References and Notes

1. J. M. Rosen and D. J. Hofmann, *J. Atmos. Sci.* **32**, 1457 (1975).
2. J. M. Rosen, *J. Appl. Meteorol.* **10**, 1044 (1971).
3. P. J. Crutzen, *Geophys. Res. Lett.* **3**, 73 (1976).
4. O. B. Toon and N. W. Farlow, *Annu. Rev. Earth Planet. Sci.* **9**, 19 (1981).
5. J. B. Pollack, O. B. Toon, C. Sagan, A. Summers, B. Baldwin, W. Van Camp, *J. Geophys. Res.* **81**, 1071 (1976).
6. J. B. Pollack, A. Summers, B. Baldwin, C. Sagan, W. Van Camp, *Nature (London)* **263**, 551 (1976).
7. For a complete description of the SAM II and SAGE systems, see M. P. McCormick, P. Hamill, T. J. Pepin, W. P. Chu, T. J. Swissler, L. R. McMaster, *Bull. Am. Meteorol. Soc.* **60**, 1038 (1979).
8. The inversion techniques used are discussed in W. P. Chu and M. P. McCormick, *Appl. Opt.* **18**, 1404 (1979).
9. P. B. Russell *et al.*, *J. Atmos. Sci.* **38**, 1295 (1981).
10. J. L. Stanford and J. S. Davis, *Bull. Am. Meteorol. Soc.* **55**, 213 (1974); M. P. McCormick, H. M. Steele, P. Hamill, W. P. Chu, T. J. Swissler, in preparation; P. Hamill, H. M. Steele, M. P. McCormick, W. P. Chu, T. J. Swissler, in preparation.
11. A. Ghazi, *J. Atmos. Sci.* **31**, 2197 (1974); P. B. Russell, W. Viezee, R. D. Hake, R. T. H. Collis, *Q. J. R. Meteorol. Soc.* **102**, 675 (1976).
12. For details of this stratospheric warming, see R. S. Quiroz, *Geophys. Res. Lett.* **6**, 645 (1979).
13. M. P. McCormick, H. M. Steele, P. Hamill, T. J. Swissler, W. P. Chu, L. R. McMaster, W. H. Mitchell, A. B. Graham, M. T. Osborn, *NASA Ref. Publ. L-14754*, in press.
14. National Space Sciences Data Center, NASA Goddard Space Flight Center, Greenbelt, Md. 20771.
15. The eruption of Soufrière on the Caribbean island of St. Vincent in April 1979 did not inject a significant amount of material into the stratosphere. It represented about a 0.5 percent increase in stratospheric aerosol mass.
16. M. P. McCormick, T. J. Swissler, W. P. Chu, W. H. Fuller, *J. Atmos. Sci.* **35**, 1296 (1978).
17. D. J. Hofmann and J. M. Rosen, *ibid.* **38**, 168 (1981).

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Superheavy Elements: An Early Solar System Upper Limit for Elements 107 to 110

Abstract. *The abundance of samarium-152 in the Santa Clara iron meteorite is found to be 108 × 10^7 atoms per gram. This quantity, if attributed to fission of a superheavy element with atomic number 107 to 109, limits the amount of superheavy elements in the early solar system to 1.7 × 10^{-5} times the abundance of uranium-238. For element 110, the limit is 3.4 × 10^{-5}*

