. The large HCN mole fraction near 600 km determined by Geballe et al. (2003) is a consequence of the large value adopted for $P_{10}$. Figure 6 shows a curve of growth for a model similar to that of Geballe et al. (2003), along with the single scattering albedo corresponding to $P_{10} = 0.1$. The calculations use an HCN mole fraction of 0.01 at pressures less than 1 µbar and the Marten et al. (2002) results at higher pressure. The large values of $P_{10}$ and $X_\infty$(HCN) in the Geballe et al. (2003) model imply that the amount of flux is absorbed is similar to that in our baseline model. In fact, our calculations of a synthetic spectrum using these model parameters agrees well with the Geballe et al. calculations. The difference then concerns only the temperature sensitivity. We find that the spectrum is insensitive to temperature changes of tens of Kelvins and that, if anything, the observations are better matched by a temperature higher than that in the baseline model. Geballe et al. (2003) claim that the spectrum is highly sensitive to temperature and that most of the scattering must take place near the mesopause in order to reproduce the low rotational temperature inferred from the observations.
Fig. 8. Sensitivity tests for C$_2$H$_2$ model parameters. The curves show the difference between the modified models and the baseline model. Only one parameter is modified at a time and the varied parameter is listed next to the curve.

We have also explored the sensitivity of the model spectra to C$_2$H$_2$ model parameters (Fig. 8). Interestingly, the spectrum is more sensitive to the abundance of C$_2$H$_2$ in the thermosphere than was the case for HCN. Holding $P_{10}$ fixed, we calculate that more than a factor of 2 increase in $X_{\infty}(\text{C}_2\text{H}_2)$ would produce more C$_2$H$_2$ fluorescence than observed. This is most apparent at 3.058 and 3.0625 $\mu$m. A value of $X_{\infty}(\text{C}_2\text{H}_2)$ a factor of two smaller causes the absorption lines to be too deep. Similarly, assuming our baseline model for the C$_2$H$_2$ distribution, we calculate that a factor of 2 variation of $P_{10}$ in either direction degrades the match between synthetic and observed spectra.

5. Summary

We have shown that the HCN emissions arise primarily from scattering in Titan’s middle atmosphere at pressures near 1 mbar. A good match to the observed spectrum is achieved with a model that incorporates the HCN distribution of Marten et al. (2002), the thermal profile of Yelle et al. (1997), and collisional de-excitation rates a factor of ten lower than the room temperature values measured in the laboratory (Hastings et al., 1983). The HCN mole fraction in the thermosphere cannot be accurately inferred from the $v_3$ band observations. Models that have mole fractions in the thermosphere from 3 x 10$^{-3}$ to 10$^{-5}$ fit the observations equally well. We also find that the spectrum is insensitive to temperature variations of tens of kelvins. Thus, the band formation region cannot be determined using relative rotational line strengths. This result differs from that presented by Geballe et al. (2003) who argued that the spectrum could only be matched by HCN emissions that arose near the mesopause. We conclude that there is no evidence for the HCN densities greatly in excess of currently accepted values, as suggested by Geballe et al. (2003). Nor do we require collisional de-excitation rates greatly in excess of laboratory measurements to explain the observations.

The lack of C$_2$H$_2$ emission features requires a low abundance of C$_2$H$_2$ in Titan’s thermosphere. Our analysis establishes an upper limit to the mole fraction of 10$^{-5}$ for $P_{10} = 10^{-4}$. This upper limit is lower if $P_{10}$ decreases with temperature. Photochemical models of Yung et al. (1984), Toublanc et al. (1995), and Lara et al. (1996) predict $X_{\infty}(\text{C}_2\text{H}_2)$ values of 10$^{-2}$, 2 x 10$^{-3}$, and 10$^{-3}$, respectively. It appears that $X_{\infty}(\text{C}_2\text{H}_2)$ is lower than photochemical predictions as long as $P_{10}$ at Titan temperatures is equal to or lower than its room temperature value. Potentially, this is an important spectral region for determining C$_2$H$_2$ mole fraction because it constrains the abundance in the thermosphere where C$_2$H$_2$ is created. The C$_2$H$_2$ $v_3$ spectrum therefore constrains the photochemical models in a region that is not strongly affected by uncertain atmospheric mixing rates. Our results are consistent with the Vervack (1997) analysis of the Voyager UVS occultation observations and can be further tested with Cassini observations.

