Luminescence Studies: Luminescence of Aqueous Ionic Solutions; Temperature Dependence of the Phosphorescence of Phenanthene in Ethanol - Effects of Gases.

Terrence Lenoir Mathers

Louisiana State University and Agricultural & Mechanical College

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LUMINESCENCE STUDIES: LUMINESCEENCE OF AQUEOUS IONIC SOLUTIONS; TEMPERATURE DEPENDENCE OF THE PHOSPHORESCENCE OF PHENANTHENE IN ETHANOL - EFFECTS OF GASES

The Louisiana State University and Agricultural and Mechanical Col.  Ph.D.  1982

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LUMINESCENCE STUDIES:
LUMINESCENCE OF AQUEOUS IONIC SOLUTIONS;
TEMPERATURE DEPENDENCE OF THE PHOSPHORESCENCE OF PHENANTHENE IN
ETHANOL - EFFECTS OF GASES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by

Terrence Lenoir Mathers
B.S., Mississippi State University, 1975
May, 1982
Dedication

to my father

William Chester Mathers
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I wish to thank Professor Sean P. McGlynn for his many helpful comments during the writing of this manuscript. I also wish to thank him for suggesting the hydroxide luminescence problem as well as the temperature dependence of the phosphorescence of phenanthrene in ethanol and for his faith in my ability and patience during the slow development of this work.

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This work could not have been performed without the technical expertise of C. Boussert, A. Delaney, L. Edelen, J. Kass, M. Richardson, L. Rogge, F. Seab and G. Sexton.

I never realized the key role played by the typist in an undertaking such as the writing of a dissertation. Carol Young did a truly outstanding job and thereby helped me beyond words. Will Fournerat drew all Figures presented in this dissertation.
In the Fall of 1972 my life was darkness; my own actions had brought me to the brink of despair. To the One who lifted me up and opened my heart, and who gives me the strength and courage to live and to love, Jesus Christ, be all glory and honor forever.
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ABSTRACT

LUMINESCENCE STUDIES:

Part I. Luminescence of Aqueous Ionic Solutions

An anomalous luminescence of aqueous solutions of I⁻, Br⁻, OH⁻ etc. is observed and appear to be characteristic of the solvent. The emission of a KBr solution is greatly reduced by purification of the KBr. However, upon addition of acids, this emission reappears. Since all of the ions involved are known to have charge transfer to solvent (CTTS) transitions, the luminescence is postulated to be due to the recombination of H₃O⁺ and e⁻. Hydroxide and hydrosulfide appear to be a special case and may be transferring a hydrogen atom to the water. Discussions of the hydronium radical and the triplet state of water are presented. Neither of these entities can account for the luminescence; however, an excited state complex between water and a hydrogen atom may be involved.

Part II. Temperature Dependence of the Phosphorescence of Phenanthrene in Ethanol - Effects of Gases

The effects of various gases upon the temperature dependence curves of intensity and lifetime of the phosphorescence of phenanthrene in ethanol are studied. A shift of both the glass transition region and crystal formation region for ethanol is observed when oxygen or nitrogen is added to the sample. Other
nonpolar gases (Ar and Ethane) do not exhibit this shift. The effect for oxygen and nitrogen is explained by invoking hydrogen bond breaking by O$_2$ and N$_2$. A discussion of glass transition and hydrogen bond breaking studies is presented and found to support this suggestion. The work is extended to the melting curves of DNA, where a similar effect is observed.
The history of luminescence spectroscopy can be said to be the history of spectroscopy itself. Many of the earliest experiments in spectroscopy consisted of placing a sample in a flame or arc and dispersing the emitted light by prism or grating. G. R. Kirchhoff and R. Bunsen were instrumental in developing this technique for use in elemental analysis.¹

In a broad sense, any emission of electromagnetic radiation might be considered a luminescence. This term, and the sub-classifications fluorescence and phosphorescence are generally reserved for emission of visible, ultraviolet, vacuum ultraviolet, and x-ray radiation resulting from the transition of an electron in a system from a higher to a lower electronic state. Thus, the emission of radiation from an oscillating dipole or accelerated charge (synchrotron radiation), described by Classical Electrodynamics are not included in the term nor is Cherenkov Radiation (described by Relativistic Electrodynamics), Bremsstrahlung or pair annihilation emission (these latter being explained by Quantum Electrodynamics). Many other types of mechanisms exist by which radiation may be emitted. The basis for our understanding of quantum effects in fact, was laid in Planck’s analysis of Blackbody Radiation.

As stated, however, the main focus in chemistry consists of luminescence arising from electronic transitions. Einstein²
developed a useful relationship for a two level system:

\[
A_{m \rightarrow n} = \frac{8\pi \hbar \nu^{3}}{c^{3}} B_{n \rightarrow m}
\]

where \( A_{m \rightarrow n} \) is the Einstein coefficient for spontaneous emission and \( B_{n \rightarrow m} \) is the Einstein coefficient for stimulated absorption (which is equal to \( B_{m \rightarrow n} \) the coefficient for stimulated emission), and \( \nu_{mn} \) is the frequency of light corresponding to the energy difference between level \( m \) and level \( n \). The Einstein coefficient of stimulated absorption can be derived by time-dependent quantum mechanics and is equal to:

\[
B_{n \rightarrow m} = \frac{2\pi}{3\hbar^{2}} |R_{mn}|^{2}
\]

where \( R_{nm} \) is the matrix element for transition from state \( m \) to state \( n \):

\[
|R_{mn}|^{2} = |X_{mn}|^{2} + |Y_{mn}|^{2} + |Z_{mn}|^{2}
\]

where,

\[
X_{nm} = e^{<\psi_{m} | x | \psi_{n}^{0}>}
\]

which is the transition dipole moment in the \( x \) direction for the single electron being considered. This derivation may be found in xy.
detail in Eyring, Walter, and Kimball. The matrix element \( R_{mn} \), being an integral over all space, vanishes unless the product of the wavefunctions and \( x \) is totally symmetric. This constraint leads (for the hydrogen atom where the symmetry of the wavefunctions is dictated by the spherical harmonics) to the dipole selection rules, \( \Delta \ell = \pm 1 \), where \( \ell \) is the angular momentum of the wavefunction. The symmetry of the wavefunctions involved can thus be used to predict whether a transition will be dipole allowed or forbidden.

