Spectroscopic Detection of Stratospheric Hydrogen Cyanide

Abstract. A number of features have been identified as absorption lines of hydrogen cyanide in infrared spectra of stratospheric absorption obtained from a high-altitude aircraft. Column amounts of stratospheric hydrogen cyanide have been derived from spectra recorded on eight flights. The average vertical column amount above 12 kilometers is $7.1 \pm 0.8 \times 10^{14}$ molecules per square centimeter, corresponding to an average mixing ratio of 170 parts per trillion by volume.

We have analyzed high-resolution solar spectra at wavelengths near 3 μm taken with a spectrometer aboard a Saheliner jet aircraft flying in the lower stratosphere. This spectral region contains the strong v3 band of HCN, with band center at 3311.48 cm$^{-1}$. A number of weak lines at the position of the HCN lines were identified. This spectral region also contains lines of H$_2$O and N$_2$O as well as some unidentified lines. The HCN lines are weak, so that the signal-to-noise ratio in a single spectrum does not permit identification of HCN, but by averaging a large number of individual scans and observing lines from P$_b$ to R$_b$ we have made a positive identification.

To our knowledge, HCN has not been observed previously in the stratosphere or unpolluted troposphere. The method of obtaining and analyzing stratospheric spectra has been reported (1). A solar tracking system directs sunlight into a high-resolution (0.06 cm$^{-1}$ full width at half-maximum, apodized) Fourier transform spectrometer. The instrument is flown aboard the Saheliner at times near sunset or sunrise to enhance the absorption path length.

Figure 1 shows a portion of the measured spectrum in the region containing the P branch of the v3 band of HCN. The HCN lines and major lines due to water are indicated. This spectral region has not been extensively studied in the past. To establish the presence of HCN absorption in the stratospheric spectrum, a wider portion of the spectrum was examined for HCN v3 lines with the line positions of Rank et al. (2). Although some lines are overlapped by other absorbers, all unobscured features for quantum number J ≤ 16 appear in the measured spectra. Recent long-path laboratory measurements (3) provided absorption spectra of O$_3$ and N$_2$O in this region. These laboratory measurements and line parameters in the Air Force Geophysics Laboratory (AFGL) compilation (4) have been used to identify most of the other features in this region and to select HCN features that are free from absorption by other molecules (5).

Six lines of HCN in the region 3270 to 3290 cm$^{-1}$ were selected as free from overlap by other absorptions and sufficiently intense to be useful in determining amounts of HCN. The six lines used in the analysis are listed in Table 1 with their line intensities measured by Jaffe (6). The intensities are estimated to be accurate to ±20 percent or better, and they agree well with band intensities given by other investigators (7, 8). To determine the amount of absorber, synthetic spectra are calculated (9) to match the observed spectra. In the absence of better information, we assumed a uniform mixing ratio of HCN above the aircraft (10). Since the lines are all weak, any other distribution would produce the same absorption for the same line-of-sight amount of HCN; any errors introduced by this assumption in the conversion of line-of-sight amounts to column amounts are negligible compared to the noise. The temperature profile of the U.S. Standard Atmosphere was used. The upper curve in Fig. 1 is a calculated spectrum based on line parameters for H$_2$O, CO$_2$, and N$_2$O from the AFGL line compilation (4) and the HCN line parameters in Table 1.

Table 2 gives details of the flight spectra that were analyzed to determine amounts of HCN. Flights were made at latitudes from 5° to 50°N in winter and summer. The errors in the determination of HCN column amounts are largely due to noise in the spectra; systematic errors due to assumptions of distribution, temperature effects, errors in line intensities or broadening coefficients, and so on are generally much smaller. To improve the signal-to-noise ratio, we averaged as many spectra as possible, even when this covered a significant range of air mass,
and used the mean air mass for conversion to a vertical column amount. The standard deviations of the column amounts measured in the six lines are shown in Table 2. The mean of all the observations, weighted by the inverse square of the individual standard deviations, gives a column amount of $7.1 \times 10^{14}$ molecules per square centimeter in a vertical column above 12 km, with a standard deviation of the mean of $0.81 \times 10^{14}$ cm$^{-2}$. This quantity corresponds to an average mixing ratio of 170 ± 20 parts per trillion by volume above 12 km. Although the measurements cover the latitude range 5° to 50°N in winter and summer, the precision of the individual points is not high enough to allow us to observe any trend with latitude. Similarly, although there is some indication that the amount is lower in the sunrise spectrum than at sunset, there are not enough sunrise data to make a definitive statement about diurnal variability; no diurnal variation is expected, as discussed below.

