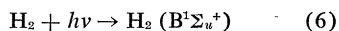
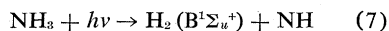


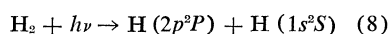
($B^1\Sigma_u^+-X^1\Sigma_g^+$) may arise from fluorescent scattering by molecular hydrogen or the photodissociative excitation of ammonia:



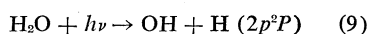
or



The Lyman- α line originates from the photodissociative excitation of NH_3 , from the resonance scattering of solar Lyman- α radiation by atomic hydrogen, or from the photodissociative excitation of molecular hydrogen:



In addition, the Lyman- α line could be produced by photodissociative excitation of any water vapor that might be present in the effluent gas:



These observations demonstrate the usefulness of making ultraviolet spectroscopic measurements of the atmospheres of the jovian planets. Fluorescence in the molecular hydrogen Lyman bands can be measured against the dark background produced by NH_3 and CH_4 which strongly absorb at wavelengths shortward of 1800 Å. All the emissions observed in this experiment can be measured on the limb and

terminator of the planets. Airglow observations of this type may be used to determine the structure of the atmosphere, as has been done for Mars (4, 7).

J. B. PEARCE

Department of Astro-Geophysics and Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder 80302

A. L. LANE

Space Sciences Division, Jet Propulsion Laboratory, Pasadena, California 91103

K. K. KELLY, C. A. BARTH
Department of Astro-Geophysics and Laboratory for Atmospheric and Space Physics, University of Colorado

References and Notes

1. J. B. Pearce, *et al.*, *Appl. Opt.* **10**, 805 (1971).
2. C. A. Barth, *Astrophys. J.* **161**, L181 (1970).
3. W. H. Smith, *J. Chem. Phys.* **51**, 520 (1969).
4. C. A. Barth, *et al.*, *Science* **165**, 1005 (1969); C. A. Barth, *et al.*, *J. Geophys. Res.* **76**, 2213 (1971).
5. L. Wallace and M. B. McElroy, *Planet. Space Sci.* **14**, 677 (1966).
6. H. Okabe and M. Lenzi, *J. Chem. Phys.* **47**, 5241 (1967).
7. We thank J. Casani, N. Medici, D. Beauchamp, E. Goldyn, R. Rowley, and D. Preska of the Jet Propulsion Laboratory's Mariner 6 and Mariner 7 staff for the considerable effort necessary to perform these experiments. We also thank H. P. Broida and G. M. Lawrence for aid in making the spectroscopic identifications. Supported by NASA grant NGL 06-003-052 and NASA contract NAS-7-100.

22 January 1971

Carbon Monoxide in Rainwater

Abstract. Concentrations of carbon monoxide in rainwater collected at widely diverse locations show up to a 200-fold supersaturation relative to the partial pressure of the gas in the atmosphere. These results indicate the existence of an additional natural source of carbon monoxide not heretofore considered. Production of carbon monoxide in clouds is tentatively attributed to the photochemical oxidation of organic matter or the slight dissociation of carbon dioxide induced by electrical discharges, or both. Methane concentrations measured in the same rainwater show that the partitioning of this gas, unlike that of carbon monoxide, is very close to a state of equilibrium.

During the past several years a number of reports have appeared on the origin and fate of atmospheric carbon monoxide. Although there is general agreement that the residence time of carbon monoxide in the atmosphere is short, it is not yet possible to specify completely the various sources and sinks which play essential roles in its geochemical cycle. In particular, it now appears that natural sources can no longer be neglected. Measurements in the Atlantic Ocean (1-3) have shown that the ocean is an important natural source of this gas; recent measurements made by us in the Pacific (4) have con-

firmed this conclusion. It is quite likely that the oceans may be the largest natural source of carbon monoxide. A conservative estimate shows that oceanic carbon monoxide, as a lower limit, contributes at least 5 percent of the amount generated by the burning of fuels by man (2); the correct value is probably much higher.

There are other natural sources which have not as yet been clearly identified. We report here the results of a series of measurements on carbon monoxide in rainwater. These measurements show a high degree of supersaturation of carbon monoxide in rain-

water, relative to the partial pressure of carbon monoxide in the atmosphere, and indicate the possible existence of an additional natural source not heretofore considered. For purposes of comparison, methane measurements made at the same time are also reported; these show that, unlike carbon monoxide, methane partition between rainwater and the atmosphere is close to a state of equilibrium.