For molecules, while these concepts are certainly useful, other possibilities exist for transitions between electronic states. An excited state of a molecule may couple through vibrational modes to a lower state and decay via a radiationless transition. This process is called internal conversion. The molecule can also change multiplicity through a process called intersystem crossing. The quantum mechanical treatment of these processes is quite complex and at least in the case of internal conversion not completely understood since radiationless decay apparently has nonzero amplitude upon extrapolation to zero pressure.

Kinetic treatments for radiationless processes are well known and relatively simple. Each process is assigned a rate constant for each mechanism by which it can take place. For example the radiationless decay rate of the lowest excited triplet state of a molecule in fluid media is given by:
\[-\frac{dT}{dt} = k_1[T] + k_2[T]^2 + k_3[T] \cdot [S_0] + \Sigma(k_Q) \cdot [M_i] \cdot [T]\]

where \([T]\) is the concentration of the triplet species, \([S_0]\) the concentration of the unexcited species, and \([M_i]\) the concentration of any phosphorescence quenching impurity (e.g., oxygen). The rate constant \(k_1\) for unimolecular decay is the sum of radiative and non-radiative rate constants:

\[k_1 = k_P + k_{NR}\]

However, in many polyaromatic molecules this latter term may be quite small in solvents even at rather low viscosities. The second term, \(k_2\), corresponds to triplet-triplet annihilation and the third \((k_3)\) to formation of an excimer. The final term \(k_Q\) represents the rate of quenching of the triplet state by each impurity species.

Luminescence techniques can thus be used to study radiation-less transitions as well as the emission itself. Furthermore, intermolecular or intramolecular interactions are also amenable, in many cases, to study by these techniques. For example, conformations of proteins as a function of temperature might be investigated. The formation of excited state complexes (exciplexes and excimers) was discovered through changes in the luminescence at higher concentrations.

The apparatus used in the following studies was an American Instrument Company (Aminco) Keirs Spectrophosphorimeter. This
instrument has two monochromators one for excitation and one for emission, the gratings of which are blazed at 300 and 500 nm, respectively. The excitation source was a 150W Xe arc focused by a parabolic condensing mirror for greater intensity. The lamp intensity maximized at 400-450 nm. The photomultiplier tube, a Hamamatsu R136 (multialkali type), had a broad efficiency maximum at 450 nm. The usable range, however, was 160-800 nm.

Thus, the basic requirements for luminescence work were met—an excitation source, dispersing element and a detector—in both the visible and ultraviolet regions. As noted earlier, the term luminescence can be applied to higher energy regions of the electromagnetic spectrum as well. However, difficulties arise, in the vacuum ultraviolet (VUV) region, for instance, since the competing processes of autoionization, photochemical change, and dissociation become dominant. Also solvents and matrices which do not themselves absorb or emit upon VUV excitation are few, indeed.

The detection of x-ray fluorescence is well known. X-ray fluorescence arises when a valence or higher shell electron fills a hole in a lower or core orbital. This technique is much used in nondestructive analysis. The process of radiative hole filling is much less efficient for light elements (e.g., C, N, and O) since the emission of secondary or Auger electrons becomes dominant. The technique is worth developing, nevertheless, not for elemental analysis but for the possible study of bulk phase systems. The information generated by a soft x-ray spectrum is comparable to
that in Photoelectron Spectroscopy (PES) and thus biological molecules, for example, could be studied in a more realistic environment (since PES must be done on gas phase molecules or surfaces under vacuum). This possibility has been discussed in the literature.\textsuperscript{7}
REFERENCES


2. A. Einstein, Physik, Zeit., 18, 121 (1917).


LUMINESCENCE STUDIES

PART I

LUMINESCENCE OF AQUEOUS IONIC SOLUTIONS
Anomalous Luminescence of Some Aqueous Salts

Ionic systems in aqueous solution have two well-recognized mechanisms by which visible and ultraviolet light may be absorbed or emitted. That is, two basic types of electronic transitions are known. In common with nonionic systems, anions or cations can undergo a localized transition to a higher electronic state. In addition, these species may form complexes in which the charge density is rearranged by excitation, leading to an increase of the electronic charge density of one of them. This charge rearrangement is termed Charge-Transfer (CT) and the resultant excitation is referred to as a Charge Transfer Transition.

The localized transitions are of two types: one in which the electronic spin state is retained and one for which it changes -- with concomitant change in the multiplicity of the system. For example, a closed shell ground state species may absorb energy and be promoted to either a higher singlet or a higher triplet state. Since a closed shell system must be in a singlet spin state these two types of promotions are termed singlet-singlet and singlet-triplet transitions. These two types of transitions may be differentiated by their respective energies, their oscillator strengths, and their emissive lifetimes.

Transition metal cations (e.g., Cr$^{3+}$) are often colored because
of low-energy excitations of d + d and f + f types. These excitations give rise to absorption bands which are both very intense and very narrow. Since the transition is intrinsic to the cation and of localized nature, environmental effects upon it are minimal.

Polyatomic anions* also exhibit internal transitions although our understanding of them is not as complete as for the transition metal cations. Often the absorption spectra of anions consist of broad, overlapping featureless bands which are very difficult to interpret.

The tetrahedral transition metal oxyanions (e.g., MnO$_4^-$ and CrO$_4^{2-}$) possess well-resolved and highly-structured absorption bands.$^{1,2}$ These highly colored anions possess visible and ultraviolet transitions which can be assigned in the tetrahedral group nomenclature as $^1T_2 + ^1A_1$ and $^1T_1 + ^1A_1$. The lowest observed energy singlet excited state of permanganate is $^1T_2$ and the $^1T_2 + ^1A_1$ transition is responsible for the purple color characteristic of permanganate. Similarly, the chromate ion has a $^1T_2 + ^1A_1$ excitation which causes the yellow-orange color of this ion.

