Further elaboration of this theory could account for the variations in the integrated pulse profile, from low radio frequencies to gamma rays, in terms of small variations of field and electron energy in different parts of the source.

The absence of optical radiation in pulsars other than the Crab Nebula pulsar is understandable as a combined effect of lower electron energy and lower magnetic field. The comparatively small population of pulsars with long periods may possibly be those with the strongest magnetic fields.

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Intense Vibrational Absorption Spectra of Trapped Triatomic Radicals

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Intense spectra of triatomic radicals have been produced by means of a surface reaction of hydrogen atoms, formed by a microwave discharge in flowing gas, with diatomic oxides. Failure of this method to produce detectable formyl radicals is attributed to existence of an activation energy greatly exceeding 200 cm^{-1} for reaction of H with CO. New NH and ND fundamental vibrations of HNO and DNO, at 2,719 and 2,043 cm^{-1}, are now consistent with the known large bond length. The weak absorption due to the bending mode of DO$_2$ has at last been located at 1,085.3 cm^{-1}, enabling a vibrational assignment for hydroperoxyl radical to be completed.

ALTHOUGH much quantitative structural information has been obtained on the free radicals formed by reacting hydrogen atoms with CO, NO or O$_2$ to form formyl, nitrosyl hydride or hydroperoxyl radicals, certain peculiarities remain. Missing vibrational fundamentals, anomalous bond-length-wavenumber correlations and activation energies for the formation reaction are some of these properties. I have extended the electric discharge method of Dewar[1], as developed by Geib and Harteck[2,3], to produce very intense vibrational absorption spectra which have provided information on these outstanding problems.

The basic apparatus is shown in Fig. 1. Gases from a standard high-vacuum manifold passed to 'Cryotip' refrigerators operated at 17 K, mounted in 'Unicam SP100G' or 'Perkin-Elmer 225' spectrometers. The quarter-wave cavity was fed with 75–125 W power at 2.45 GHz from a 'Microtron' generator to maintain a stable discharge in gas at 20–30 N m^{-2}. Both inlet systems operated with comparable efficiency. Hydrogen or deuterium (mol fraction 1–4% in argon) was discharged, whereas the oxide (CO, NO or O$_2$, 5–20% in Ar) was not.

When H atoms were reacted with molecular oxygen, very intense absorption at 1,389.0, 1,101.0 and another fairly intense absorption at 3,410.5 cm^{-1} were observed (Fig. 2*A*). When D atoms were used instead, intense absorptions appeared at 1,020.2 and 2,529.7 cm^{-1} (Fig. 2*B*). All these wavenumbers agree conclusively with those measured previously in photolysis experiments[4–6] in which hydroperoxyl product absorptions were much less intense. To complete the assignment, careful scrutiny of several minor absorptions was necessary. Characteristic absorptions of H$_2$O, H$_2$O$_2$, D$_2$O, D$_2$O$_2$ and O$_3$ were readily recognized. I believe the ozone observed to be derived from reaction of oxygen atoms, produced by bombardment of the silica tube in the discharge region by energetic argon ions, with oxygen molecules. (Correspondingly CO$_2$ and NO$_2$ were observed in experiments with CO and NO.) Weak absorptions at 830 and 760 cm^{-1} may be attributed to D$_2$O$_4$ [7], presumably formed by combination of DO$_2$ radicals. All these absorptions were of variable intensity relative to the 1,020 cm^{-1} line of DO$_2$ in various experiments, whereas the 1,085.3 cm^{-1} line had an intensity ratio constant within experimental error. Also notable is a linewidth phenomenon. For all three fundamentals of HO$_2$ and the other two of DO$_2$, widths at half maximum intensity were always significantly greater than those of other species detected in the same spectral scans, such as H$_2$O, D$_2$O, O$_3$. The 1,085.3 cm^{-1} absorption shares this greater linewidth property. Thus both intensity ratios and linewidths support assignment of this line to DO$_2$.

This assignment can terminate a controversy between earlier predictions of the order of fundamentals, which generally placed ν_3 (O–O stretching) at greater wavenumbers than ν_2 (bending) and previous incomplete data from photochemical experiments[4]. The only reasonable assignment now consistent with all experimental data places ν_2 of HO$_2$ above ν_3. The intensity differences, small between ν_2 and ν_3 of HO$_2$ but large for DO$_2$, are similar to those for HCN and DCN vapours.