The rainwater and air samples were collected at three different locations—in Washington, D.C., over the Pacific Ocean, and on the island of Hawaii. In Washington the rain was collected at rooftop level at the Naval Research Laboratory (NRL) by means of a V-shaped trough, inclined at a 20° slope so that the rain could be easily collected in a glass sample bottle. In a moderate rainfall, filling of the bottle took less than 2 minutes. Samples of air were taken simultaneously at the same location. Samples over the Pacific were taken aboard ship by means of the same collection technique while en route from Panama to Hawaii in June 1970. Care was taken to place the V-shaped trough well forward of the ship's stacks; during collection of the samples, the ship was always headed into the wind. Both in Washington and aboard ship, all samples were analyzed immediately after collection.

On the island of Hawaii, samples were collected at two locations, the Cloud Physics Observatory (CPO) on the Hilo campus of the University of Hawaii (5), and along Saddle Road which runs between the volcanic peaks of Mauna Loa and Mauna Kea. Samples were collected during the period from 16 to 22 June 1970. Saddle Road is an excellent sampling site in the interior of the island with minimum danger of pollution, since there is very little traffic during the day and virtually none at night. Sampling sites along this road were located along the windward side, facing the oncoming trade winds, and at a considerable distance upward from the active volcano sites on Mauna Loa. Orographic rain samples were taken at various altitudes, ranging from 1500 to 5000 feet (460 to 1500 m) above sea level. Several of the samples, both rainwater and air, were taken within the clouds, which in the interior are generally found at altitudes between 2000 and 5000 feet. Samples collected at CPO were analyzed immediately; those collected along Saddle Road were analyzed at the CPO laboratory within 1 to 2 hours after collection.

Table 1. Carbon monoxide and methane in rainwater and the atmosphere. Numbers of samples are indicated in parentheses.

Location and number of samples	Carbon monoxide						Methane					
	Concentration in rain (10 ⁻⁵ ml/liter)			Concentration in air (ppm)			Concentration in rain (10 ⁻⁵ ml/liter)			Concentration in air (ppm)		
	Av.	Range		Av.	Range		Av.	Range		Av.	Range	
Washington, D.C. (NRL)†												
Day (17)	32.0	9.7-140.0		1.49	0.8-2.7		7.3	1.9-32		8.8	7.5-9.8	
Pacific Ocean§												
Day (4)	16.0	14.5-18.9		0.10	0.08-0.12		73	56-110		5.4	5.3-5.7	
Night (1)	4.1			.11			17			5.1		
Hawaii (Saddle Road)												
Day (9)	33.0	11.0-55.0		.12	0.09-0.16		123	55-210		4.7	4.3-5.4	
Night (13)	15.0	5.0-28.0		.15	0.07-0.30		52	16-105		4.7	4.4-5.4	
Hawaii (CPO)¶												
Day (13)	20.0	6.0-46.0		.22	0.10-0.25		41	17-86		5.0	4.0-5.7	
Night (4)	19.0	13.0-25.0		.25	0.19-0.36		26	21-34		5.0	4.4-5.4	

* Ratio of the measured concentration of carbon monoxide in rainwater to the calculated concentration based on the partial pressure of carbon monoxide in the atmosphere (at equilibrium, $R=1$).
† Samples collected at Naval Research Laboratory between December 1969 and April 1970.
‡ Samples collected aboard ship during June 1970 while en route from Panama to Hawaii. Atmospheric concentrations shown refer only to the five samples taken at the time of rainfall (see text).
§ Samples collected in the interior of the island at altitudes between 1500 and 5000 feet (see text).
|| Samples collected at the Cloud Physics Observatory, University of Hawaii, Hilo campus (approximately at sea level). Hawaiian samples were collected 16 to 22 June 1970.
¶ Samples collected at the Cloud Physics Observatory, University of Hawaii, Hilo campus (approximately at sea level). Hawaiian samples were collected 16 to 22 June 1970.

The carbon monoxide in both air and rainwater samples was analyzed by gas chromatography (6). In the laboratory calibration was carried out by saturating distilled water at a measured temperature with pure carbon monoxide at a pressure of 1 atm. Aliquots of this saturated solution were then diluted 270-fold with carbon monoxide-free distilled water to give a final carbon monoxide concentration close to the measured values found in rainwater. The diluted samples were then processed in exactly the same manner as the rainwater samples. Solubility coefficients for carbon monoxide in distilled water used in calculating the calibration factors were those of Lange and Forker (7). We used a similar technique for methane calibrations, and the solubility coefficients were also those of Lange and Forker (7). The precision of the method in the laboratory was found to be ± 1.3 percent, expressed as the relative standard deviation of a single determination. In the field a standard gas mixture was used for calibration, consisting of air containing known amounts of carbon monoxide [0.60 part per million (ppm)] and methane (1.50 ppm). Aliquots of this gas, as well as samples of distilled water saturated with the gas, were used for calibration. The precision of the method in the field, based on calibrations made twice daily over a period of 2 weeks, was ± 3 percent at the concentrations given.

