The vibrational fundamentals and structure of triatomic radicals formed by photolytic hydrogen-atom reactions: formyl, nitrosyl hydride and hydroperoxyl*

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(Received 23 June 1966)

Abstract—The infra-red spectra of formyl and hydroperoxyl radicals and nitrosyl hydride trapped in matrices of argon and neon at 4°K have been re-investigated. All three radicals result from the reaction of hydrogen atoms from photolysed hydrogen iodide with the appropriate diatomic oxide. The formyl radical has been shown to be decomposed photochemically by visible radiation. Suggested by the infra-red absorption spectrum, an improved (τ_0) structure for HCO X²A' has from rotational constants of HERZBERG and RAMSAY been determined to be r(CH) = 1.148 Å, r(CO) = 1.1765 Å and interbond angle 123.3 degrees. The r_1 fundamentals of HNO and DNO have been established to 3450 and 2565 cm⁻¹ respectively. In the case of the hydroperoxyl radical only two fundamentals are confirmed; an alternative assignment of these vibration frequencies, and the question of the presence of other absorbing species in the hydrogen–oxygen system are discussed. The available experimental evidence is insufficient for a definite structure for HO₂ to be determined. The methoxyl radical and nitrosyl iodide have possibly been detected by their infra-red spectra.

THE reactions of hydrogen atoms with diatomic oxides and other small molecules have been studied extensively for forty years from the first experiments of BONHOEFFER and BOEHM in the gas phase [1]. The reaction of hydrogen atoms with a solid carbon monoxide matrix provided probably the first certain detection of a small trapped radical [2] by infra-red absorption spectroscopy. The latter method seemed to furnish a useful test of apparatus and procedure in further experiments in which trapped radicals were to be produced photochemically, as well as to permit some investigation of the reaction and trapping processes which can occur under cryogenic matrix conditions. It was planned to extend the reaction of hydrogen atoms from photolysed hydrogen iodide to nitric oxide and diatomic oxygen in argon matrices. In the case of NO the stable molecule HNO was known to exist from other studies, whereas for oxygen the hydroperoxyl radical had not previously been directly detected. During the course of this investigation, three articles were published which dealt with these topics [3-5]. Nevertheless, the project was

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^{*} Presented in part at the eighth European Congress of Molecular Spectroscopy, Copenhagen, August 1965.

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^[1] E. BOEHM and K. F. BONHOEFFER, Z. Physik. Chem. Leipzig 119, 385 (1926).

^[2] G. E. EWING, W. E. THOMPSON and G. C. PIMENTEL, J. Chem. Phys. 32, 927 (1960); 34, 1067 (1961).

^[3] D. E. MILLIGAN and M. E. JACOX, J. Chem. Phys. 41, 3032 (1964).

^[4] D. E. MILLIGAN, M. E. JACOX, S. W. CHARLES and G. C. PIMENTEL, J. Chem. Phys. 37, 2302 (1962).

^[5] D. E. MILLIGAN and M. E. JACOX, J. Chem. Phys. 38, 2627 (1963); 40, 605 (1964).

continued for the practical aspects of the work. Also, the hydroperoxyl radical is of such great importance in the chemistry of combustion systems that experimental confirmation of its fundamental frequencies is entirely justifiable. From the results that have emerged from this investigation, certain points of interest arose which had not been fully developed in previous articles. These matters, concerning vibrational assignments and structural deductions, constitute the principal issues of the present article.

EXPERIMENTAL

The required materials were prepared as listed in Table 1. Their purity was checked by vapour pressure measurements and by both infra-red and ultra-violet spectroscopic analysis after distillations from or through efficient traps at appropriate temperatures. All chemicals used were of analytical grade if available, particular precautions being taken in the case of HI to exclude bromides. Mixtures of HI with

Reagent	Method of preparation	Comments	Impurities found	
HI	48% aqueous HI + P ₂ O ₅	good yield	CO ₂ , occasionally H ₂ O	
	$KI + H_3PO_4$ (warmed)	poor yield	н ₂ О, СО ₂	
	$KI + HPO_{s}$ (warmed)	poor yield	CÕ	
	$I_2 + red P_4 + H_2O$	good yield		
0 ₂	KMnO ₄ heated in silica tube		none	
NO	$\frac{\mathrm{KNO}_{8} + \mathrm{KNO}_{8} + \mathrm{Cr}_{2}\mathrm{O}_{3}}{\mathrm{NaNO}_{3} + \mathrm{H}_{2}\mathrm{SO}_{4} + \mathrm{Hg}}$	[6] purified according to	N ₂ O	
		reference [7]	none	
CO	$Zn + CaCO_{a}$ heated in			
	silica tube	[8]	none	

Table 1. Preparation of chemicals for hydrogen atom reactions

one of CO, NO or O_2 were measured in a 5-l. bulb, and matrix gas was added to give final proportions similar to HI:CO:Ar::1:5:200. These mixtures were stable at ambient temperatures for at least several hours, but active reagents were neither frozen together in cold fingers nor heated.