Superheavy elements (SHE's) are elements with atomic numbers greater than 106 which may have been produced in stars by the same processes that produced thorium, uranium, and plutonium. Myers and Swiatecki (*1*) suggested that a region of relative stability, which would permit some of these elements to have appreciable half-lives, existed near atomic number $Z = 114$ and neutron number $N = 184$. More recent calculations, in which alpha and beta decay were considered in addition to spontaneous fission, suggest that the most stable nuclide is $^{294}110$, with a half-life ($t_{1/2}$) of 10^5 to 10^9 years (*2*). Numerous attempts have been made to synthesize SHE's in the laboratory and to search for them in nature. The possibility of an SHE with $t_{1/2} \approx 10^9$ years has led many investigators to search for extant SHE's; claims have been made for their discovery in halos in mica (*3*), in meteorites (*4*), and in hot springs (*5*), but these claims have been criticized (*6*). Other investigations are discussed in several reviews (*7*); there is currently no strong evidence for extant SHE's. Anders and co-workers (*8, 9*) claimed evidence for an extinct SHE with $Z = 115$ (or 114 or 113) in the Allende meteorite, based on xenon isotopic abundances that appear to be due to fission of an unknown transuranic nuclide. This result is difficult to understand in terms of calculated half-lives for these nuclides, all of which are less than 1 year, based on the more recent calculations (*2*). However, the calculated half-lives are uncertain by many factors of 10 (*10*).

We designed an experiment to look specifically at element 110, the only one expected to have a half-life long enough to have survived until the formation of the solar system. We chose an iron meteorite, Santa Clara, for our study because elements 107 through 110 are expected to be siderophilic, that is, concentrated in metallic phases, whereas the rare earth fission decay products are not. Santa Clara was chosen because it contains evidence for decay of extinct ^{107}Pd ($t_{1/2} = 6.5 \times 10^6$ years) (*11*). Because this meteorite apparently formed very early after nucleosynthesis, it may contain evidence for SHE's with half-lives as short as a few million years. In order to explain the applicability of meteorites in addressing this problem, we will describe the mechanism by which iron meteorites are thought to have formed.

Initially, solid grains of metals and silicates condensed out of a hot solar nebula. These grains accreted to form larger bodies that eventually melted. The metal grains sank and coalesced to form an iron-nickel core with a silicate mantle. Later collisions with other bodies fragmented the object. A sample of this core was eventually perturbed into an earth-crossing orbit, and fell as a meteorite.

By considering the thermodynamic properties of the elements, one can calculate the fraction of an element condensed into the grains as a function of temperature. Santa Clara is a typical member of the group IVB irons, which, on the basis of several elements, give a self-consistent grain condensation temperature of 1270 K at a pressure of 10^{-5} atm (*12*). At this temperature Fe and Ni are about 10 percent condensed, while Re, Os, Ir, and Pt, congeners of SHE's 107 to 110, are totally condensed. This work is mainly aimed at SHE 110, the only element expected to have a long half-life, but because the calculated half-lives for fission are so uncertain, elements 107 to 109 are also considered.

To consider the properties of the SHE's in detail and to calculate the fraction condensed, we require estimates of their enthalpy (ΔH_v) and entropy (ΔS_v) of vaporization. Following other investigators (*8, 13*), we extrapolate values from congeners in other rows of the periodic table. The values of ΔH_v are plotted in Fig. 1 (*14*). The extrapolation for elements 107 to 109 appears straightforward, with a clear monotonic trend toward increasing ΔH_v with increasing period. For element 110 the extrapolation is less certain. We arbitrarily chose a value as indicated, but any value from 100 to about 180 kcal is plausible. For comparison, the value chosen by Anders *et al.* (*8*) for element 111 in a similar situation is indicated. Following the procedures of Kelly and Larimer (*12*), we calculated the fraction of each SHE condensed at 1270 K and 10^{-5} atm. Even the most volatile element, element 110, is 99.98 percent condensed under these conditions. Deviations from ideal solid solution, if similar to Pt in Ni (*15*), would increase the amount of element 110 condensed. Because the extrapolation of ΔH_v for element 110 is uncertain, we will be conservative and assume that it is only 50 percent condensed; this is the observed fraction condensed of Pd, the most volatile congener of element 110 (*16*).