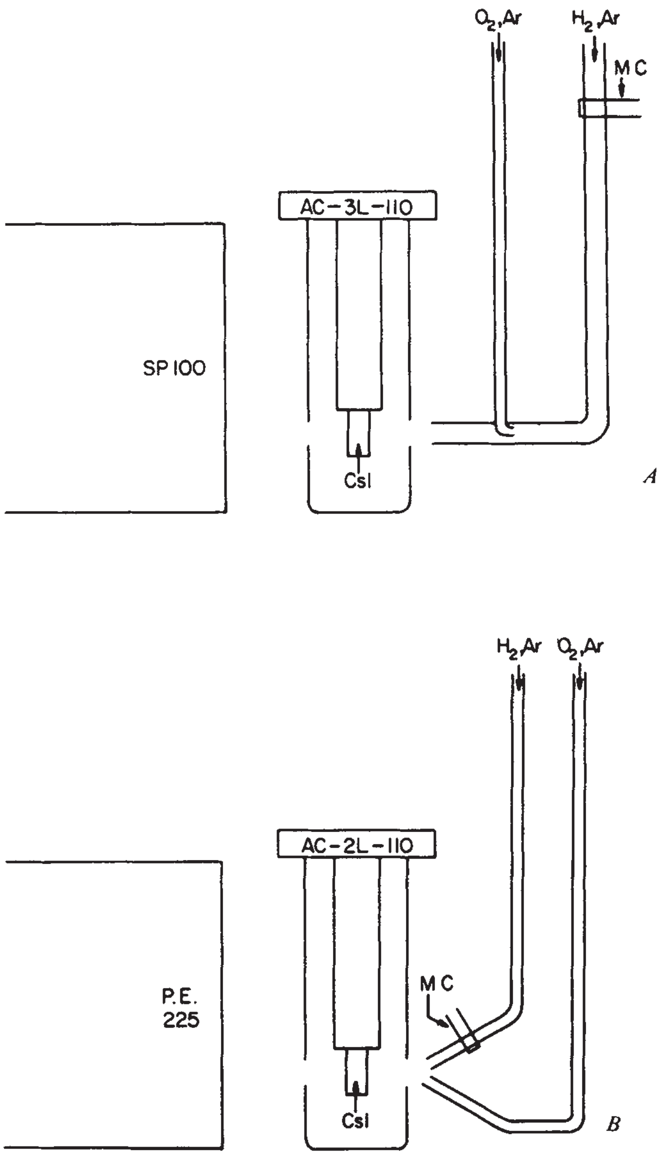


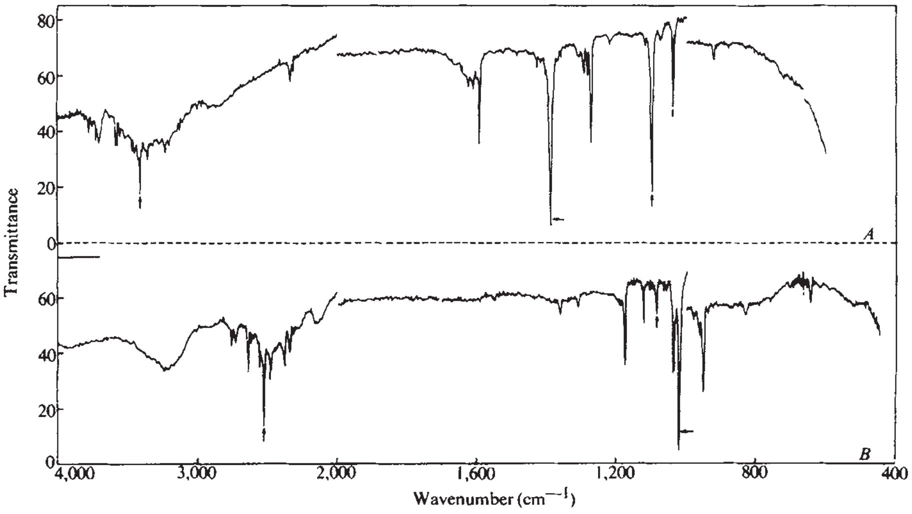
Fig. 1 Diagrammatic representation of inlet systems used to obtain intense spectra. MC, microwave cavity.