The site of the chemical reactions herein reported was the surface of a caesium bromide crystal maintained at the required temperature by thermal contact through a copper block with liquid helium at its normal boiling point. The cryostat, based on the design of DEURIG and MADOR [9], required $3 \pm \frac{1}{2}$ l. of liquid helium for cooling (from less than 100°K) and filling, a single charging permitting a working period of approximately 12 hr before the refrigerant was exhausted. The temperature of the copper block below the window was measured by a Au: 2·1% Co vs. Ag: 0·37% Au thermocouple [10], of which the thermoelectric potential relative to a similar reference junction submerged in liquid nitrogen was displayed on a variable-range

^[6] J. D. RAY and R. A. OGG, J. Am. Chem. Soc. 78, 5993 (1956).

^[7] E. E. HUGHES, J. Chem. Phys. 35, 1531 (1961).

^[8] S. WEINHOUSE, J. Am. Chem. Soc. 70, 442 (1948).

^[9] W. H. DEURIG and I. L. MADOR, Rev. Sci. Instr. 23, 421 (1952).

^[10] R. L. POWELL, M. D. BUNCH and R. J. CORRUCCINI, Cryogenics 1, 139 (1961).

A.E.I. potentiometric recorder. The radiation shield of the cryostat held 2 l. of liquid nitrogen which would last 17 hr per filling.

Infra-red absorption spectra were recorded with an evacuated Unicam SP100G spectrophotometer [11], modified [12] to allow scanning from 375 to 5000 cm⁻¹ with spectral slit widths usually less than 4 cm⁻¹ and frequency accuracy 3 cm⁻¹. Calibration was effected by reference to standard tables [13]. Ultra-violet spectra of gases in a 10-cm cell with pure synthetic fused silica windows were recorded on a Unicam SP800C spectrophotometer and checked on other instruments. Recording of spectra was usually done on absorbance paper (ruled linear or non-linear in absorbance units, log I_0/I), so that intensities could be read directly as the difference of the absorbances at the absorption maximum and at the interpolated base line.

Two sources of ultra-violet radiation for photolytic purposes were employed. A Philips HPK or MBL/U lamp, operating with mercury at 8 atm pressure and consuming 125 W electrical power through a Philips L4125 series ballast, had its emission focused by mirrors near the sample through two KBr crystal plates and the sample substrate. The other source was a specially constructed low-pressure mercury lamp situated adjacent to the radiation shield within the cryostat, drawing 25 mA at 280 V from a 10 kV stray-field transformer.

RESULTS

The formyl radical

In the present studies of this radical, an argon matrix (containing 5% neon) was used, and the low-pressure mercury lamp provided ultra-violet radiation to decompose the hydrogen iodide in the presence of carbon monoxide. The infra-red absorption features which appear after photolysis are listed (with intensities) in Table 2. First of all, the appearance of the same frequencies as in other investigations [2, 3] proves that free radicals can be formed and trapped under the present experimental conditions. Secondly, identification of methanal by comparison with published spectra of this substance in argon [14] (small frequency shifts being easily compatible with the presence of neon, iodine atoms or molecules etc.) demonstrates that secondary reactions at the effective matrix ratio of 200 are not negligible, particularly in the case that the photolytic hydrogen atom from HI has considerable excess energy after dissociation [15].

Because there was little optical scattering in the experiment to which the data in Table 2 belong, spectrophotometric measurements were profitably continued as the sample warmed from 4°K. Near 20°K the 1091 cm⁻¹ line began to decrease in intensity, as the neon was being pumped away, and similarly the 1862 cm⁻¹ feature, but the 1100 cm⁻¹ line began to increase and attained an absorbance of 0.08 near 38° K, just before all absorbing species were pumped away with the argon. The 1871 cm^{-1} line did not increase; the only other notable spectral change involved the broadening and shifting of the 1732 cm⁻¹ band to 1710 cm⁻¹, as expected for

^[11] C. S. TARBET and E. F. DALY, J. Opt. Soc. Am. 46, 603 (1959).

^[12] J. F. OGILVIE, J. Sci. Instr. 42, 352 (1965).

^[13] I.U.P.A.C., Commission of Molecular Structure and Spectroscopy, Pure Appl. Chem. 1, 537 (1961).

^[14] K. B. HARVEY and J. F. OGILVIE, Can. J. Chem. 40, 85 (1962).

^[15] R. M. MARTIN and J. E. WILLARD, J. Chem. Phys. 40, 2999 (1964).