The cyanate ion is another example of this type. This species was studied by Rabalais et al.$^{3,4}$ and found to have a transition assigned as $^1Σ^- + ^1Σ^+$ at 197.3 nm (50,684 cm$^{-1}$). A small shift was noted (approximately 2,000 cm$^{-1}$) upon change of the associated

*Monoatomic anions such as Br$^-$, Cl$^-$, etc., are believed not to possess bound excited states.
cation from sodium to lead. A second transition of the cyanate ion was also studied and it was found that this absorption peak varied from 285 to 300 nm again depending upon the cation involved. These systems also emitted, yielding a phosphorescence at 77K. The luminescence assignment was taken to be $3\Gamma^+ \rightarrow 1\Gamma^+$ because of the increase of oscillator strength, $f$, and decrease of lifetime, $\tau$, caused by cadmium, mercury and lead cations.

An idealization of the behavior of internal transitions is known as The Principle of Additivity of Ionic Colors.\textsuperscript{5,6} This principle states that the color obtained upon combining a colored cation and a colored anion is merely the sum of both colors. This supposition is thought to pertain to all spectral regions.

Deviations from this idealization have been discussed.\textsuperscript{7-9} These deviations can arise by one or several of the following mechanisms:

1. Spin-orbit enhancement of the intensity of $T_1 \leftrightarrow S_0$ transitions of the anions.

2. Alteration of energy of certain anionic transitions because of perturbations by the cation — perturbations which arise from either polarization or distortion of the anion by the cation.

3. New transitions arising from charge rearrangement of the ionic complex, that is Charge Transfer (CT) transitions.

The last mechanism, presumably characteristic of all anions, does not require post-transition element cations. Absorption bands
which are sensitive to the cation of the anion/cation system are indicative of CT transitions. An example can be found in the nitrate ion. The spectra of several nitrate salts were reported by Maria et al.\textsuperscript{10} In most but not all cases, they assigned the lowest-energy band as CT. The CT assignment was bolstered by the observed effects of solvent polarity, since CT transitions are also very sensitive to the characteristics of solvent. In the work cited, the CT band maximum shifted from 28,330 cm\textsuperscript{-1} for the ferric salt to 40,980 cm\textsuperscript{-1} for that of the mercuric, and the CT transition of the cupric salt shifted from 33,800 cm\textsuperscript{-1} to 37,000 cm\textsuperscript{-1} upon changing solvent from dioxane to ethanol.

Luminescence of a CT state has not been demonstrated although some anions which exhibit CT bands do show emission. The nitrate ion, for instance, shows an emission of light; however, this luminescence has been assigned to spin orbit enhancement of the lowest singlet $\leftrightarrow$ triplet transition. Indeed, the radiationless decay of CT bands is probably very fast\textsuperscript{9} making the emission of these bands either very weak or non-existent.

A luminescence which is not easily assigned has been observed in low temperature aqueous solutions of some acids and salts. A very similar blue emission (maximum $\sim$400 nm) is observed upon photolysis of aqueous hydroxide ion solutions. This long lived radiance has been attributed to the $^4I^-$ state of the hydroxyl radical by Maria and McGlynn.\textsuperscript{11} Problems with this assignment have been pointed out by Merkel and Hamill,\textsuperscript{12} who argued that the lowest
triplet of the hydroxide ion may be responsible.

The difficulty in assigning this luminescence is not surprising in light of some of the unusual features it possesses. For example, two decay components have been reported to exist: a fast one of \(~0.1 s\), and a slow one of \(~1 s\). Additionally, while the excitation maximum of the luminescence depends strongly upon the anionic species in the solution, the emission band shows almost no dependence on this factor. Finally, no cationic dependence is shown, either by the emission or the excitation maxima, although the emissive lifetimes are shortened by heavy-metal cations.

The interpretation of this luminescence as a low-lying triplet state of the hydroxide ion is questionable. The emissive state (3.11 eV above the ground state) is considerably higher in energy than the ionization potential of hydroxide ion at 1.8 eV. Also, in concentrated acid solutions, the life-time of the hydroxide ion even at 77K, would probably be considerably shorter than 0.1s.

The argument against the luminescence being due to the hydroxyl radical is an energetic one -- the excitation onset is far too low in energy to allow both ionization and excitation of the hydroxide ion. A two photon process is doubtful both on an experimental and a theoretical basis.\(^{11,12}\)

Because of these observations we will consider the possibility that the solvent, namely water, is itself involved in the phenomenon of interest.
Relationship to the 4.5 eV Absorption in Water Systems

A luminescence has been attributed to water in both the radiolysis\textsuperscript{13-15} and electron impact excitation\textsuperscript{16,17} of low-temperature ices. The reported emission spectra bear a strong resemblance to those observed for aqueous ionic solutions. Therefore, we inquire into the relationship, if any, which exists between these phenomena.

Several experimenters have reported an absorption in water systems in the 4.5 eV region\textsuperscript{18}. A tentative assignment for the excited state involved in this absorption is either the $^3B_1$ or $^3A_2$ state of water. The luminescence of ice has been supposed to initiate in the same low-lying triplet state of the water molecule. However, this assignment has never been corroborated by theoretical calculations.

The luminescence, while not understood, appears to be real and not artifactual: other techniques yield similar results. Bernas and Truong,\textsuperscript{19-21} for example, observed an emission, $\lambda_{\text{max}} \approx 380$ nm, upon illumination of gamma irradiated ice. These workers also observed an extremely weak luminescence upon mercury sensitization of ice.

**Thesis -- The Hydronium Radical as Causitive Factor**

An hypothesis which may explain the phenomena reported for both aqueous salt luminescences and pure water systems invokes the presence of the hydronium radical, $\text{H}_3\text{O}^+$. Since hydrogen atoms are readily produced upon reaction of water with electrons, as well as in the radiolysis of water, this supposition is not unreasonable.
The existence of the $\text{H}_2\text{O}^*$ radical has been a topic of considerable debate. These arguments will be presented in the discussion following the presentation of our experimental results and of our calculational data set for this species.