Observations with a higher signal-to-noise ratio and less contamination by telluric absorption might place useful constraints on the temperature in Titan’s atmosphere. In the past, the temperature in Titan’s middle atmosphere has been stud-
ied with space-based observations of the CH$_4$ $v_4$ band. Inference of the temperature through HCN observations would complement the CH$_4$ studies and might provide a useful way to monitor temperature from ground-based observatories.

The temperature dependence of the collisional de-excitation rates is the primary uncertainty in our analysis. The analytic approximations to $P_{10}$ in common use (Landau and Teller, 1936; Schwartz et al., 1952) predict that $P_{10}$ decreases with decreasing temperature (Yelle, 1991); however, these approaches were developed for V–T reactions while it appears that the $v_3$ states of both HCN and C$_2$H$_2$ are de-excited by V–V reactions. Further laboratory studies of these processes would enhance the value of observations of fluorescence in the C–H stretch modes of hydrocarbons in planetary atmospheres.

Acknowledgment

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Appendix A

Inspection of the spectrum shown in Fig. 1 reveals significant overlap between the HCN emission and C$_2$H$_2$ absorption lines. We therefore derive a radiative transfer equation that incorporates overlap of two vibrational bands assuming rotational LTE. The formulation is an extension of that described by Yelle (1991). We write the absorption coefficient as

$$k_{\nu} = k_{\nu}^A + k_{\nu}^B,$$

(A.1)

where the superscripts $A$ and $B$ denote the bands. The emission coefficient is

$$j_{\nu} = \frac{B_{\nu} k_{\nu}^A}{B^A k^A} \int k_{\nu}^A \left( \frac{\tau_{\nu}^A}{4\pi} e^{-\tau_{\nu}^A} \right) \, d\nu,$$

$$+ \frac{B_{\nu} k_{\nu}^B}{B^B k^B} \int k_{\nu}^B \left( \frac{\tau_{\nu}^B}{4\pi} e^{-\tau_{\nu}^B} \right) \, d\nu,$$

(A.2)

where $J_{\nu}$ is the mean intensity, $F_{\nu}$ is the solar flux at solar zenith angle $\cos^{-1}(\mu)$, and $B_{\nu}$ is the Planck function. The single scattering albedo for the band is given by

$$\bar{w}^{A,B} = \frac{A_{10}^{A,B}}{A_{10}^{A,B} + C_{10}^{A,B}},$$

(A.3)

where $A_{10}^{A,B}$ and $C_{10}^{A,B}$ are the radiative and collisional de-excitation rates for the upper vibrational states of the bands.

Variables without the $\nu$ subscript are band averages,

$$k^{A,B}_{\nu} = \int k_{\nu}^{A,B} \, d\nu,$$

$$B^{A,B}_{\nu} = \int \frac{k_{\nu}^{A,B} B_{\nu}}{k_{\nu}^{A,B}} \, d\nu.$$

(A.4)

The source function is given by

$$S_{\nu} = S_{\nu}^0 + U_{\nu}^A J^A + U_{\nu}^B J^B,$$

(A.5)

where

$$S_{\nu}^0 = (1 - \bar{w}_{\nu}) B_{\nu} + U_{\nu}^A \int \frac{w_{\nu}^A F_{\nu} e^{-\tau_{\nu}^A/\mu_{\nu}}}{4\pi} \, d\nu,$$

$$+ U_{\nu}^B \int \frac{w_{\nu}^B F_{\nu} e^{-\tau_{\nu}^B/\mu_{\nu}}}{4\pi} \, d\nu,$$  

(A.6)

$$U_{\nu}^{A,B} = \bar{w}^{A,B} F_{\nu} \frac{B_{\nu}}{B^A B^B},$$

(A.7)

$$w_{\nu}^{A,B} = \frac{k_{\nu}^{A,B}}{k_{\nu}^A + k_{\nu}^B},$$

and

$$\bar{w} = p^A + p^B \bar{w}^B.$$  

The mean intensities and source functions for each band are defined as

$$J_{\nu}^{A,B} = \int u_{\nu}^{A,B} J_{\nu} \, d\nu,$$

(A.10)

and

$$S_{\nu}^{A,B} = \int u_{\nu}^{A,B} S_{\nu} \, d\nu.$$

(A.11)