Frequency (cm ⁻¹)	Intensity	Assignment	
1091	0.055	НСО	
1100	0.015	H.CO	
1356	0.015 br*		
1772	0.01		
1862	0-095	нсо	
1872	0.01 br		
2482	0.02	HCO	
1263	0.005	H.CO	
1498	0.01	н.со	
1724	0-02 sh	H.CO	
1729	0.03 ah	H.CO	
1732	0.04	H.CO	
1740	0.02	H.CO	
2810	0.01 vbr	H	
2850	0-01 vbr	H.CO	

Table 2. Analysis of infra-red spectra produced after photolysis of HI and CO in Ar + Ne

* The abbreviations br, sh, v, w, m and s, which appear in this and succeeding Tables, signify broad, shoulder, very, weak, medium and strong, respectively.

methanal [14]. The satellite absorptions near the principal HCO lines may be due to HCO radicals in other sites in the micro-crystalline lattice. However, the band at 1100 $\rm cm^{-1}$ of which the intensity increases during warm-up cannot belong to HCO or to any other carbonyl compound because there is no corresponding increase in the region from 1680 to 1900 cm⁻¹. A possible carrier of this frequency is the methoxyl radical plausibly formed by reaction of mobile hydrogen atoms with methanal as the temperature rises. On the other hand the continued existence of this trapped radical while both formyl and isolated methanal begin to disappear is difficult to rationalize. Nevertheless, 1100 cm^{-1} cannot be assigned to any likely stable molecule, and is very reasonable for the methoxyl radical of which the C-O stretching frequency, expected to be its most intense absorption, would be greater than for methanol, 1035 cm^{-1} , because of the smaller effective reduced mass of the oxygen atom and also hyperconjugation effects. For the other unassigned frequencies, no other carriers are easily assigned; in particular ethanedial can be positively excluded because its most intense fundamentals [16] have no close counterparts in the matrix spectra.

In previous papers there have been comments regarding the photolysis of the formyl radical itself. In the electron spin resonance experiments in which methanal in argon exposed to a low-pressure mercury lamp served as a source of formyl radicals, only a limited radical concentration was produced; the cause stated [17] was that the very small extinction coefficient of H_2CO at 39413 cm⁻¹ worked in favour of producing HCO less efficiently than of destroying it because of the greater absorption coefficient presumed at this frequency. MILLIGAN and JACOX [3] asserted that attempts to prepare HCO in an argon matrix (employing a medium-pressure mercury lamp) failed because most hydrogen atoms were reduced to thermal energies before encountering carbon monoxide molecules, for reaction with which an appreciable activation energy was deduced. That the latter hypothesis is

^[16] R. K. HARBIS, Spectrochim. Acta 20, 1129 (1964).

^[17] F. J. ADRIAN, E. L. COCHRAN and V. A. BOWERS, J. Chem. Phys. 36, 1661 (1962).

incorrect is demonstrated by the present experiments in which the intensities of HCO radical absorption lines are as great as in a previous investigation in which no inert matrix was utilized [2].

The solution to this conundrum is indicated in the results of another experiment in which HI and CO in argon were exposed first to the low-pressure and then to the high-pressure mercury lamps. The data are listed in Table 3. Thus the action of the lamp emitting many intense lines and an underlying continuum in the visible and

lines					
Frequency (cm ⁻¹)	Intensity before high-pressure Hg lamp	Intensity after high-pressure Hg lamp			
1088	0.025	0.01			
1861	0.05	0.022			
2482	0.012	0.005			

Table 3. Effect of high-pressure lamp on HCO absorption lines							
	T-4	T. (

ultra-violet region is seen to consist of decomposing the formyl radical more rapidly than it is formed, adequate hydrogen iodide still remaining so that the synthetic reaction was still possible. HCO and DCO are known to absorb in the visible region but not in the ultra-violet between 27000 and 45000 cm⁻¹ [18]. Therefore in the ESR investigation of methanol photolysis in argon [17], the usually negligible emission of the low-pressure lamp in the visible region sufficed to limit the concentration of HCO to a small steady-state amount. When the medium-pressure lamp was used the steady-state concentration was too small to be detected by the relatively insensitive infra-red technique [3]. The fact that hydrogen iodide absorbs 39413 cm^{-1} radiation approximately 100 times as strongly as methanal allows formyl radicals to be observed in these experiments, comparison of results with the ESR work being made. Because the ground state of the formyl radical has now been shown [19] to be the ${}^{2}A'$ state, the formyl radical can be formed directly in this state from hydrogen atoms and carbon monoxide in their ground states [20], although an activation energy is still required which is probably small compared with the amount of excess energy available after the photodissociation of hydrogen iodide at 39413 cm^{-1} .

Additional support for this explanation comes from other work of MILLIGAN and JACOX [21] in which ClCO radicals were produced in an argon martix by photolysis of chlorine in the presence of carbon monoxide. In this case, there is no visible or near ultra-violet absorption of ClCO [21] so that MILLIGAN and JACOX have not found it necessary to postulate an activation energy for reaction. The advantage inherent in the use of the almost monochromatic source (the low-pressure mercury lamp) in conditions such that reactants, but not products, absorb reasonably intensely at the source frequency is immediately manifest.

The assignment of the fundamental frequencies of the formyl radical will now

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^[20] G. HERZBERG and D. A. RAMSAY, Proc. Roy. Soc. London A288, 34 (1956).