The origin of HCN and its role in atmospheric chemistry are not completely clear. Although it was not detected previously in the stratosphere or free troposphere, HCN is a known combustion product (15) and can be produced by microbes and plants. Atmospheric HCN apparently originates at ground level from these sources (12). Although mechanisms exist for its in situ atmospheric production (12), they appear to be inadequate to explain the concentrations we observed. Similarly, direct injections of HCN from high-flying aircraft (13) are too small to account for our data. Once in the atmosphere, HCN is not very reactive because of its strong bonds. Because the bond dissociation energy $D(H-CN) = 119.9$ kcal/mole there are few, if any, possible atmospheric hydrogen-abstractation reactions; for instance, reaction with OH is slow (14) and endothermic. Although the reaction HCN + ClO $\rightarrow$ HCl + NCO is exothermic, one expects four-centered reactions to be extremely slow in the atmosphere because of their high activation energies (15). Also, HCN is photodissociated only by short-wavelength (< 200 nm) light (6) and its Henry’s law coefficient implies that clouds and rain are ineffective scavengers of HCN vapor. Accordingly, the atmospheric residence time of HCN is measured in years, and so its vertical distribution is largely controlled by transport and no diurnal variations should be observable in the stratosphere. These points are discussed more quantitatively in (12). The concentration in the troposphere should be as high as that in the stratosphere, but spectroscopic detection there will be difficult due to interference by water vapor.

Recently, the presence of CH$_3$CN in the stratosphere was inferred from positive-ion mass spectra (17), and CN$^-$ (hydrated) appears faintly in stratospheric negative-ion spectra (18). The decomposition of stratospheric CH$_3$CN cannot produce much HCN because CN reacts quickly with O$_2$ to form NCO, which absorbs visible light (12), cleaving the C–N bond. Also, while CN$^-$ and HNO$_3$ can react to form HCN, this HCN source appears small. Finally, because the atmosphere cannot synthesize CH$_3$CN from HCN, it seems likely that the atmospheric chemistries of CH$_3$CN and HCN are uncoupled.

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Table 2. Details of flights for which HCN amounts have been derived. All flights were at sunset. Latitudes, longitudes, and solar elevations are means for all spectra used, weighted by air mass of the individual spectrum.

| Date          | Latitude (°N) | Longitude (°W) | Solar elevation (deg) | Number of spectra averaged | HCN column amount above 12 km (10$^{14}$ cm$^{-2}$) | Standard deviation of column amount (10$^{14}$ cm$^{-2}$) |
|---------------|---------------|----------------|-----------------------|---------------------------|--------------------------------------------------|--------------------------------------------------|
| 10 February 1978 | 9.3           | 85.3           | 6.7                   | 20                        | 9.76                                             | 2.52                                             |
| 11 February 1978 | 21.3          | 95.6           | 8.0                   | 35                        | 5.35                                             | 1.90                                             |
| 12 February 1978 | 32.9          | 102.1          | 8.2                   | 25                        | 7.62                                             | 1.46                                             |
| 30 June 1978   | 5.1           | 80.4           | 3.3                   | 12                        | 4.24                                             | 1.75                                             |
| 2 July 1978    | 21.9          | 96.7           | 9.8                   | 14                        | 13.20                                            | 5.10                                             |
| 11 July 1978   | 40.8          | 108.1          | 10.5                  | 20                        | 13.50                                            | 3.08                                             |
| 12 December 1979 | 48.8         | 117.3          | 3.2                   | 25                        | 5.25                                             | 2.57                                             |
| 9 February 1980 | 49.8          | 118.0          | 6.8                   | 24                        | 15.90                                            | 8.42                                             |