To solve this system of equations we write the radiative transfer equation in the Feautrier form

$$\mu^2 \frac{\partial^2 u_{\nu}}{\partial \tau_{\nu}^2} = u_{\nu} - S_{\nu},$$

(A.12)

where $u_{\nu}(\mu) = \frac{1}{2}(I_{\nu}(+\mu) + I_{\nu}(-\mu))$. Substituting the expression for the source function and rearranging terms we have

$$u_{\nu} - \mu^2 \frac{\partial^2 u_{\nu}}{\partial \tau_{\nu}^2} = S_{\nu}^0 + U_{\nu}^A J^A + U_{\nu}^B J^B.$$  

(A.13)

We now switch notation and use bold symbols to denote vectors and matrices containing the depth variation of the variables and the subscript $i$ to denote a frequency-angle point. The radiative transfer equation becomes

$$\textbf{T}_i \cdot \textbf{u}_i = \textbf{S}_i^0 + \textbf{U}_i^A \cdot \textbf{J}^A + \textbf{U}_i^B \cdot \textbf{J}^B,$$

(A.14)

where $\textbf{T}_i$ represents $1 - \mu^2 \partial^2 / \partial \tau_{\nu}^2$, $\textbf{U}_i^{A,B}$ is a diagonal matrix containing the values of $U_{\nu}^{A,B}$ and $\textbf{S}_i^0$ is a vector containing the values of $S_{\nu}^0$. The mean intensities are related to
the Feautrier variables through

$$J^{A, B} = \sum_i \omega_{i}^{A, B} u_i,$$  \hspace{1cm} (A.15)

where $\omega_i$ is a diagonal matrix containing the weights for the integration over frequency and angle. Eliminating $u_i$ from Eq. (A.14), we obtain two coupled equations for the mean intensity

$$\left(1 - \sum_i \omega_{i}^{A, B} T_i^{-1} U_i^{A, B}\right) J^A = \left(\sum_i \omega_{i}^{A} T_i^{-1} U_i^{A}\right) J^A + \sum_i \omega_{i}^{A} T_i^{-1} S_i^A,$$

$$\left(1 - \sum_i \omega_{i}^{B, A} T_i^{-1} U_i^{B, A}\right) J^B = \left(\sum_i \omega_{i}^{B} T_i^{-1} U_i^{B}\right) J^B + \sum_i \omega_{i}^{B} T_i^{-1} S_i^B.$$  \hspace{1cm} (A.16)

We now define

$$M^{A, B} = 1 - \sum_i \omega_{i}^{A, B} T_i^{-1} U_i^{A, B},$$

$$N^{A B, RA} = \sum_i \omega_{i}^{A} T_i^{-1} U_i^{B, A},$$

and

$$L^{A, B} = \sum_i \omega_{i}^{A, B} T_i^{-1} S_i^A.$$  \hspace{1cm} (A.17) \hspace{1cm} (A.18) \hspace{1cm} (A.19)

The coupled equations become

$$M^A J^A = N^{A B} J^B + L^A,$$

$$M^B J^B = N^{B A} J^A + L^B,$$  \hspace{1cm} (A.20) \hspace{1cm} (A.21)

where the $N^{A B}$ matrices represent the coupling between the bands. $N^{A B}$ is significant if $k^A_v$ and $k^B_v$ are correlated. In the limit of no overlap equations (A.20) and (A.21) reduce to the expression for independent bands. The solution to Eqs. (A.20) and (A.21) is

$$J^A = \left(1 - \left(M^A\right)^{-1} N^{A B} \left(M^B\right)^{-1} N^{B A}\right)^{-1} \left(M^A\right)^{-1} \times \left(N^{A B} M^B \left(M^B\right)^{-1} L^B + L^A\right),$$

$$J^B = \left(1 - \left(M^B\right)^{-1} N^{B A} \left(M^A\right)^{-1} N^{A B}\right)^{-1} \left(M^B\right)^{-1} \times \left(N^{B A} M^A \left(M^A\right)^{-1} L^A + L^B\right).$$  \hspace{1cm} (A.22) \hspace{1cm} (A.23)

References