^[21] M. E. JACOX and D. E. MILLIGAN, J. Chem. Phys. 43, 866 (1956).

be considered. First, the fundamental frequencies of the free radical will undoubtedly closely resemble the frequencies of the observed absorption lines in the argon matrix, at 2482, 1088 and 1861 cm⁻¹, and can be designated to be probably 2475, (1083) and 1865 cm⁻¹ for v_1 , v_2 and v_3 respectively, by comparison with methanal [14] and with matrix shifts in general [22]. From the electronic spectrum, the ground state bending fundamental was discovered to be 1083 cm⁻¹, but an estimate for v_3 from an uncertain assignment of a "hot" band invoked the value 1820 cm⁻¹ [19]. The latter frequency is almost certainly incorrect because the shift from argon matrix to gas phase is invariably small for non-hydrogenic motions, as is illustrated even in the case of ν_2 . The very weak gas-phase band at 17694 cm⁻¹ can then better be assigned to H¹³CO, v' = 11, as previously mentioned but then rejected [19]; the difference between the calculated isotope shifts, 75 ± 5 cm⁻¹, and the observed shift, 63 cm⁻¹, is much less than the difference between the projected r_3 " frequency, 1820 cm⁻¹, and the observed matrix absorption line position, 1862 cm^{-1} . This assignment is in any case consistent with the contours of the diffuse bands [19] calculated on the basis of 313°K, a gas temperature at which is entirely negligible the equilibrium thermal population of the $v_3'' = 1$ state.

The fundamental frequencies of HCO having been established, the proposed frequencies of isotopic molecules can be considered. Vibrational modes involving hydrogen atoms are invariably markedly anharmonic, the effect for hydrogen bondstretching motion being so great as to require an explicit correction in the calculation of deuterium frequencies. Force constant calculations in which all frequencies from all available isotopic species are included produce values of stretching force constants which are of little general application because of the constraints applied to the calculation to overcome the effects of anharmonicity. A simple procedure of correction for anharmonicity can be readily devised. A search of the table of diatomic hydrides in HERZBERG's definitive volume [23] reveals that the ratio of the principal anharmonicity term, $2\omega_s x_s$, in the vibrational energy level equation to the anharmonic or fundamental vibration frequency is equal to 0.040 ± 0.0045 for eighteen different protiated molecules and 0.029 ± 0.0036 for seventeen different deuterated molecules. However, for the first-row diatomic hydrides, BH, CH, OH and HF, the anharmonicity fraction (as defined above) is 0.0456 ± 0.0015 , and 0.0331 ± 0.0005 for the deuterides, significantly larger than the over-all average. In the usual approximation that hydrogen bond-stretching frequencies are sufficiently large to be separated from the other factors in the FG matrix method [24, 25] the simple expression relating the harmonic frequencies of HXY molecules (X and Y being first-row atoms) is obtained as follows:

$$\frac{(\omega_1'')^{\rm H}}{(\omega_1'')^{\rm D}} = \left(\frac{\mu^{\rm D}}{\mu^{\rm H}}\right)^{1/2} = \frac{1.0456 \, r_1^{\rm H}}{1.0331 \, r_1^{\rm D}}$$

$${m v_1}^{
m D} = 0.71573 \, {m v_1}^{
m H} \left\{\!\!\! rac{m_{
m D} + m_{
m X}}{m_{
m H} + m_{
m X}}\!\!\!\!\!
ight\}^{\!1/2}$$

[22] G. C. PIMENTEL and S. W. CHABLES, Pure Appl. Chem. 7, 111 (1963).

- [24] J. W. LINNETT, Trans. Faraday Soc. 41, 223 (1945).
- [25] H. J. BERNSTEIN, Spectrochim. Acta 18, 161 (1962).

or

^[23] G. HERZBERG, Spectra of Diatomic Molecules (2nd Edition) Van Nostrand, Princeton (1959).

in which ω , ν , m and μ represent respectively the harmonic and fundamental frequencies, atomic and reduced masses, superscripts indicating protiated or deuterated molecules. The application of this formula, which is in accordance with DENNISON's rule [26], to a molecule of which the calculated deuterium-stretching frequency is 2200 cm⁻¹ with no account taken of anharmonicity causes an increase of 26 cm⁻¹ in the calculated ν_1^{D} . This increment is much greater than what might be due to Fermi resonance interactions if the closest perturbing frequency (of appropriate symmetry species) is at least a few hundred cm⁻¹ distant.

The calculation of v_1 of DCO by the application of the derived formula leads to a value of 1839 cm⁻¹. This frequency is so close to the carbonyl-stretching frequency that an appreciable Fermi resonance exists to make the energy levels "repel" one another, all vibrational modes of the bent non-symmetric triatomic molecule (in the isolated state) having the same symmetry species. Therefore the values of 1937 and 1800 cm⁻¹ for v_1 and v_3 of DCO [3] are reasonable. If an allowance for the Fermi resonance interaction be made, one obtains a crude estimate of 0.20 ± 0.05 for the anharmonicity fraction for v_1 of HCO, a value compatible with the small bond dissociation energy of HCO in the ground electronic state. In summary, all the frequencies assigned by MILLIGAN and JACOX [3] to the various isotopic formyl radicals can be found to be reasonable.