Briefly, three different mechanisms could give rise to $\text{H}_3\text{O}^*$.

First, electrons produced upon photolysis of anions present in aqueous acid solutions could recombine with the "hole" $\text{H}_3\text{O}^+$. Electron-Hole recombination luminescence is very well known.\textsuperscript{\textsuperscript{22}}

Again, in basic solutions, the hydroxide ion may dissociate into $\text{O}^-$ and $\text{H}^*$. Indeed, interstitial hydrogen atoms have been reported upon excitation of hydroxide-doped KBr.\textsuperscript{\textsuperscript{23}} Finally, hydrogen atoms may be produced, as stated earlier, by reaction of electrons and water. Hydrated electrons and hydrogen atoms may even be said to be interchangeable.\textsuperscript{\textsuperscript{24}} These hydrogen atoms could then react with water to form $\text{H}_3\text{O}^*$.

Some theoretical support exists for this hypothesis. As shall be discussed later, Bader and Gangi\textsuperscript{\textsuperscript{25}} found a metastable conformation for the hydronium radical with a lowest excited state 4.4 eV above the ground state. Since the barrier to dissociation was found to be 6.6 Kcal/mole, this species might exist at low temperatures. Even if the ground state of this species is not stable, an excited state of it, in the form of an exciplex (excited state complex) between water and hydrogen, might be.
CHAPTER II
THE 4.5 eV ABSORPTION IN WATER SYSTEMS

Experimental Work

An absorption of energy by water at energies below the first optically-allowed transition (which occurs at 7.45 eV) was originally reported by Schulz in 1960. Schulz used the "Trapped Electron" (TE) method, which is a type of electron impact spectroscopy.* In the TE technique, the inelastically scattered electrons with less than 0.3 eV energy are collected by a grid-plate arrangement; the resultant current is plotted versus the incident electron kinetic energy. A small flat peak was observed beginning at an incident electron energy of 3.5 eV and continuing up to the onset

*Electron Impact Spectroscopy (EIS) differs in two essential ways from an Electron Scattering (ES) experiment. In EIS, the incident electron energy is varied, usually from near zero energy to energies slightly higher than the first ionization potential (IP) (so that the first nonrelativistic Born approximation does not apply). In ES, on the other hand, the energy is held constant at a level somewhat higher than the first IP (so that the Born approximation is valid). The methods of detection differ also: in EIS the inelastically scattered ("slow") electrons are trapped in a potential well (such as a grid-plate arrangement), whereas in ES the electrons are analyzed for both angular and energetic distribution.
of the first large peak. A number of maxima, all thought to correspond to optically-observed transitions, were found at 7.3, 9.2, 10.1, and 12.4 eV.

Eleven years later, Knoop et al. improved the technique and reinvestigated the water spectrum. Their method which they termed "Double Retarding Potential Difference", gave better energy resolution and also eliminated the negative ion current in Schulz's work. In their apparatus, both incident and detected electrons passed through energy analyzers. The collision chamber, surrounded by a mantle held at a positive potential, acted as a potential well for negative ions. Futher separation of the electrons and ions was effected by a magnetic field parallel to the beam of the electrons. Using a potential well of 2 eV they substantiated the work of Schulz: they found a small maximum between 4.4 and 4.6 eV incident electron energy. This peak was tentatively assigned as a transition from the ground state of water to a low-lying triplet state with B1 or A2 symmetry.

In a different electron impact method, inelastically-scattered electrons were scavenged by SF6 and the resultant SF6 ions were counted using time-of-flight mass spectroscopy. Once more a small broad absorption was noted: onset at 4.1 with continuation to 6.1 eV where, again, the distinct maximum at 7.45 eV began. The broadness of the 4.5 eV band was supposed to arise from dissociation of the water above 5.1 eV, which is the bond dissociation energy.

The Low Energy Electron Reflection (LEER) spectrum of ice was
reported in two papers by Lewis et al.\textsuperscript{30,31} In this technique, electrons are incident on a thin film of sample at 45°. Electrons which are reflected by the sample and which pass a retarding grid are collected by a Faraday cup. Lewis found a large drop in the collected current for ice in the 4-5 eV range. This work was thought to be corroborative of the existence of a low-lying triplet state of water.

A feature similar to the one found in EIS was observed by several groups in electron scattering experiments on water.\textsuperscript{18,32-34} Typical results are found in the paper by Trajmar et al.\textsuperscript{18} These scientists found an increase of two orders of magnitude in the 4.5 eV band (normalized to the 7 eV peak) upon going from 0-90° scattering angle and the incident electron energy equal to 20 eV. This large variation of band intensity with angle has been found to be typical of spin forbidden transitions.\textsuperscript{35}

A more recent study\textsuperscript{34} has shown that the 4.5 eV phenomenon is real but that it probably arises from contamination of the collision chamber by interaction of the sample and the walls. This conclusion was based on several findings. The first anomaly was the lack of a peak in the 4-6 eV region of H\textsubscript{2}O in H\textsuperscript{+} and H\textsubscript{2}\textsuperscript{+} scattering experiments: these techniques are of use in detecting triplet states in other systems. Secondly, the 4-6 eV absorption increased greatly after the collision chamber had been saturated with water vapor. Furthermore, heating of the sample chamber caused a significant reduction of the 4.5 eV signal. Finally,
time-of-flight mass spectroscopy measurements confirmed that the
signal arose from inelastically scattered electrons and not from a
negative ion current, in agreement with the results of Lassetre and
Huo.\textsuperscript{33}

**Optical Spectroscopy**

An extremely weak absorption in the UV region was reported by
Larzul et al.\textsuperscript{36} This absorption which had a maximum at 276 nm ($\nearrow4.5$
eV), was observed by the differential pathlength absorption method.\textsuperscript{†}
The sample cells were made of nickel and the net pathlength was 79.2
cm. The water used was doubly distilled and the deuterioxide had an
isotopic purity of 99.76%. The small maximum for water at 276 nm
was increased several-fold upon deuteration. While the authors did
not interpret the spectra, this paper was frequently cited as
additional evidence of a triplet state at $\nearrow4.5$ eV.