Results of the analyses are shown in Table 1. The measured concentrations are presented in terms of the average values calculated for each group of samples listed in the first column, and also in terms of the range of values encountered. The quantity R is a measure of the extent of supersaturation in the rainwater; it is the ratio of the measured concentration to the concentration calculated on the assumption that equilibrium conditions prevail and that the atmosphere is the sole source of the gas in question. Calculated concentrations of carbon monoxide in rainwater were determined by multiplying the measured partial pressures of carbon monoxide in the atmosphere by the appropriate solubility coefficient (7). The solubility coefficients used in making these calculations were those for the measured temperatures of the rainwater samples at the time of collection. Values of R greater than unity thus indicate supersaturation.

As might be expected, atmospheric carbon monoxide concentrations at

NRL, which is located on the outskirts of Washington, D.C., are comparatively high and show a large range of values because of pollution. To a much lesser extent, the values obtained at Hilo (CPO) also show some expected contamination. Along Saddle Road in the interior, both day and night samples show lower average carbon monoxide concentrations than those at CPO. Of particular interest are the atmospheric concentrations observed over the Pacific, far from any land masses, since these may be regarded as free from pollution. The average atmospheric carbon monoxide concentration of 53 samples taken between Panama and Hawaii was 0.14 ppm with a range of 0.08 to 0.17 ppm (4). The average atmospheric concentration of 0.10 ppm in Table 1 for the five samples from over the Pacific taken at the time of rainwater collection is slightly less but within the overall range just given.

The most striking characteristic of the data is the unexpectedly large amount of carbon monoxide found in the rainwater, and the extent of supersaturation as shown by the values of R . Surprisingly, the supersaturation appears to be highest in the regions where pollution is the lowest, that is, over the Pacific and along Saddle Road. It might be expected that supersaturated raindrops would lose carbon monoxide as they fall through the atmosphere; if so, a significant difference should be found between the extent of supersaturation of the Saddle Road samples collected within the clouds at altitudes from 2000 to 5000 feet and those collected at CPO, which is approximately at sea level. In general, this tendency is what was observed, as shown by the R values for carbon monoxide.

In contrast to the supersaturation observed for carbon monoxide, the data for methane are easier to interpret. The average concentration of methane in the atmosphere at NRL is only slightly higher than that over the Pacific or in Hawaii, although the range of values at NRL is much greater. The close proximity of NRL to the Washington, D.C., sewage treatment plant may account for the latter fact. The values for methane in the atmosphere over the Pacific are in close agreement with the concentrations of 1.33 ppm found by us over the Atlantic (4) and with those reported by Junge (8). Of particular significance is the fact that the R values for methane are close to the equilibrium value of unity. The R values for methane over the Pacific are

slightly higher than those at the other sampling sites. This may be the result of a temperature effect, that is, a warming of the rain as it falls through the atmosphere. This warming effect did not occur to any great extent in the mountain rain samples of Hawaii, or at the NRL sampling site. A measurable degree of warming was observed for some of the CPO daytime rain samples, however. To determine the possible effect of this warming on the precision of our field data, a series of six consecutive rain samples was collected at CPO during a 1-hour heavy rainfall. Treating these as replicate samples, we obtained relative standard deviations of ± 8 and ± 30 percent for the methane and carbon monoxide results, respectively. However, the recorded temperature spread in these samples at the time of sampling was 21° to 26°C . It is clear that this warming effect, when it occurs, introduces an additional source of variability in the rainwater data. This warming effect is sufficient to explain the variations in the methane results, but not in the carbon monoxide data. The wide spread of the latter values in Table 1 must be attributed to other causes.

In the case of the atmospheric samples collected in the vicinity of cities, pollution is the most probable cause of the widespread variations in the carbon monoxide data. In the case of the unpolluted Pacific air, however, the range of values shown is significantly greater than what can be explained in terms of the precision of our method; we believe this to be due to diurnal variations in the quantity of carbon monoxide released to the atmosphere by the ocean (1, 4). The atmospheric concentrations of carbon monoxide in the interior of Hawaii upwind of active volcanic sites appear to be typical of unpolluted marine air.

The high degree of carbon monoxide supersaturation in the rainwater is difficult to explain. Since a progressive decrease in the degree of supersaturation can be expected as the rain falls through the atmosphere, we suggest that the sources of the excess carbon monoxide are in the region where the rain is first formed in the clouds.