An explanation of the broad nature of the v_1 fundamental absorptions in the matrices is desirable. The usual cause of such diffuseness in electronic spectra is predissociation to an energetically close unstable state. Because there are no such close states for the ground state of formyl, the application of this effect to the present case is untenable. The half-width of v_1 of HCO in the argon-neon mixed matrix experiments is approximately 10 cm^{-1} , a magnitude which may be significantly less than that estimated from MILLIGAN and JACOX's spectra [3] for the carbon monoxide matrix. In contrast, all of the other bands of small isolated species in argon matrices have band widths comparable to the spectral slit widths of the spectrometer at those frequencies. Yet the assignment of the carrier of the 2482 cm^{-1} absorption to a non-isolated species is compatible with the carrier being the formyl radical only if nearest neighbours are other than formyl or hydrogen iodide. An explanation invoking a phenomenon of partial bonding of the hydrogen atom of HCO with adjacent carbon monoxide molecules in the CO matrix can be dismissed because the frequency of r_1 in the argon matrix is less than in the CO matrix, whereas some analogy to hydrogen bonding would require the opposite effect. The anomalous bandwidth is probably connected with the large amplitude and anharmonicity of this vibration. In the case of DCO, the Fermi resonance with v_3 acts to mix the vibrational modes so that the vibrational energy of v_1 is distributed between the CD and CO bonds, with consequent narrowing of the absorption line.

Concerning the structure of the formyl radical, HERZBERG and RAMSAY [20] obtained the geometrical parameters r(CH) = 1.08 Å, r(CO) = 1.20 Å and the interbond angle 120 degrees. The first bond length was assumed, and the other parameters were calculated from the rotational constants B''_{000} and C''_{000} of each isotopic species, because explicit solution of all parameters was stated to be not

^[26] D. M. DENNISON, Rev. Mod. Phys. 12, 175 (1940).

possible [20]. There was relatively poor agreement of structure between the two isotopic species, the large discrepancies being ascribed to a non-zero inertial defect. However, by reference to correlations of stretching frequency for C---H bonds with bond length and dissociation energy [25], the choice of 1.08 Å as the assumed bond length can be seen to have been unfortunate. The frequency, 13200 cm^{-1} , of the first missing sub-band in the infra-red electronic transition [20] has been taken as an upper limit of the bond-dissociation energy. Both this upper limit and the value



Fig. 1. Graph of (a) bond angle and (b) CO bond length vs. CH and CD bond lengths for HCO and DCO.

of 2475 cm⁻¹ for r_1 " seem suitable to a C—H bond length of approximately 1.16 Å. To check the effect of such a long bond on rotational constants, moments of inertia were generated by the University of Cambridge Titan computer programmed to vary r(CH) from 1.02 to 1.30 Å, r(CO) from 1.10 to 1.46 Å, and the bond angle from 90 to 140 degrees, for both HCO and DCO. In order that economy of computing time might be effected, the relatively coarse intervals of 0.02 Å for the bond lengths and 3 degrees for the angle were chosen for the first run through the entire range. In further runs the increments of bond parameters were reduced, finally to 0.001 Å for r(CH), 0.0005 Å for r(CO) and 0.1 degrees for the angle, and the range searched was correspondingly reduced. As shown in the figure, there is an intersection of the curves of r(CH) and r(CD) vs. r(CO) for values of these variables constrained to reproduce the experimental rotational constants within reasonable experimental error; the curves for the HCO and DCO angles appear not to intersect in the same region, ~ 1.14 Å for r(CH) and ~ 1.18 Å for r(CO). Thus, in agreement with the analysis of HERZBERG and RAMSAY, no unique solution of the structural parameters has been obtained from the equations relating them to the rotational constants. However on the fine scale that the present computations have been made, the constraint of the parameters to such values as would satisfy simultaneously rotational constants of both HCO and DCO would lead to fallacious results because the available rotational constants refer to the zero-point energy state; in this circumstance, significant deuterium isotope effects are invariably found in accurate structure determinations. Therefore those values of the molecular dimensions were selected which gave coincident CO bond lengths and bond angle, but a CH bond length slightly larger than the CD one. These parameters and the rotational constants calculated and experimental are listed in Table 4. The accuracy of the parameters is difficult to determine,

	1	ICO	I		
Constant	Calc.	Exp.	Cale.	Exp.	Units
A 000	22.37	22·36 ₅ [20]	13.61,	13·64 ₁ [20]	cm ⁻¹
Booo	1.494,	1.494, [20]	1.281,	1.281, [20]	em^{-1}
C	1.400	1.400 [20]	1.171	1.171, [20]	em ⁻¹
¥1	v	2482	^	1937 [3]	cm^{-1}
г. У.,		1083		847 [20]	cm^{-1}
ř.		1861		1800 [3]	cm^{-1}
r(CH)	1.148	(1.08) [20]	1.145	(1.08) [20]	Å
ricoj	1.1765	(1.193) [20]	1.1765	(1.202) [20]	Å
angle	123.3	(119) [20]	123.4	(120) [20]	degree

Table 4. Summary of molecular constants for HCO and DCO in the ${}^{2}A'$ state

partially because the experimental error of the rotational constants is not explicitly assigned [20]. From the computer results the errors of ± 0.002 Å in the bond lengths and ± 0.4 degrees in the angle will reproduce rotational constants within 0.2 per cent. The non-zero inertial defect and experimental inaccuracies in the rotational constants (fairly large by microwave determination standards) undoubtedly cause even less accuracy of the bond lengths than is indicated by these estimates but the true (r_0) bond lengths are certainly much closer to these calculated values than the original set of HERZBERG and RAMSAY [20], listed in parentheses in Table 4.