A recent paper by Quickendon and Irvin,\textsuperscript{37} in which the dif­
f erential path method was also used, found no evidence of a maximum
for water in this wavelength region. Instead, a monotonically
increasing absorption from 320 to 196 nm was observed. This absorp­
tion could be attributed almost completely to the sum of Rayleigh

\textsuperscript{†}The differential path absorption method is a double beam experiment
in which samples of slightly different pathlengths are placed in
both beams. A net absorption is observed. The corrections,
mandatory to this technique, for scattered light and wavelength
dependent window reflections are fully discussed in reference 37.
scattering and the low energy tail of the $\tilde{A} \text{^1B}_1 \rightarrow \tilde{X} \text{^1A}_1$ transition. The net pathlength in these later experiments, only 9 cm, was shown to be sufficient to reproduce the earlier work. It was concluded that organic impurities were the probable explanation for the peak observed in Reference 36 since, in the distillation procedures of Quickenden et al. these impurities were thoroughly eliminated.

**Luminescence Studies**

The electron impact and scattering work may be explained in terms of water-saturated walls and the optical absorption relegated to impurities; however, a luminescence is found in low temperature ices (e.g., 77K) upon radiolysis, mercury photo sensitization, photo bleaching after $\gamma$-irradiation, and electron impact on thin films and this luminescence has not been explained. Some of these results have been attributed to a low-lying triplet state of water.

For example, Merkel and Hamill observed that ice films at 77K show two emission bands, one at ~280 nm which was attributed to the hydroxyl radical and a second at ~380 nm which was suggested to be the $\text{^3B}_1 \rightarrow \text{^1A}_1$ transition of water. The two peaks apparently do not arise from the same mechanism since the 280 nm peak appeared at incident electron energy $\geq 9.1$ eV whereas the 380 nm peak appeared only at incident electron energy $\geq 12$ eV.

This work was confirmed and improved by later workers who found that the 380 nm maximum was composed of three separate peaks at ~400, 440, and 490 nm. The excitation of these maxima was found
to onset at ~12.6 eV, identical, within experimental uncertainty, to the first ionization potential for water. These peaks were tentatively assigned as non-Frank-Condon transitions for the ion-electron recombination luminescence arising from the $\tilde{A} \, ^3A_1$ or $^3B_1$, $\tilde{B} \, ^1A_1$ or $^1B_2$, and $\tilde{C} \, ^1B_1$ or $\tilde{D} \, ^1A_1$ states respectively. Finally, the hydroxyl radical luminescence, previously assigned$^{16}$ at 280 nm, was found$^{17}$ to lie at 306 nm (e.g., at the same wavelength as the gaseous hydroxyl radical emission).

An almost identical luminescence has been observed upon charge neutralization of $\gamma$-irradiated ices.$^{19-21}$ In charge neutralization, electrons generated during the $\gamma$-irradiation are detrapped from the lattice by photo-bleaching and may recombine with any positive ions present. Two bands were evident in ice. A 305 nm band, again due to the $^2e^+ \rightarrow 2\pi$ transition of hydroxyl, and a 380 nm band suggested to be a $T_1 \rightarrow S_0$ emission of water produced by the mechanism

$$H_2O + h\nu \gamma \rightarrow H_2O^+ + e^-_m$$

The symbol $e^-_m$ denotes an electron trapped in the ice matrix. Hydronium ion production proceeds as

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH^-$$

Upon photo-bleaching, the electron may recombine with the hydronium ion according to

$$H_2O^+ + e^-_m \rightarrow H_2O$$
\[
H_3O^+ + e^- \xrightarrow{\text{hv}} H^* + H_2O^*
\]

which then decays to the ground state with production of an \( H_2O \) luminescence

\[
H_2O^* \rightarrow H_2O + h\nu_F
\]

The recombination of the electron with the hydronium ion could also proceed differently

\[
H_3O^+ + e^- \rightarrow H_2 + OH^* \]

\[
OH^* \rightarrow OH + h\nu_F
\]

and give rise to an hydroxyl radical emission.

An extremely weak luminescence was also reported\textsuperscript{19,20} upon mercury photosensitization of water. In this experiment, water and mercury were stored in two separate branches of a three branch suprasil vessel and then condensed simultaneously by dipping the third branch in liquid nitrogen. The condensed ice-mercury mixture was then illuminated using the 254 nm \( ^3P_1 \) emission line of a low pressure mercury arc. The luminescence was centered at \( \approx 380 \) nm. Triplet-triplet energy transfer from the mercury to the water (which then emitted) was suggested as an explanation for the presence of this band.

Finally, ice has also been reported to luminesce upon radio-lysis.\textsuperscript{13-15} This emission exhibited a maximum at 373 nm and
possessed two decay components (possibly indicative of two mechanisms for luminescence production), one quite fast, the other somewhat slower. The band contours for both fast and slow components were found to be identical. Both components showed an increase upon addition of NaCl, NaBr, NaI, and HCl and a decrease upon addition of H$_2$O$_2$ and AgNO$_3$. No effect was found when CCl$_3$COONa or CH$_2$ = CHCONH$_2$ (acrylamide) was added in concentrations as large as 1 M, even though these are known to be good traps for solvated electrons and hydroxyl radicals.

Deuteroxide, in addition to the 373 nm band, exhibits a second band with maximum at ~534 nm. This new band is not affected by addition of H$_2$O$_2$ and only slightly by AgNO$_3$. Thus, a different mechanism must be involved in the production of the 534 nm band. This idea is supported by the different temperature dependences of the 373 and 534 nm bands. The 373 nm band also exhibited two lifetime decay components as mentioned, while the 534 nm emission was short lived.