When H atoms were reacted with nitric oxide, no absorption in the 3,200–3,600 cm^{-1} was found to obey the intensity criterion, a consistent absorbance ratio with the characteristic 1,564 cm^{-1} feature of HNO, in experiments with varied conditions. A line at 2,719 cm^{-1} did, however, obey this criterion, and one correspondingly at 2,043 cm^{-1} for DNO, as shown in Fig. 3. These lines can be attributed to no other species known to be present, such as nitrogen oxides, nitrous acid, etc. The isotope wavenumber shift is as expected. As these NH and ND fundamentals are considerably weaker than the NO fundamentals, the intense spectra made possible by the flow discharge method were invaluable for these assignments. Furthermore the isolation of HNO or DNO molecules, surrounded by only argon atoms in most sites, prevents intermolecular interactions which could lead to wavenumber shifts. When HNO is produced on photolysis of methyl nitrite or nitromethane (unpublished results) for instance, the carbonyl fundamental of cage partner H_2CO is significantly displaced from the wavenumber for unambiguous isolation in other experiments; to expect a corresponding perturbation of HNO absorption wavenumber is entirely reasonable.

When H or D atoms were reacted with carbon monoxide under similar conditions, no trace of HCO or DCO was obtained in these flow discharge experiments, but minor absorptions due to impurities, as well as major absorption of CO, were easily detected.

The spectra in Figs. 2 and 3 make clear that this method can make possible relatively concentrated samples of matrix-isolated radicals. Consideration of gas pressure, both in the reaction zone and downstream, and available time, between mixing of reagents and freezing on the CsI substrate, precludes the reaction of, for example, H with O_2 in the gas phase; known specific velocities from gas kinetic studies and the requirement of a third body (M), $H+O_2+M\rightarrow HO_2+M$, mean that such a homogeneous reaction is impossible with either reactor in Fig. 1. Therefore the synthetic reactions must occur at or just below the surface layers of the deposit as it builds up while incident gases freeze thereon. The efficiency of production of radicals to produce intense spectra in short deposition periods (2–4 h) with small amounts of reactants means that mobility on the freezing surface must be possible, but also the relative scarcity of radical dimers (such as D_2O_4) indicates only a limited mobility. Consistent with these results is the hypothesis that H or D atoms are very mobile species, even when having only 200 cm^{-1} of kinetic energy (thermal energy for 300 K), so that they can diffuse across and into the argon surface layers for some brief period. Of course the surface layers at time of formation cannot be considered to be representative of the bulk of the sample. Proof that reaction occurs heterogeneously is provided in other experiments in which H or D atoms were reacted with NO_2; observed products included *s-cis* and *s-trans* rotamers of HONO but no trace of OH radicals. In the gas phase, the rapid bimolecular reaction[8] $H+ONO\rightarrow OH+NO$ is known to be much more efficient than the termolecular combination reaction $H+ONO+M\rightarrow HONO+M$. But even

Fig. 2 Infrared absorption of products of reaction of (*A*) H and (*B*) D atoms with molecular oxygen. Arrows mark features attributed to HO_2 and DO_2.



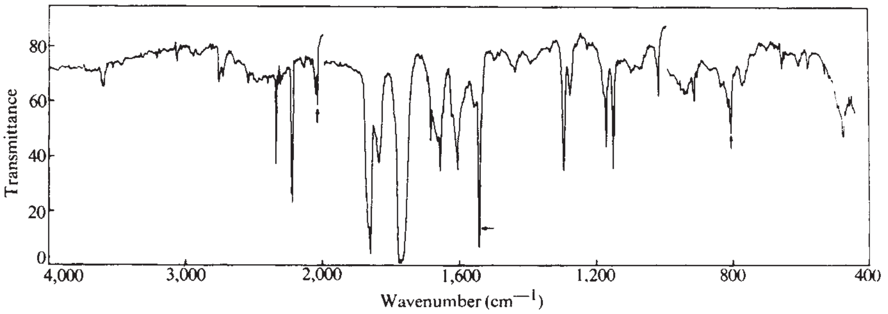


Fig. 3 Infrared absorption of products of reaction of D atoms with nitric oxide. Arrows mark features attributed to DNO.