Abundances of the rare earth elements were determined by neutron activation analysis with radiochemical separation (*17*). The results are given in Table 1. Neutron activation analysis can only determine the quantity of the target nuclide; except for monoisotopic elements, the technique generally does not directly determine the total amount of the element present. The assumption of normal isotopic abundance to infer the total quantity of an element may not be appropriate in this instance, since significant amounts of several of the isotopes may be made by spontaneous fission.

In order to estimate the amount of SHE that could account for the observed rare earth element abundances, we need to know the fission yield of the SHE in the rare earth mass region. Steinberg and Wilkins (*18*) developed a theoretical model for mass distribution in fission. Their model explains the observation that as the mass of the fissioning nuclide increases, the heavy mass peak remains fixed at 88 neutrons (around mass 142), while the mass of the lighter fragment increases (*19*). They calculated the expected mass distribution for fission of $^{298}114$ and showed that the stability of the 88-neutron mass peak is preserved, and the other fragment, now heavier, has a mass distribution with a broad peak near mass 157. Element $^{294}110$ is expected to have a heavy mass peak near mass 153. Allowing for several neutrons puts the peak in the distribution slightly lower than the masses examined in this work, but as the peaks are quite flat, with a full width at half-maximum of about 20 mass units, the fission yield for ^{152}Sm is expected to be near the maximum. We assume a fission yield of 4 percent for ^{152}Sm (*20*).

To calculate a limit, we assume that all of the ^{152}Sm is due to SHE decay. The observed ^{152}Sm abundance implies a limit to the SHE abundance of 2.7×10^{10} atoms per gram. If the SHE totally condensed into Santa Clara as discussed above, the SHE/Ir ratio in Santa Clara will be equal to the ratio in the early solar system (*21*). Taking the observed Ir concentration in Santa Clara (*22*) and the solar Ir/U ratio (*23*) yields a limit to the solar SHE/^{238}U ratio (atomic) of 1.7×10^{-5}. If the SHE were so volatile that it was only partially condensed, the limit would be higher. The assumption of 50 percent condensation for element 110 discussed earlier sets an upper limit to the 110/^{238}U ratio of 3.4×10^{-5}. Other estimates could be made on the basis of the other nuclides in Table 1, but the higher abundances would not further constrain the limit of SHE in Santa Clara. The nuclide with the lowest abundance, ^{176}Lu, is shielded from fission.

Runcorn (*24*) suggested that siderophile SHE's with half-lives of ~ 10^8 years were present in the early moon. The energetic decay of these elements supposedly melted the lunar interior and powered a lunar magnetic dynamo. Runcorn argued that remanent magnetism observed in lunar rocks was thermoremanent magnetism produced by cooling the rocks in a strong (~ 1 gauss) dipole field. He estimated that 3×10^{13} atoms per gram would be required to power the dynamo. Our upper limit is about a factor of 10^3 less than this, suggesting that a lunar dynamo powered by SHE's 107 to 110 cannot be the source of lunar remanent magnetism.

Table 1. Abundances of rare earth elements in the Santa Clara meteorite.

Nuclide	Atoms of nuclide per gram* (× 10^{-7})	Grams of element per gram† (× 10^{12})	Fraction of cosmic abundance‡ (× 10^6)
^{152}Sm	108 ± 18	1.0	0.23
^{151}Eu	420 ± 100	2.0	1.3
^{159}Tb	<340	<0.9	<0.8
^{165}Ho	<100	<0.3	<0.16
^{174}Yb	<400	<3.0	<0.7
^{176}Lu	3.9 ± 2.4	0.44	0.46

*Uncertainties are 1 standard deviation (S.D.) based on counting statistics. Upper limits are 3 S.D. †Assuming normal isotopic composition. ‡Based on 18 μg of iridium per gram in Santa Clara (*26*) and cosmic ratios of rare earth elements to iridium (*27*).