Finally, a thermoluminescence with maximum at ~335 nm was observed and reached its maximum intensity upon warming to 120K. This band was reduced by the electron scavengers sodium trichloroacetate and acrylamide. It was also found to increase if the ice was annealed at -25°C for 24 hours prior to cooling to 77K. Steen suggested that this band and not the one at 373 nm was due to $T_1 \rightarrow S_0$ emission of water.
Luminescence of Aqueous Ionic Compounds

A luminescence of aqueous ionic systems was reported by Maria and McGlynn. This luminescence was quite similar to that of ice. Indeed, Grossweiner and Matheson found that the luminescence of ice upon radiolysis was both intensified and shifted to lower energies by the addition of ionic solutes. For example, they reported that the maximum for the luminescence of ice was shifted about 12 nm and intensified by a factor of about six upon addition of NaOH or NaCl. These authors believed this luminescence to arise from recombination of the cations (Na⁺, K⁺, etc.) with a solvated electron. This idea was dismissed by Steen and Holteng who showed the intensification was probably due to the anions (Cl⁻ < Br⁻ < I⁻). The previous authors (Grossweiner and Matheson) also found a second peak at ~478 nm when the cations Rb⁺ and Cs⁺ were present. Neither Steen and Holteng nor Maria and McGlynn investigated this finding.

As discussed in the earlier section, Maria and McGlynn suggested that the observed emission was due to the \( ^4\Sigma^- \) state of the hydroxyl radical produced in acid and salt solutions by the mechanism

\[
\begin{align*}
X^- + \text{hν} & \rightarrow X^*_{\text{aq}} + e^-_{\text{aq}} \\
 e^-_{\text{aq}} & \rightarrow H^*_{\text{aq}} + (OH^-)^*_{\text{aq}} \\
(OH^-)^*_{\text{aq}} & \rightarrow OH^*_{\text{aq}} + e^- \\
OH^*_{\text{aq}} & \rightarrow OH^- + \text{hν}
\end{align*}
\]
This mechanism can explain some of the observed phenomena but, as stated previously the excitation energy (≈5.0 eV) is far below that required to produce excited hydroxyl radicals from either water (≈9.1 eV) or hydroxide ions (≈9.0 eV). Finally, this quartet state is dissociative in the gas phase and probably does not exist long enough in low temperature ices to give rise to a long-lived luminescence (≈1s).

In all of these experiments two common factors exist: free electrons and water. The spectrum of electrons in water and ice is well known and no emission of such systems has been reported. Other common elements are also present in the same systems: H*, OH*, and OH-. These species will be considered in the discussion.

Review of Theoretical Work

Many calculations have been done on the ground and excited states of water. These computations have used various types of basis sets and approximations. It is beyond the scope of this discussion to evaluate all of these calculations since, in many instances, water merely served as a convenient test case for new computational modes and theories. Therefore, only those papers which deal directly with the question of a low-lying triplet state of water will be discussed.

One of the earliest papers on extended basis set Hartree-Fork calculations of the lowest excited states of water was that by Horsley and Fink. In this work, a minimum basis set of Gaussian functions (GTO's) was supplemented by the addition of a diffuse
orbital centered on the oxygen. A ground state energy of -75.9117 hartrees was calculated and the lowest excited state \(3\beta_1\) symmetry) was found lie 7.3 eV higher (vertical excitation, i.e., same geometry as ground state). The potential surfaces of the \(\bar{B}^1,3\alpha_1\) states were also studied. Both of these excited states were found to be planar, the triplet lying at 7.22 eV (adiabatic transition, i.e. geometry rearrangement). In addition, the dissociation of these two states was investigated. Other excited states were not studied with respect either to their potential surfaces or their dissociation behavior.

Calculations for \(\text{H}_2\text{O}\) and \(\text{H}_2\text{O}^-\) were done shortly afterwards by Claydon, Segal and Taylor.\(^{40}\) They used the INDO approximation,\(^{41}\) in a Hartree-Fock SCF mode, and a minimum basis set which did not include diffuse orbitals. The lowest triplet state, of \(B_1\) symmetry, was found to be 6.22 eV above the ground state. A minimum energy of 4.76 eV above the ground state was found for this state upon geometry optimization (adiabatic transition). The ground state energy was not given so the quality of these calculations can not be judged by this means. The importance of diffuse functions in calculations of excited states of water, however, is now well established.\(^{42}\) Furthermore, the INDO approximation, which was developed for closed shell ground state systems, is not a good approximation for excited states. This work has historical significance, nevertheless, since these were the only calculations ever reported for which an excited state of water was found lower
than 6 eV above the equilibrium ground state.

More rigorous calculations in the Hartree-Fock scheme were done by Hunt and Goddard\textsuperscript{43,44} using their "Improved Virtual Orbital" (IVO) technique. In this method, the standard Fock operator,

\[ H_{\text{HF}} = \sum_{\mu} h_{\mu} + \sum_{j} (J_{j} - K_{j}) \]

where \( h_{\mu} \) is the one electron operator

\[ h_{\mu} = -\frac{1}{2} \nabla_{\mu}^{2} - \frac{Z}{r_{\mu}} \]

and \( J_{j} \) and \( K_{j} \) are the coulomb and exchange operators, respectively,

\[ J_{j}(\mu)\phi_{j}(\mu) = \langle \phi_{j}(v) | \frac{1}{r_{\mu v}} | \phi_{j}(v) \rangle \phi_{j}(\mu) \]

and

\[ K_{j}(\mu)\phi_{j}(\mu) = \langle \phi_{j}(v) | \frac{1}{r_{\mu v}} | \phi_{j}(v) \rangle \phi_{j}(\mu) \]

is modified by deleting the self-coulomb and self-exchange operators (i=j). This yields

\[ H_{\text{EX}} = \sum_{\mu} h_{\mu} + \sum_{j \neq i} (2J_{j} - K_{j}) + J_{i} + K_{i} \]

where the positive sign gives the excited singlet state operator and the negative sign that of the excited triplet state. Since the self coulomb and self-exchange terms are deleted, the ground state gives
virtual orbitals which are variationally correct approximations to
the excited states (vertical excitations). Hence these energies may
be obtained by adding (or subtracting) the coulomb and exchange
integrals for the orbital desired. In the resultant calculations of
water several diffuse functions were added to approximate the
Rydberg character of the excited states. A lowest excited state
(A^3B_1) was found at 6.68 eV above the ground state. No potential
surfaces were studied.