Although the new value of the C—H internuclear distance is less than what was predicted from frequency correlations, the considerable extrapolations involved in those estimates must lead to great uncertainty. The new C—O bond length fits well on the graph of force constant vs. bond length in the paper of EWING *et al.* [2], supporting the computed results. Thus the formyl radical has probably been shown to have the largest C—H bond length, approximately 1.14 Å, of any ground state molecule.

Nitrosyl hydride

The ground state of nitrosyl hydride has been shown to be ${}^{1}A'$ from flash photolysis studies, and the structure was accurately determined from the rotational

constants obtained in the same work [27, 28]. However, no vibrational frequencies for the ground state could be determined directly. HNO has in the present investigation been prepared from HI and NO in argon (containing 5% neon); in other studies [28] both HNO and DNO have been observed after photolysis of methyl and methyl- d_3 nitrites in argon at 4°K. The frequencies measured are presented in the fifth and sixth columns of Table 5. Another band beside those listed in the fifth

HNO	[31]	[29]	[4]	Present results	[30]
¥1	3300 (0-09)	3596	3375	3401 (0.006)	3447 (0.035)
v	1125 (0.06)	1110	1126	1098 (0.003)	1107 (0.07)
-	1110 (0.29)				
va	1570 (0.25)	1562	1570	1563 (0.017)	1554 (0.05)
•				1566 (0.014)	, ,
DNO				•	
¥1	2481 (0.08)	2680	2565		2569 (0.01)
v2	822 (0.02)	820	838		832 (0.01)
ν_{2}	1560 (0.06)	1550	1561		1543 (0.05)

Table 5. Frequencies attributed to HNO and DNO in the ground state ${}^{1}A'$ (Intensities in parentheses)

column of Table 5, at 1795 cm⁻¹, was also observed after the photolysis of hydrogen iodide in the presence of nitric oxide. It is assigned to nitrosyl iodide, unstable at ambient temperature, but previously detected as a transient absorption at 23000 cm⁻¹ in the flash photolysis of iodine in the presence of nitric oxide [32]; the corresponding fundamentals of NOCl and NOBr are respectively 1800 and 1801 cm⁻¹ [33]. This 1795 cm⁻¹ band was not produced when nitric oxide at similar concentrations in argon was photolysed in the absence of hydrogen iodide.

As is clear from Table 5, sufficient evidence has accumulated that there can be no doubt concerning the frequencies of v_2 and v_3 of both HNO and DNO, apart from small matrix shifts. In the case of v_1 of both isotopic species there are several different values, and their range is very large. Because 3447 cm⁻¹ has been observed on several occasions in different experiments, even though it has not been previously assigned to v_1 of HNO from such data [31, 4] the coincidence of this frequency with $3450 \pm 30 \text{ cm}^{-1}$ observed in chemiluminescent emission [34] both as $(1, 0, 0)'' \rightarrow$ (0, 0, 0)'' and as $(0, 0, 0)' \rightarrow (1, 0, 0)''$ ensures that this assignment is correct. In particular the reason for the non-assignment of 3450 cm^{-1} to v_1 of HNO was stated by BROWN and PIMENTEL [31] to be that the absorption appeared too broad, even with the NaCl prism optics used; however the repetition of the methyl nitrite experiment [28] produced an absorption at 3447 cm^{-1} with a bandwidth of about

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5 cm⁻¹, comparable with the effective spectral slit width of the spectrometer at that frequency. From other chemiluminescent work [35] the relations $v_1' - v_1'' =$ -560 cm⁻¹ for HNO and -380 cm⁻¹ for DNO have been reported; combined with the frequencies of the upper state observed directly in absorption, these equations yield 3414 and 2556 cm⁻¹ as estimates of unknown accuracy for the fundamentals being discussed. In fact anharmonicity effects will probably mean that these estimates constitute lower limits to the correct frequencies. A calculation of v_1 of DNO by the formula devised for DCO and based on 3450 cm⁻¹ for HNO yields the result 2555 cm⁻¹, in satisfactory agreement with both the preceding estimate [35] and some of the matrix infra-red absorption frequencies. The fundamentals and structural parameters for HNO and DNO are summarized in Table 7.

