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T. B. Pierce
P. F. Peck
W. M. Henry

Analytical Chemistry Branch,
Atomic Energy Research Establishment,
Harwell, Berks.

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Infra-red Absorption of the Hydroxyl Radical

ALTHOUGH the vibration–rotation structure of the hydroxyl radical emission spectrum in the infra-red has been observed both from flames[1] and from the chemiluminescent reaction[2] of hydrogen atoms with oxygen molecules:

$$H \cdot + \cdot O_2 \cdot \rightarrow HO_2 \cdot$$
$$H \cdot + HO_2 \cdot \rightarrow 2 \cdot OH \dagger$$
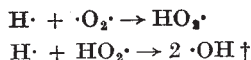
(where $\cdot OH\dagger$ denotes a vibrationally excited hydroxyl radical), there has been no report of the infra-red absorption spectrum of $\cdot OH$. The purpose of this communication is to suggest that the absorption of both $\cdot OH$ and $\cdot OD$ has been recorded without the identity of the carrier being discovered.

In investigations[3-5] concerned with the infra-red absorption of water molecules trapped in noble gas matrices at 4° K, there have been observed two sharp absorption lines, at 3,574 cm^{-1} in H_2O experiments and 2,635 cm^{-1} in the case of D_2O, both of variable intensity relative to other spectral features. These frequencies are close to the zero lines of the gas phase, calculated from electronic spectra[6] to be 3,569·6 cm^{-1} and 2,632·5 cm^{-1} for $\cdot OH$ and $\cdot OD$, respectively.

Again, in experiments[7] in which were frozen at 4° K the products from a discharged mixture of 50 per cent hydrogen (or deuterium) and 50 per cent argon reacted with a small amount of nitric oxide, an absorption band at 3,596 cm^{-1} (or 2,680 cm^{-1}) was observed besides the other absorption bands conclusively assigned[5,8,9] to nitroxyl, HNO. (In connexion with the assignment in ref. 9 of 3,380 cm^{-1} as the N—H stretching fundamental of HNO, better agreement with the infra-red emission from the hydrogen atom–nitric oxide reaction[10] would result from the alternative assignment of the feature at 3,450 cm^{-1} as this fundamental.)

There are three points to be considered in the proposed assignments for the hydroxyl radical: the mechanisms of formation, the frequency shifts in the solid matrices, and the absence of vibration–rotation structure.

In the case of the hydrogen atom reaction with nitric oxide, the hydroxyl radical could result from reaction of hydrogen atoms with nitrogen oxide impurities stated[7] to be present:

$$H \cdot + \cdot NO_2 \rightarrow \cdot OH + \cdot NO$$

or

$$H \cdot + N_2O \rightarrow \cdot OH + N_2$$
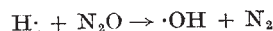
the former bimolecular reaction being particularly rapid[11]. Less easily solved is the mechanism of hydroxyl production in experiments in which 0·2–0·35 per cent water

in argon is simply deposited on a window at 4° K (refs. 3–5). Possibly significant are the facts that the 3,574 cm^{-1} absorption feature is absent when H_2O in argon is deposited at 20° K (refs. 12, 13), and that the thermal conductivity of solid argon is a maximum at 8° K (ref. 14), enabling greater deposition rates without loss of optical transmission and isolating power. A possible mechanism is that the friction of the gas mixture flowing about 5 m/sec through glass tubing toward the cold window could produce static electricity in the form of discharges in the gas, noble gases having comparatively small breakdown potentials. The principal effect of these discharges would be to cause dissociation of water in the gas phase either directly or sensitized by metastable argon atoms in the $^3P_1$ state. The energy of the metastable argon atoms could also be transferred to the water in the solid[15] through the intense band systems existing in solid noble gases[16]. The necessity for the discharge to be weak or sporadic is indicated by the results[5] of an experiment in which the products deposited at 4° K from a leak-tester discharged mixture of 0·5 per cent H_2O in argon showed no infra-red absorption attributable to hydrogen–oxygen species.

The observed frequencies of the matrix-trapped hydroxyl radicals are in all cases blue-shifted, being 3–4 cm^{-1} for H_2O and D_2O in argon[3-5] and 26 and 48 cm^{-1} for H_2O and D_2O in the argon–hydrogen mixed matrix[7]. The shift in the former case is small, and comparable to the shifts experienced with water itself[3,5]. In the latter case, the presence of about 50 per cent hydrogen in the solid causes the lattice sites to be smaller, thereby augmenting repulsive interactions of the trapped radical and hence tending to increase its stretching frequency, again in general concord with spectra of both water[3,5] and formaldehyde[17] bond-stretching fundamentals for these substances in noble gas matrices.

By analogy with HCl in argon at 4° K (ref. 18), one might expect to observe additional lines due to some reorientation process of $\cdot OH$, particularly in the argon matrix. However, no absorptions near 3,611 cm^{-1} or 2,655 cm^{-1}, the expected positions of $R(0)$ for H_2O and D_2O, have been observed, despite the intense absorptions at the Q-branch positions. That the observed matrix absorptions are blue-shifted is again relevant in that rotation of a solute molecule is unlikely if matrix conditions cause the molecule to be compressed.

Finally, the presence of the paramagnetic hydroxyl radicals in solid argon matrices also containing water provides a simpler mechanism for ortho-para nuclear spin conversion than the postulated oxygen impurity[3,4] certainly present (unless deliberately added) in a much smaller concentration than hydroxyl.

J. F. Ogilvie

Department of Physical Chemistry
and Emmanuel College, Cambridge.

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