H or D atoms can be trapped in argon; the absorption at 643 cm^{-1} in Fig. 2*B* is probably due to trapped D[9]. No absorption at 905 cm^{-1} is seen in Fig. 2*A*, but the scanning procedure used may have precluded observation[10].

Lack of formyl radicals in these experiments is positive proof of an activation energy exceeding 200 cm^{-1} (2.4 kJ mol^{-1}) for the synthesis reaction. Earlier evidence[11] for such an activation requirement was ill-founded[4]. When hydrogen iodide was photolysed (39,413 cm^{-1}) as a source of hydrogen atoms[4], 14,800 cm^{-1} of excess energy remained after 24,600 cm^{-1} was used in dissociating HI into ground-state atoms[12,13]; most of this excess energy must, by conservation of momentum, be left to the hydrogen atom as kinetic energy. The energy of activation of self-diffusion of metals is often estimated[14] to be two-thirds the energy of sublimation. If motion through the argon lattice required such an energy, 430 cm^{-1}, per step, and if almost all the excess energy available from that photodissociation had to be dissipated in this manner, H or D atoms could travel many steps from the site of production. Alternatively, a number of such translational steps could still occur while leaving the diffusing atom considerable energy for reaction initiation purposes. Radical concentrations attained in photochemical experiments suggest that the average transfer of "hot" hydrogen atoms consists of only a short motion. On the other hand, the quantity 430 cm^{-1} may be an underestimate, as infrared radiation at 905 cm^{-1} seems far more effective in causing loss of hydrogen atoms, presumably eventually by recombination, than at 644 cm^{-1} (for D atoms)[9]. In any case, we conclude that the flow discharge method is effective in producing radicals by synthesis only when at most a very small activation energy is required.

The vibrational and structural parameters of all three radicals are collected in the table for purposes of comparison. The structure of the formyl radical, previously reconsidered because of the vibrational spectra of trapped radicals[4] but calculated purely from gas-phase rotational constants[15], has now been accepted[16]. An alternative procedure[17], based on minimization of error in calculated vibrational wavenumbers, lacks physical justification. For nitrosyl hydride, previous assignments of the HN stretching fundamental, 3,300–3,600 cm^{-1}, were severely inconsistent with the large known bondlength and small dissociation energy (upper limit of 17,000 cm^{-1}), according to Bernstein's correlations[18]. This discrepancy has now been resolved satisfactorily on the basis of the new assignments.

Table 1 Structures and Fundamental Vibrations of Triatomic Radicals

	HCO	DCO	HNO	DNO	HOO	DOO
r_0(X-H), pm	114.5*		106.28†		98.5	
r_0(X-O), pm	117.65		121.16		136	
angle, degrees	123.3		108.58		106	
v_1, cm^{-1}	2,482	1,926‡	2,719	2,043	3,410.5	2,529.7
v_2, cm^{-1}	1,088	850	1,122	811.7	1,389.0	1,085.3
v_3, cm^{-1}	1,861	1,803	1,564	1,547.3	1,101.0	1,020.2

* Results from ref. 3.
† Results from ref. 14.
‡ Results from ref. 10.

The structure of HO_2 has been newly estimated on the basis of the definite vibrational assignment; the OH distance is derived from Bernstein's correlation[18], the OO distance from Orville-Thomas's correlation[19], whereas the interbond angle is based on theoretical results but is consistent with rough rotational constants estimated for HO_2 [20]. A complete normal coordinate analysis will be published elsewhere.

Finally, the alleged absorption of trapped hydroxyl radicals[21] (3,452.3 and 3,428.2 cm^{-1} for OH, or 2,543.2 and 2,526.2 cm^{-1} for OD) is inconsistent with both earlier direct observation[22] (at 3,574 or 2,635 cm^{-1}) and combination differences (of 3,573 for 2,634 cm^{-1}) in fluorescence spectra[23] of radicals trapped in neon.

Absorption spectra in the latter experiments are closely related to those of OH or OD in the gas phase, so there can be no doubt of the identity of the carrier. Purported spectra[20] of hydroxyl radicals are almost certainly due to hydroxyl anions, OH^- or OD^-. The method of production, vacuum ultraviolet photolysis during deposition, is known to lead to anions in other cases; for example, C_2^- has been obtained from HCCH in this manner[24].

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