The hydroperoxyl radical

With the exception of the experiments of MILLIGAN and JACOX [5], attempts to obtain directly optical spectra of this important intermediate have been generally unsuccessful. The only positive spectrum consisted of two broad, diffuse and exceedingly weak bands near 10000 cm⁻¹ of which the indistinct separation seemed appropriate to a bending vibration frequency [36]. Although the previous cryogenic investigation of trapped hydroperoxyl was an extensive and thorough study [5], some missing fundamentals and a particularly curious statement that the filtering effect of halogen was the cause of reduced yields of this radical would have prompted the review of this subject.*

The two variations of the synthetic method used in the present experiments are similar to the procedures of MILLIGAN and JACOX [5]: irradiation with the lowpressure mercury lamp was either simultaneous with deposition of the 0.5% HI:2.5% $O_2:97\%$ Ar mixture or followed spectral scanning of the deposited mixture of 1% HI:2.5% $O_2:5\%$ Ne:91.5% Ar both at 4°K. In the former case, the infra-red absorption spectrum from 375 to 7000 cm⁻¹ showed absorption features only at 1100, 1389 and 3572 cm⁻¹. The latter frequency can be definitely assigned to the hydroxyl radical, as previously postulated [37].

In these HO_2 experiments the mechanism of formation of hydroxyl may be similar to that responsible for chemiluminescent emission [38, 39]:

$$\begin{aligned} \mathrm{HI} &+ h\nu = \mathrm{H} + \mathrm{I} \\ \mathrm{H} &+ \mathrm{O}_{\mathrm{2}} = \mathrm{HO}_{\mathrm{2}} \\ \mathrm{H} &+ \mathrm{HO}_{\mathrm{2}} = \mathrm{2OH}. \end{aligned}$$

^{*} Because halogen atoms, bromine or iodine in this case, do not absorb in the near ultraviolet, and even at their far ultra-violet resonant absorption frequencies the absorption line of the trapped atom would be very narrow, "halogen" [5] is presumed to imply diatomic molecules which ought not to be produced in significant yield if hydroperoxyl radicals are to be successfully trapped.

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Because oxygen may be dissociated by the 53800 cm^{-1} mercury resonance radiation from the low-pressure lamp, the following reaction sequence cannot be excluded:

$$\begin{aligned} \mathbf{O_2} + h\mathbf{v} &= \mathbf{2O} \\ \mathbf{O} + \mathbf{HI} &= \mathbf{OH} + \mathbf{I}, \end{aligned}$$

but the former scheme is more probable because of the small emission at the true resonance frequency. A by-product of the former reaction would be expected to be hydrogen peroxide, but none was detected, nor any water.

The 3572 cm^{-1} line having been properly assigned, the remaining frequencies which have been measured can be considered. The data are listed in Table 6, of which the footnotes explain the source of the frequencies in each column; frequencies known to belong definitely to H₂O and HNO have been omitted. A similar table, but much more extensive, has been included in a recent review of discharged water systems [40].

Comparison of the last three columns of Table 6 shows a consistency for the lowfrequency vibrations. The frequency near 1100 cm⁻¹, although associated with a weaker band than for 1389 cm⁻¹, is the only one in Table 6 reported only during experiments in which HO₂ was actually sought. As is emphasized in Table 7, this frequency coincides with one each of HNO and HCO. This frequency will now be assigned to v_2 , the bending vibration, of HO₂. The intensity of 1389 cm⁻¹ varies consistently with that of 1100 cm⁻¹ under the two conditions of production in this

Н ₈ О ₃ *	H ₂ O ₃ †	H ₂ O ₂ ‡	H ₂ O§	HNO	HO ₂ [5]	но,¶	Н0 ₁ **
3608				·			
3599				0700		BEER (0.04)	
	3578 (B)		3574 (VB)	3596		3572 (0.06)	
	3542 (w)						
		3469					
		3458					
	3417 (m)	(3417)	3416 (vw)		3414		3412 (0-01)
1380	1385 (vvw)	•	• •		1389-5	1389 (0-18)	1395 (0-07)
1266	1292 (vs)						· ·
					1101	1100 (0-11)	1104 (0-04)
880	870 (vvw)						,
500	595 (www)						
022	395 (vvv)						
371	300 (V8)						

Table 6. Frequencies measured in hydrogen-oxygen system experiments

* Fundamentals in gas phase [41]. Low-frequency bands in gas phase [42].

† H₂O₂ in N₂ matrix [43].

H₃O₃ in argon matrix (MOBROW and HARVEY, unpublished results, 1961) [44].

- § H₂O in argon matrix [45].
- || Ar, H, matrix [46].

¶ Argon matrix; irradiation with low-pressure Hg Lamp during deposition; present results.

** Ar, Ne matrix: irradiation after deposition; present results.

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	r(XH) (Å)	v 1 (cm ⁻¹)	Angle (degrees)	"; (cm ⁻¹)	r(XO) (人)	ν ₂ (cm ⁻¹)
HCO	1-148*	2482*	123-3*	1083 [20]	1-1765*	1861*
DCO	1.145*	1937 [3]		847 [20]		1800 [3]
CH	1.120 [23]	2733 [23]				
co					1.128 [23]	2143 [23]
HNO	1.063 [28]	3450*	108-6 [28]	1110*	1.212 [28]	1563 ¥
DNO		2565 [4]		830 [4]		1650 [4]
NH	1.047 [47]	3126 47				
NO					1.151 [23]	1878 [23]
HOO	(1.01)†	(3414) [5]	(100)†	1101†	(1-25)	1385 🛉 🗍
D00		(2530) [5]	· · · · ·	(1020) [5]		
OH	0.970 [23]	3570 [23]				
00		· · · ·			1-207 [23]	1556 [23]

Table 7.	Summary o	of structure	and fun	damentals	for	triatomio	radicals
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* Present results; see text.