The results of this work can be used to set limits on the SHE production rate or half-life (but not both). The recent discoveries of evidence for in situ decay of ^{26}Al ($t_{1/2} = 7.3 \times 10^5$ years) (*25*) and ^{107}Pd (*11*) indicate that meteorites formed relatively soon (a few million years) after the last nucleosynthesis event. The nuclides above, however, are made by processes other than the *r*-process, which is suggested for the formation of SHE. Two *r*-process nuclides, ^{129}I ($t_{1/2} = 1.6 \times 10^7$ years) and ^{244}Pu ($t_{1/2} = 8.3 \times 10^7$ years), are found in meteorites in amounts that suggest a period of ~ 10^8 years from the last *r*-process nucleosynthesis to meteorite formation (*26*). If we assume, for illustrative purposes only, that the SHE half-life is identical to that of ^{244}Pu, then the SHE/^{238}U limit of 1.7×10^{-5} found in this work, combined with a Pu/^{238}U ratio of 0.015 (*27*), yields a limit to the SHE/^{238}Pu production ratio of 0.0011. If, on the other hand, we assume that the production rates of ^{244}Pu and the SHE are identical, we get a half-life of 1.2×10^7 years, assuming continuous nucleosynthesis and 10^8 years of free decay.

It has been suggested that neutron-induced fission may terminate the *r*-process before it reaches SHE masses (*28*), but Schramm and Fiset (*29*) noted that *r*-process synthesis of SHE's was strongly dependent on a surface asymmetry parameter. They suggested that reasonable values would permit synthesis of SHE's. Steinberg and Wilkins (*18*) noted that the peak in cosmic abundances around mass 165, most likely due to fission at the termination of *r*-process nucleosynthesis, requires that the *r*-process terminate beyond mass 300. It is not clear, however, that these high mass species can attain the region of stability through beta decay, because spontaneous fission may effectively compete with beta decay.

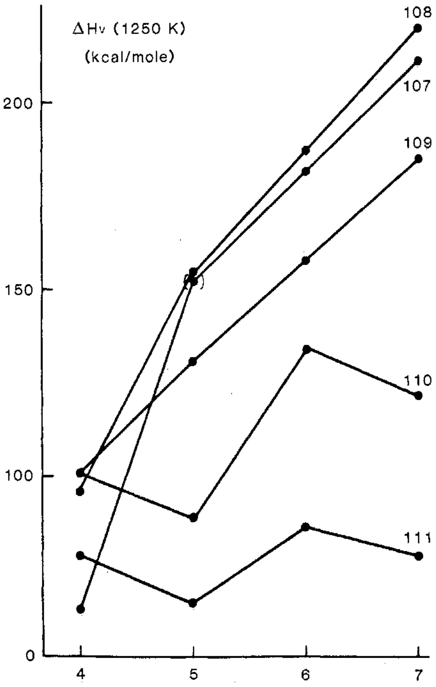

Fig. 1. The enthalpy of vaporization of the congeners of elements 107 to 109 increases monotonically with row in the periodic table. The extrapolation for element 110 is less certain, but as long as ΔH_v of 110 is greater than about 90 kcal/mole, at least 50 percent of it will have condensed into the metal grains that formed Santa Clara. The extrapolated value for element 111 chosen by Anders and co-workers (*8*, *9*) is shown for comparison.