Fig. 1. Observed and calculated stratospheric spectra in a region containing the strongest lines of the P branch of the v$_3$ band of HCN. The lower curve is the average of 80 individual spectra recorded on three consecutive days in February 1978. The mean latitude was 22°N and the mean solar elevation 8°. The HCN lines are identified with their transition; short vertical bars indicate water vapor absorptions. The upper curve, which is displaced vertically for clarity, is a calculated spectrum for 8° solar elevation based on line parameters from the AFGL compilation plus the HCN lines listed in Table 1. The HCN mixing ratio is $2 \times 10^{-10}$. The intensity scale is arbitrary. The observed line at 3289.6 cm$^{-1}$ is probably of solar origin.
Substance P in Principal Sympathetic Neurons: Regulation by Impulse Activity

Abstract. Regulation of the putative peptide neurotransmitter substance P was examined in the superior cervical sympathetic ganglion of the neonatal rat. Surgical decentralization (denervation) of the superior cervical ganglion increased ganglion substance P content. In cultured ganglia, the amount of substance P increased more than 50-fold after 48 hours, and this rise was dependent on protein and RNA synthesis. Veratridine prevented the increase in substance P in vitro, and tetrodotoxin blocked the veratridine effect; this suggests that sodium influx and membrane depolarization prevent substance P elevation. Immunohistochemical analysis of cultured ganglia indicated that substance P was present in the perikarya of principal sympathetic neurons and in ganglionic nerve processes. Transsynaptic impulses, through the mediation of postsynaptic sodium influx, may decrease substance P in sympathetic neurons.

Traditional concepts of neuronal specificity and brain function have been dramatically altered by recent work suggesting that peptides act as neurotransmitters (1, 2). It is now apparent that peptidergic neurons are distributed throughout the neuraxis and that peptides and well-recognized transmitters, such as norepinephrine, may coexist in the same neurons (2). In order to examine the functional implications of these observations, we studied peptidergic expression and metabolism in a relatively simple neuronal structure, the rat superior cervical sympathetic ganglion (SCG).

Traditional teaching maintains that sympathetic ganglion neurons use only norepinephrine or acetylcholine as transmitters and that nerves innervating ganglia are cholinergic (3). However, the recent demonstration of putative peptide transmitters in sympathetic ganglia (4, 5) suggests that the biochemical organization of the sympathetic nervous system is more complicated. For example, the undecapeptide substance P has been detected in ganglion nerve fibers (4), and application of substance P to sympathetic neurons elicits membrane depolarization and neuronal discharge (6). Moreover, since the peptide is released from ganglia by a high potassium stimulus in a calcium-dependent manner, substance P appears to subserve a physiologic role in sympathetic ganglia (7).

Recently, we found that surgical decentralization (denervation) of the SCG in the adult rat, or pharmacological blockade of transmission, increased sub-

Fig. 1 (left). Effects of ganglion decentralization in the neonate. Unilateral surgical detachment of the SCG was performed on the day of birth. The denervated and contralateral control ganglia were examined 36 hours later for substance P content. Values of substance P are expressed as means ± standard error (S.E.) for eight animals. *Differs from control at P < .001. Fig. 2 (right). (A) Time course of ganglion substance P accumulation in culture. Ganglia were placed on filter paper rafts in Ham's nutrient mixture F12 with 10 percent fetal calf serum, penicillin (50 U/ml), and streptomycin (50 μg/ml). Cultures were maintained at 37°C in an atmosphere of 95 percent air and 5 percent CO2 at nearly 100 percent relative humidity. Ganglia were examined after varying times in culture for substance P content. Substance P values are expressed as means ± S.E. for eight animals. (B) Effects of metabolic inhibitors. Ganglia were cultured in the presence of cycloheximide (2 μg/ml), camptothecin (2 μg/ml), actinomycin D (1 μg/ml), or arabinosylcytosine (2.4 μg/ml). After 12 hours, ganglia were examined for substance P content; N = 8. *Differs from 0 time control at P < .001. **Differs from 12 hour control at P < .001. ***Differs from both 0 time control and 12 hour control at P < .002. ****Differs from 0 time control at P < .001. (C) Effects of membrane depolarization. Ganglia were cultured in the presence of veratridine (2 × 10⁻³ M), tetrodotoxin (10⁻⁷ M), or both. After 24 hours, ganglia were examined for substance P content; N = 8. *Differs from 0 time control at P < .001. **Differs from 24 hour control at P < .001.