† Proposed assignment; bond lengths are based on spectra-structure correlations.

work. This band has of course been reported in the earlier article on HO₂ [5]. It will now be assigned to HO₂, as previously, but to the O—O stretching frequency, r_3 . With this assignment to HO₂ in Table 7, one can now recognize the similar fraction of reduction, about 13 per cent (with a standard deviation of 2·3 per cent), of the X—O stretching frequency from the diatomic oxide XO to the triatomic radical HXO in the three cases. This reduction can reasonably be taken to correspond to the removal of one bonding electron from X—O π -bonds to pair with the hydrogen 1s electron in forming the H—X bond. This comparison tacitly assumes similar structures of the three species, HCO, HNO and HO₂, but WALSH has predicted this from application of simple molecular orbital theory [48]. WALSH has, in addition, predicted that HO₂ in a bent form should have a low-lying allowed transition from the ground state. This might be correlated with the very weak emission recorded by CLYNE and THRUSH [36], but a recent flash photolysis study failed to produce the corresponding absorption spectrum [49].

The ordering of the low frequencies in the above assignment for HO₂ is the same as in two recent estimates of the frequencies, but no structure was explicitly stated to be the basis of these estimates [50, 51], which are as follows for HO₂ (and DO₂): $v_1 = 3700$ (2650), $v_2 = 950$ (650) and $v_3 = 1230$ (1230) cm⁻¹. The new assignment differs sharply from that of MILLIGAN and JACOX [5]. A particularly critical test of these assignments would require the observation of the bending frequency of DO₂, but this was not reported [5]. The data of these authors on oxygen-18 substituted radicals seem to indicate unequivocally that the oxygen atoms of the hydroperoxyl radical are non-equivalent, thus eliminating the two structures in which the hydrogen atom is either central in the linear radical, as in FHF⁻, or at the apex of an acute isosceles triangle, as suggested in some molecular orbital computations [52]. Application of the formula, used earlier to calculate v_1 of DCO and DNO, with 3414 cm⁻¹ [5]

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as the O-H stretching frequency of some species yields 2514 cm⁻¹ for the O-D stretching frequency, so that the measured value of 2530 cm^{-1} is consistent in the previous assignment [5]. Because secondary reactions in the formyl radical system have been, by methanal formation, demonstrated to occur, an obvious extension would be the production of hydrogen peroxide in the present case. Although the O--H stretching fundamentals of H_2O_2 vapour are at 3599 and 3608 cm⁻¹ [41], bands at these positions have been observed in neither argon [44] nor nitrogen [43] matrices. In argon, hydrogen peroxide at matrix ratios of approximately 100 gave two bands at 3458 and 3469 cm^{-1} immediately after deposition, but these quickly disappeared as the sample was exposed to the glowing silicon carbide spectrometer source and were replaced by a broader band at 3417 cm^{-1} [44]. Apparently the heat from the source was sufficient at the matrix ratio employed to cause limited diffusion in the solid. Although the separation of the initial two bands, which matched that of the gas-phase fundamentals, and the diffusion characteristics make tempting the assignment of 3458 and 3469 cm⁻¹ to monomeric hydrogen peroxide, the matrix shift from the band centres of the carefully analysed vibration-rotation bands is anomalously large. In the nitrogen matrix [43], not only 3417 (medium intensity) but also 1385 (very very weak) and 3578 cm^{-1} (strong) were recorded. The presence of an intense band at 385 cm^{-1} strongly indicates by its breadth [43] that the hydrogen peroxide was not effectively isolated even at the stated matrix ratio of 500, although a less pronounced band-width behaviour has been attributed to hydrogen bonding with the nitrogen matrix [53]. On the other hand, if the observation of absorption at frequencies appropriate for hydroxyl and hydroperoxyl radicals points to their presence, then reasonable isolation in the matrix was achieved. The entire problem of decomposition processes of hydrogen-oxygen substances in cryogenic experiments is worthy of further intensive examination.

Conclusions

An improved structure has been calculated for the formyl radical suggested by deductions from the infra-red spectra of the radical trapped in cryogenic matrices. The frequency of the r_1 fundamental vibration of both HNO and DNO has been established. In the case of the hydroperoxyl radical an alternative assignment of the two observed low-frequency fundamentals has been proposed, but this is based on the assumption of the nitrosyl hydride structure. Further study of this system is required to settle the outstanding problems. The methoxyl radical and nitrosyl iodide may also have been detected by their infra-red absorption bands. The revised structural and vibrational assignments are presented in Table 7.

Acknowledgements—The author is grateful to Professor R. G. W. NORRISH, F.R.S. and his colleagues for their support of this work and to Mr. T. C. FLETCHER, Mr. C. OATES and Mr. C. SMITH for their technical assistance.

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