indirectly from the recombination of nitrogen atoms.

When the glowing nitrogen gas is condensed at liquid helium temperature, the principal emission spectrum arises from ^2D—^4S transition of atomic nitrogen although many other bands are observed (*4*). The ^2P—^2D transition of atomic nitrogen has been found in the near infrared emission spectrum (*27*). It is interesting that the $B^3\Pi_g$———$A^3\Sigma\overset{+}{u}$ transition which dominates the gas phase afterglow is not observed. Unfortunately, impurities account for much of the spectrum observed, and several false starts toward interpretation of the results are attributable to this fact. Thus, one of the principal sets of bands originally attributed to one of the nitrogen transitions was later definitely proved to be due to the $^1S_0$—$^1D_2$ transition of atomic oxygen present as an impurity (*28*). It is significant that the emission spectra of trapped N and O were shifted slightly toward lower energies, suggesting some kind of stabilizing interaction with the solid lattice. Milligan *et al.* (*29*) obtained infrared absorption spectra on the glowing solid and attributed certain bands to the radical, N_3. However, both energy and spin orbital correlation considerations cast some doubt upon N_3 as an important method of stabilizing N atoms. Thus, we have no spectral observations on the most important free radical species presumably present in the solid—namely N^4S—and must rely on other methods for its detection.

Perhaps the most positive identification of trapped nitrogen atoms has been made by electron spin resonance. Both Cole *et al.* (*30*) and Foner *et al.* (*31*) measured the electron spin resonance spectrum of the condensed nitrogen afterglow, Table 2. Both obtained a triplet similar to that of N^4S in the gas. Foner *et al.* also studied the effect of hydrogen and methane as the trapping matrix and found a small shift in the hyperfine splitting, the shift increasing as the binding strength of the matrix increased. All of the investigators found satellite lines which have not yet been satisfactorily explained.

Oxygen atoms, NH, NH_2, HO_2, and OH radicals have been the subject for numerous investigations, but unfortunately the evidence bearing on all of them is incomplete. Thus, as was mentioned above, O atoms have been found as impurities in the glowing nitrogen solid but as yet they have not been identified in oxygen that has been condensed after passing through a discharge. Ozone is evolved in copious quantities when the solid is warmed (*32, 33*), indicating that O atoms were present at some time but there is no convincing evidence that they are trapped in the solid. The NH radical has been tentatively proposed (*1, 2*) to explain the blue color of the solid obtained when hydrazoic acid vapors are partially decomposed and immediately condensed at 77°K. However, its presence has not yet been proved although it now seems definite that, at most, it can be present only in small concentrations (*34, 35*). However, Robinson and McCarty (*36*) have detected both NH and NH_2 by the absorption spectra of the products of a discharge through hydrazine and argon condensed at 4°K. The OH and, especially, the HO_2 radicals have been sought as explanations for the behavior of the solid obtained by freezing the gases leaving an electric discharge in water vapor or hydrogen-oxygen mixtures. Electron spin resonance data on such solids (*37*) might be attributed to OH or HO_2, but the assignment is not definite and the data do not agree with electron spin resonance measurements on gamma-irradiated ice (*22, 38*) which have also been attributed to these radicals. Iodine atoms, CS, ClO, and benzyl have been trapped in hydrocarbon glasses irradiated with ultraviolet light at 77°K, and their presence identified spectroscopically, Table 3 (*39, 40*).

Several studies have been made in an effort to trap and identify organic radicals in various matrices. Unfortunately, few of these are completely convincing and, in fact, the only satisfactory studies have been of the methyl and benzyl radicals. In all cases except benzyl, attempts at identification have consisted of measurement of the electron spin resonance spectrum of a solid at low temperatures. In most instances the solid is first irradiated with gamma rays to bring about dissociation and the formation of radicals.

When protons are present in a free radical, they will couple or resonate with the spin of the unpaired electron. If all of the protons couple equally, the spectrum will show one line more than the total number of protons in the radical. Thus, the spectrum of hydrogen atoms is a doublet and of methyl, a quartet. With equal coupling the relative intensities of the lines are also predictable, the ratios being those of the coefficients of the binomial expansion to the power of the number of protons involved. These considerations form the basis for most of the identifications of organic free radicals entrapped in various matrices. Thus, Gordy and McCormick (*41*) found a quartet in the electron spin resonance spectrum of zinc dimethyl irradiated with x-rays at 77°K. Smaller and Matheson (*42*) and Wall *et al.* (*43*) irradiated solid methane with gamma rays and found a quartet with intensities of the expected order, namely in the ratio 1:3:3:1. Jen *et al.* (*18*) passed methane through a mild discharge and trapped the products at 4°K. They similarly irradiated methyl iodide with ultraviolet at 4°K. In both cases they obtained a quartet in the electron spin resonance spectrum. The data thus show rather conclusively a methyl radical as the species trapped, Table 4.

Table 2. Identification of trapped nitrogen atoms.

STATE	MATRIX	T°K	METHOD
^4S	H_2, N_2, CH_4	4	esr
^2D	N_2	4	emission spectra
^2P	N_2	4	emission spectra

Table 3. Identification of various trapped inorganic radicals.

RADICAL	MATRIX	T°K	METHOD
O	N_2	4	emission spectra
I	glass	77	absorption spectra
ClO	glass	77	absorption spectra
N_3(?)	N_2	20	absorption spectra
NH	A	4	absorption spectra
NH_2	A	4	absorption spectra

Several investigators have studied more complex systems and have attributed the resulting spectra to various possible individual free radicals. Thus, Gordy and McCormick (*41*) obtained a symmetrical sextet from irradiated mercury diethyl which they attributed to the ethyl radical. Smaller and Matheson (*42*) obtained a quartet of triplets on irradiation of ethane, ethylene, and ethyl chloride at low temperatures, and decided that their results were similar to those of Gordy and McCormick, except that the latters' spectra involved line broadening due to the influence of the matrix. They also attributed their spectrum to the ethyl radical. It is not clear why other radicals would not also be formed in a system of this kind. Smaller and Matheson (*42*) have irradiated several hydrocarbons in this way and Luck and Gordy (*44*) have irradiated various alcohols, amines, and mercaptans. In each case, the spin resonance spectra were attributed