Potential surfaces were calculated for the ground and first ^3B_1
state by Bader and Gangi.\textsuperscript{45,46} They found a vertical excitation of
6.11 eV from the ground to the higher state. The linear molecule
did show a decrease of this energy difference to 4.53 eV but the
experimental work indicates a vertical transition from the
equilibrium geometry of the ground state. Two hundred and fifty
points were calculated in the potential surfaces of these states
with a small (5,3/2) basis.\textsuperscript{**} An extended basis set (10,5,2/4,1)
contracted to (5,3,2/2,1)\textsuperscript{†} was used for selected points. Their
equilibrium ground state energy was found for the larger basis to be
-76.045 hartrees only 0.044 hartrees below the estimated
Hartree-Fock limit.

\textsuperscript{**}This notation means 5 s-orbitals on the oxygen along with 3 p-
orbitals. The hydrogen atoms had 2 s-orbitals. They added an
additional diffuse s function for the ^3B_1 state.

\textsuperscript{†}As above, with 2 d-orbitals added on oxygen and 1 p-orbital added
on the hydrogens.
Studies with Configuration Mixing

The potential energy surfaces were calculated beyond the Hartree-Fock level by Hosteny et al. They used a 4-31G basis set with added diffuse s and p functions centered on the oxygen, all with exponent of 0.026. The Hartree-Fock ground state energy (with bond angle 105° and bond lengths of 0.9525 Å) was found to be -75.9126 Hartrees with the $3B_1$ state 6 eV above this energy (-75.9126 H) for vertical excitation. Slater determinants for seven double excitations were added in the multi-configuration self-consistent field (MCSCF) step. The configurations added were thought to express most of the correlation energy due to molecular formation. The first $3B_1$ state of water was lowered 0.63 eV (to -75.7152 H) by this correlation energy at the aforementioned geometry. The potential surface for various bond lengths was calculated and the $3B_1$ state was found to be dissociative. The bond angle was, however, fixed at 105° while the true equilibrium bond angle for the $3B_1$ state is probably 180°.

Extensive configuration interaction (CI) calculations for the ground and $3B_1$ states were presented in a paper by Winter et al. These calculations included all of the single and double excitations from each symmetry orbital except $1a_1$ (which corresponds to the 1s orbital of the oxygen atom). The contracted (4s, 2p/2s) basis of Dunning's was used with additional diffuse s and p

$^\dagger$The orbital exponents of which were both 0.028.
functions centered on the oxygen. The Hartree-Fock ground state energy (-76.01114 H) was lowered by 3.47 eV (-76.13869 H) while the B state of water (Hartree-Fock energy of -76.7908 H) was only lowered 2.21 eV (to -76.87193 H). The vertical excitation energy from the ground to \( ^3B_1 \) state was thus increased from 6.0 to 7.26 eV. Several higher excited states were also calculated and found to be in good agreement with the known experimental energies.

Restricted Hartree-Fock calculations were carried out by the author in conjunction with A. Liakus using a lobe\* gaussian program (written by G. A. Gallup). A \((4,5,2/2,1)\) contracted Dunning's basis set with added diffuse s functions on oxygen (exponents equal to 0.025 and 0.010) and hydrogen (exponents equal to 0.010) was used. This basis set gave a ground state energy of -76.0503 H. The potential energy curve for the \( ^3B_1 \) state (with fixed bond lengths of 0.9572Å) for a symmetric bending mode was calculated. The minimum energy was found at bond angle 110°, at which point the energy was 6.25 eV (-75.8205 H) above the ground state. This

\*Lobe gaussian functions differ from cartesian ("normal") gaussian functions in the angular dependence representation. In a certain gaussian program this dependence is input as an algebraic expression, while in a lobe gaussian program this dependence is calculated by numerical differentiation of the gaussian basis function. This technique allows greater flexibility in the basis set. See Whitten, reference 81.
energy difference was found to increase upon configuration mixing in agreement with the results of Winter et al. These calculations were not pursued further.

The theoretical work on the $^3B_1$ state of water shows that the assignment of the luminescence of low-temperature aqueous systems to a low lying triplet state of water is almost assuredly incorrect. The related luminescence of aqueous ionic solutions may hold the key to an understanding of this phenomena, since the luminescence observed from ice under ionizing radiation could arise from a number of mechanisms.
Hydroxide Solutions

The luminescence of aqueous hydroxide solutions was reinvestigated by the author in order to try to resolve the controversy concerning its assignment. As shown in figure 1, the first excitation band of the 400 nm emission, onsets below 210 nm and maximizes between \( \lambda \sim 245-250 \text{ nm} \). Furthermore, a small shoulder is apparent in the region of 280 nm. This shoulder, which appears stronger in some spectra than others (see figures 2-4), is not understood. However, it produces an identical emission as excitation at 245 nm.

The emission band (cf. figure 1) is similar to virtually all emission bands observed for aqueous systems. This band onsets around 350 nm, increases very rapidly to a maximum between 400-410 nm and then declines quite slowly, exhibiting a long, low-energy "tail" which finally disappears around 600 nm.* Little intensity variation was observed in this spectrum in the concentration range \( 10^{-4}-10 \text{ M} \).

Figure 2 displays the effects of various cationic species on this luminescence. As reported previously,\(^{11}\) the intensity

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*This spectrum and the others following it have not been corrected for either lamp output or phototube response.
Excitation and Emission Spectra of 0.5 M NaOH @ 77K. Excitation monitored with emission wavelength of 405 nm. Emission monitored with excitation wavelength of 245 nm.
Relative Intensity

NaOH
0.5 M

EX  EM

Wavelength nm
increases somewhat for the heavier cations, possibly indicative of a spin-forbidden transition. The various cations have very little effect on band shapes or maxima, although the shoulder at ~280 nm appears to have intensified in the LiOH spectrum.