Recent investigations indicate the presence of organic matter in rainwater at concentrations between 2 and 12 mg/liter (9). Wilson *et al.* have shown (10) that the photochemical oxidation of organic matter in seawater leads to the formation of carbon monoxide. The highest concentration of car-

bon monoxide found in our Hawaiian rainwater samples was 6×10^{-4} mg/liter. It is evident that there is an abundant excess (more than a thousand-fold) of dissolved organic carbon in rain available for photochemical reactions which could lead to the production of carbon monoxide.

Electric discharges within the clouds may also lead to a slight dissociation of carbon dioxide. It is well known that ion recombination processes and corona discharges from charged droplets occur within the precipitation regions of clouds (11), and that chemical dissociation of carbon dioxide takes place in an electric discharge. Although it is unlikely that the dissociation of carbon dioxide in itself could account for the amounts of carbon monoxide found in the rainwater, the process may nevertheless be a contributing factor. However, in the absence of supporting data, these suggestions must be regarded as highly speculative, and further field investigations are required to confirm or refute such mechanisms.

J. W. SWINNERTON
R. A. LAMONTAGNE
V. J. LINNENBOM

Naval Research Laboratory,
Washington, D.C. 20390

References and Notes

1. J. W. Swinnerton, V. J. Linnenbom, C. H. Cheek, *Environ. Sci. Tech.* **3**, 836 (1969).
2. J. W. Swinnerton, V. J. Linnenbom, R. A. Lamontagne, *Science* **167**, 984 (1970).
3. W. Seiler and C. Junge, *J. Geophys. Res.* **75**, 2217 (1970).
4. R. A. Lamontagne, J. W. Swinnerton, V. J. Linnenbom, paper presented at the meeting of the Geological Society of America, 11 November 1970, Milwaukee, Wis.
5. We thank Dr. C. M. Fullerton, director of the Cloud Physics Observatory, University of Hawaii, Hilo campus, for allowing us the use of laboratory facilities during our stay in Hawaii.
6. J. W. Swinnerton and V. J. Linnenbom, *J. Gas Chromatogr.* **5**, 570 (1967); —, C. H. Cheek, *Limnol. Oceanogr.* **13**, 193 (1968).
7. N. A. Lange and G. M. Forker, Eds., *Handbook of Chemistry* (Handbook Publishers, Sandusky, Ohio, ed. 9, 1956), p. 1969.
8. C. E. Junge, *Air Chemistry and Radioactivity* (Academic Press, New York, 1963), p. 3.
9. H. Schiesser and K. E. Chave (personal communication) report concentrations of dissolved organic carbon (DOC) of 2 to 12 mg/liter in rain collected on Saddle Road at an elevation between 700 and 3000 feet; our measurements of DOC in rain collected at NRL averaged 8 mg/liter. C. E. Junge (8, p. 317) quotes values of approximately 2 mg/liter for the total content of organic matter. Surface ocean water around Hawaii has an average content of organic matter of 1 mg/liter.
10. D. F. Wilson, J. W. Swinnerton, R. A. Lamontagne, *Science* **168**, 1577 (1970).
11. R. Gunn, *Proc. Inst. Radio Eng.* **45**, 1331 (1957).
12. We thank G. Ortman of the Environmental Protection Agency, formerly the National Air Pollution Control Association, Raleigh, N.C., for his invaluable assistance in the collection of samples during our stay in Hawaii. We also thank R. A. Carr and T. B. Warner of NRL for their contributions.

4 January 1971; revised 26 February 1971

Crystal Structure of L-N-Acetylhistidine Monohydrate: An Open and Closed Case

Abstract. L-N-Acetylhistidine crystallizes from aqueous solution as the monohydrate. The crystals are triclinic, space group $P1$, with two formula units per cell. The structural solution was accomplished by direct methods. The two independent molecules have very different conformations, one open and one closed. These two conformations are compared with those found in other histidine structures.

The amino acid histidine is of particular importance in enzyme chemistry because of the frequency with which it is found to be associated with active sites. In particular, histidine seems to be directly involved in the proteolysis mechanisms of papain, subtilisin (subtilopeptidase A), chymotrypsin, trypsin, and other proteolytic enzymes. With crystal-structure results for several of these enzymes becoming available, it is now feasible to study the mechanism of proteolysis by model building based on electron density Fourier maps. For such purposes, reliable knowledge of the geometry of the histidine residue, including its conformational features, is necessary.

The crystal structures of L-histidine

hydrochloride (1), L-histidine (2), and DL-histidine hydrochloride (3) have previously been reported. The histidine moieties in these structures show major conformational differences, being in an extended, "open" form in crystals of L-histidine and DL-histidine hydrochloride and in a compact, "closed" form in L-histidine hydrochloride. We here report briefly on a derivative of histidine, L-N-acetylhistidine (I), which crystallizes as a mixture of two conformers, one open and one closed.

