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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 Sabreliner jet aircraft flying in the lower stratosphere. This spectral region contains the strong ν_3 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_2O and N_2O 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_{16} to R_{16} 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 instrumentation is flown aboard the Sabreliner 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 ν_3 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 ν_3 lines with the line positions of Rank *et al.* (2). Although

some lines are overlapped by other absorbers, all unobscured features for quantum number $J \leq 16$ appear in the measured spectra. Recent long-path laboratory measurements (3) provided absorption spectra of O_3 and N_2O 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_2O , CO_2 , and N_2O 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,

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16. Based on observed Pd (11) and Ir (22) contents and the solar Pd/Ir ratio (23).
17. The sample was etched with dilute aqua regia before irradiation at a flux of $1.5 \times 10^{14} \text{ cm}^{-2} \text{ sec}^{-1}$ for 24 hours. After irradiation it was again etched (0.4 percent of the mass removed) and then dissolved with rare earth carriers. The rare earth fraction was separated as a group, counted on a Ge(Li) detector, and compared with chemically prepared standards. Radiochemical yield was determined by reactivation of mixed carrier solution. The nuclides ^{139}La , ^{140}Ce , and ^{146}Nd , normally measured by neutron activation, could not be determined because their (n, γ) activation products had a significant contribution from neutron-induced fission of ^{235}U .
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20. The possibility of ternary fission was considered for 20 nuclides in the region around $Z = 114$ and $N = 184$ and it was found that the highest probability for ternary fission was only 1 percent of that for binary fission [H. Schultheis and R. Schultheis, *Phys. Lett. B* 58, 384 (1975); *Phys. Rev. C* 15, 1601 (1977)].
21. Recent work shows that the nebula was not entirely well mixed; some inclusions in carbonaceous chondrites have a record of addition of small amounts (~ 0.1 percent) of heavy elements with nonsolar isotopic composition [reviewed by T. Lee, *Rev. Geophys. Space Phys.* 17, 1591 (1979)]. These samples are quite rare, however, and for the most part the nebula appears to have been well mixed in heavy elements to better than 0.01 percent. The evidence for ^{107}Pd in Santa Clara (10) suggests that this meteorite received any late addition of recently synthesized elements. The limit for SHE's in Santa Clara can therefore be related to average solar system material, but the possibility of rare materials with higher amounts cannot be excluded.
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30. We thank R. Frazier and D. Rollins for assistance, A. Meyer and the staff of the Missouri Research Reactor Facility for performing irradiations, R. Reedy for helpful discussions, and C. Lewis and C. Moore of Arizona State University for the sample of Santa Clara. This work was supported in part by NASA grant NSG-7436. The gamma counting was performed at the Arizona Gamma-Ray Analysis Facility, established by NSF grant EAR 78-02708.

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Table 1. Lines in the ν_3 band of HCN used for analysis. The line positions are from Rank *et al.* (2) and the intensities are based on measurements by Jaffe (6); the band intensity inferred from the line intensities given by Jaffe agrees within 3 percent of that from Hyde and Hornig (7).

Line	Position (cm^{-1})	Intensity at 296 K ($\text{cm}^{-1}/\text{column amount}^*$)
P_{13}	3271.45	2.822×10^{-19}
P_{12}	3274.65	3.026×10^{-19}
P_{11}	3277.83	3.219×10^{-19}
P_{10}	3280.99	3.446×10^{-19}
P_9	3284.13	3.625×10^{-19}
P_8	3287.25	3.450×10^{-19}

*Molecules per square centimeter.

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 7.1×10^{14} molecules per square centimeter in a vertical column above 12 km, with a standard deviation of the mean of $0.81 \times 10^{14} \text{ cm}^{-2}$. 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 (11) 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 $D(\text{H-CN}) = 119.9 \text{ kcal/mole}$ there are few, if any, possible atmospheric hydrogen-abstraction reactions; for instance, reaction with OH is slow (14) and endo-

thermic. Although the reaction $\text{HCN} + \text{ClO} \rightarrow \text{HCl} + \text{NCO}$ 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 ($< 200 \text{ nm}$) light (16) 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_3CN 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_3CN 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_3CN from HCN, it seems likely that the atmospheric chemistries of CH_3CN 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 ($^\circ\text{N}$)	Longitude ($^\circ\text{W}$)	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

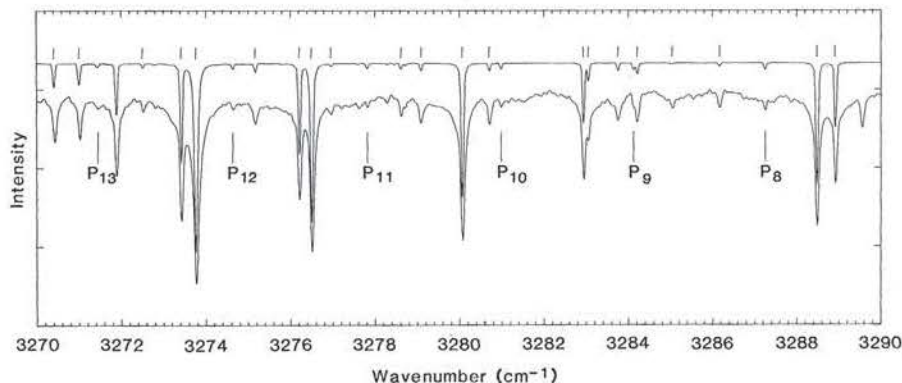


Fig. 1. Observed and calculated stratospheric spectra in a region containing the strongest lines of the P branch of the ν_3 band of HCN. The lower curve is the average of 80 individual spectra recorded on three consecutive days in February 1978. The mean latitude was 22°N and the mean solar elevation 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 2×10^{-10} . The intensity scale is arbitrary. The observed line at 3289.6 cm^{-1} is probably of solar origin.

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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-

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 neurotrans-

mitters (1, 2). It is now apparent that peptidergic neurons are distributed throughout the neuraxis and that peptides and well-recognized transmitters,

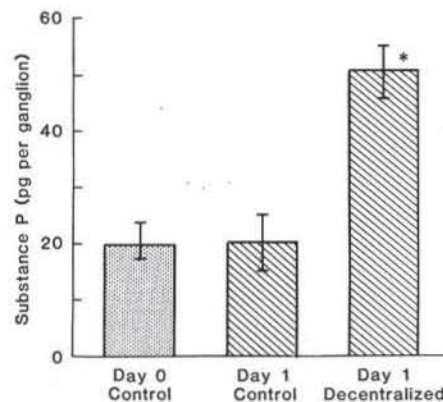


Fig. 1 (left). Effects of ganglion decentralization in the neonate. Unilateral surgical denervation of the SCG was performed on the day of birth. The denervated and contralateral control ganglia were examined 36 hours later for substance P content. Values of substance P are expressed as means \pm standard 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 μ g/ml). Cultures were maintained at 37°C in an atmosphere of 95 percent air and 5 percent CO_2 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 \pm S.E. for eight animals. (B) Effects of metabolic inhibitors. Ganglia were cultured in the presence of cycloheximide (2 μ g/ml), camptothecin (2 μ g/ml), actinomycin D (1 μ g/ml), or arabinosylcytosine (2.4 μ g/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 ($2 \times 10^{-7}M$), 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 $P < .001$.