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References and Notes

1. W. D. Myers and W. J. Swiatecki, *Nucl. Phys.* **81**, 1 (1966).
2. E. D. Fiset and J. R. Jix, *Nucl. Phys. A* **193**, 647 (1972); J. Randrup, S. E. Larson, P. Miller, A. Sobiczewski, A. Tukasik, *Phys. Scr.* **10A**, 59 (1974); A. Sobiczewski, in *Superheavy Elements*, M. A. K. Lodhi, Ed. (Pergamon, New York, 1978), p. 274.
3. R. V. Gentry, *Science* **169**, 670 (1970); ______, T. A. Cahill, R. G. Flocchini, *Phys. Rev. Lett.* **37**, 11 (1976).
4. G. N. Flerov, G. M. Ter-Akop'yan, A. G. Opoeko, B. V. Fefilov, V. G. Subbotin, *Sov. J. Nucl. Phys.* **26**, 237 (1977).
5. G. N. Flerov, preprint (1977).
6. F. Bosch, A. El Goresy, W. Kratschmer, B. Martin, B. Povh, R. Nobiling, K. Traxel, D. Schwamm, *Phys. Rev. Lett.* **37**, 1515 (1976); G. Flynn, P. Fraundorf, J. Shirck, R. M. Walker, *Lunar and Planetary Science IX* (Lunar and Planetary Institute, Houston, 1978), p. 341.
7. G. Hermann, *Phys. Scr.* **10A**, 71 (1974); G. T. Seaborg, W. Loveland, D. J. Morrissey, *Science* **203**, 711 (1979).
8. E. Anders, H. Higuchi, J. Gros, H. Takahashi, J. W. Morgan, *Science* **190**, 1262 (1975).
9. E. Anders, *Proc. R. Soc. London Ser. A* **374**, 297 (1981).

10. P. Hodgson, *New Sci.* **75**, 152 (1977).
11. W. R. Kelly and G. J. Wasserburg, *Geophys. Res. Lett.* **5**, 1079 (1978); T. Kaiser, W. R. Kelly, G. J. Wasserburg, *ibid.* **7**, 271 (1980).
12. W. R. Kelly and J. W. Larimer, *Geochim. Cosmochim. Acta* **41**, 93 (1977).
13. O. L. Keller, Jr., *et al.*, *J. Phys. Chem.* **74**, 1127 (1970); O. L. Keller, Jr., C. W. Nestor, Jr., B. Fricke, *ibid.* **78**, 1945 (1974).
14. The data are from R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley, D. D. Wagman, *Selected Values of the Thermodynamic Properties of the Elements* (American Society for Metals, Metals Park, Ohio, 1973). Extrapolations for ΔS_v were performed similarly; they have a much smaller effect on the fraction condensed.
15. R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley, *Selected Values of Thermodynamic Properties of Binary Alloys* (American Society for Metals, Metals Park, Ohio, 1973).
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 1.5×10^{14} cm^{-2} 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.
18. E. P. Steinberg and B. D. Wilkins, *Astrophys. J.* **223**, 1000 (1978).
19. D. C. Hoffman and M. M. Hoffman, *Annu. Rev. Nucl. Sci.* **24**, 151 (1974); D. C. Hoffman, J. B. Wilhelmy, J. Weber, W. R. Daniels, E. K. Hulet, R. W. Lougheed, J. H. Landrum, J. F. Wild, R. J. Dupzyk, *Phys. Rev. C* **21**, 972 (1980); C. E. Bemis, Jr., R. L. Ferguson, F. Plasil, R. J. Silva, F. Pleasanton, R. L. Hahn, *ibid.* **15**, 705 (1977).
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.
22. A. Kracher, J. Willis, J. Wasson, *Geochim. Cosmochim. Acta* **44**, 773 (1980).
23. A. G. W. Cameron, *Space Sci. Rev.* **15**, 121 (1973).
24. K. Runcorn, *Earth Planet. Sci. Lett.* **39**, 193 (1978).
25. T. Lee, D. A. Papanastassiou, G. J. Wasserburg, *Astrophys. J.* **211**, L197 (1977).
26. F. Podosek, *Annu. Rev. Astron. Astrophys.* **16**, 293 (1978).
27. ——, *Geochim. Cosmochim. Acta* **36**, 755 (1972).
28. V. E. Viola, Jr., and G. J. Matthews, in *Superheavy Elements*, M. A. K. Lodhi, Ed. (Pergamon, New York, 1978), p. 499.
29. D. N. Schramm and E. D. Fiset, *Astrophys. J.* **180**, 551 (1973).
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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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 ± 0.8 × 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*).

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 (cm^{-1}/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.

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 Jaffee (*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,