The deuter oxide ion produces the spectrum shown in figure 3. The hydroxide and deuter oxide samples were prepared by reaction of metallic sodium with triply distilled water in the first case and commercial D$_2$O (99.8% isotopically pure) in the second. In both cases, the concentration was ~0.1 M. A shift is observed in the excitation spectra for NaOD. The first maximum appears to blue shift by ~5 nm (~800 cm$^{-1}$) to 240-245 nm, while the shoulder at 280 nm has apparently increased and red shifted by approximately the same amount. Some of this shift can be attributed to the greater resolution of the NaOD spectrum due to the increase of the second band. Tinti$^{50}$ has observed, however, that, for hydroxyl radicals trapped in a neon matrix, the 0,0 absorption and emission lines were blue shifted from 308.12 to 307.12 nm upon deuteration. A similar shift is possible for the hydroxide ion.

Since the 0,0 band for hydroxyl has been found around 280 nm in ice systems,$^{16,19}$ we might postulate a build-up of hydroxyl radicals as the explanation of the shoulder and its intensification upon deuteration. Further discussion of this possibility will be included in Chapter V.

The intensity of the luminescence increases gradually with time for non-degassed samples whereas the intensity is constant when the
Figure 2

Excitation and Emission Spectra, nongassed, of 0.5 M CsOH, of a saturated solution of Ba(OH)$_2$·8H$_2$O (≈0.3 M), and of 0.34 M LiOH. Emission monitored with excitation wavelength of 250 nm. Excitation monitored with emission wavelength of 400 nm.
Figure 3

Emission and Excitation Spectra of 0.0818 M NaOH and of 0.10 M NaOD. Excitation monitored with emission wavelengths of 410 and 400 nm, respectively. Emission monitored with excitation wavelengths of 245 and 288 nm, respectively. The emission of NaOD with excitation of 240 nm was found to be identical to that with excitation of 288 nm.
sample is degassed. It had been reported\textsuperscript{11} previously that removal of oxygen increased the luminescence intensity. This effect was attributed to oxygen quenching of the phosphorescence. The slow temporal increase observed in non-degassed samples is indicative of a different mechanism. Since oxygen is a good trap for both solvated electrons and hydrogen atoms, the slow increase in time may be indicative of depletion of the oxygen via reaction with intermediate species. Hydroxide is known to decompose to hydroxyl radicals and electrons as well as to hydrogen atoms and oxide ions\textsuperscript{23} upon photolysis, and some of these entities may well be the requisite intermediate species.'

Hydrogen peroxide is also a good trap for electrons and H-atoms but not for hydroxyl radicals. Therefore, a sample containing 0.5 M NaOH and \textasciitilde0.9 M H\textsubscript{2}O\textsubscript{2} was prepared.* No luminescence was observed, suggesting as does the slow temporal increase just discussed, that either the solvated electron or the hydrogen atom is a precursor to the luminescence event.

Several additional solvents were investigated. Methyl alcohol exhibited considerable solvent luminescence even after extensive purification. Distillation over sulphanilic acid was finally found to reduce this self-emission. Upon addition of \textasciitilde0.1 M NaOH, a luminescence identical to the solvent self-luminescence reappeared. This spectrum is shown in figure 4. This luminescence is somewhat

*3\% H\textsubscript{2}O\textsubscript{2} by weight.
Figure 4

Excitation and Emission Spectra of 0.1 M NaOH in MeOH. Excitation
monitored for 390 nm emission wavelength. Emission monitored for
225 nm excitation wavelength.
NaOH in MeOH

Relative Intensity

EX    EM

Wavelength nm
different from that observed in aqueous systems. The excitation shows an intense peak at 220-225 nm with a much smaller one at ~265 nm. The emission is also blue shifted from aqueous systems, the onset occurring at ~325 nm and the maximum at ~380-385 nm. Again, a rather long "tail" persists. This emission was also considerably stronger than that observed for aqueous systems.

The fact that an identical luminescence was observed before treatment with sulphanilic acid prevents us from ruling out the methoxide ion as the possible emitting species at this time. Even though this ion is a much stronger base than hydroxide, a small amount may have been formed when the solution was made. In either case this spectrum is interesting.

Ethanol was also investigated as a solvent. NaOH is slightly soluble in this solvent and it forms a good glass at 77K. No emission was observed. Ethanol does not trap free electrons but can react with both hydrogen atoms and hydroxyl radicals. Since hydrogen peroxide traps electrons and hydrogen atoms and ethanol traps hydroxyl radicals and hydrogen atoms, the fact that neither system exhibits luminescence tends to suggest that the luminescence precursor is either the hydrogen atom or a combination of OH· and e−.

Acetonitrile and glycerol were also investigated as solvents but both exhibited unacceptable amounts of self-emission.

Luminescence of Acids and Salts

A luminescence similar to that of the hydroxide ion is found in
Excitation and Emission Spectra of 0.092 M KBr and of 0.18 M KI.
Excitation monitored with emission wavelengths of 430 and 420 nm, respectively. Emission monitored with excitation wavelengths of 270 and 280 nm, respectively.
aqueous systems of some salts and acids. For example, in figure 5, the luminescence spectra of KBr and KI are shown. The onset for both is \( \approx 350 \text{ nm} \), as is observed for hydroxide. The maxima have shifted somewhat (to 420-430 nm) but the band shape and the low energy "tail" for each are very similar to that observed for hydroxide.

While the emission spectra of both salts are similar to hydroxide, the excitation spectra of all three entities are very different. The bromide excitation spectrum is fairly symmetric with a single maximum near 260 nm and a FWHM* of approximately 70 nm. The excitation spectra for iodide, on the other hand, is both lower in energy, with maximum near 280 nm, and narrower, with FWHM of 30 nm than that of bromide.

The bromide emission was found to be greatly reduced upon recrystallization from water thus implying that some water soluble impurity is involved in the emission of these salts. Since the emission of hydroxide systems is quite similar to that of the unpurified KBr, it might be reasoned that the impurity in question for bromide systems is the hydroxide ion itself. As can be seen in figure 6, however, the luminescence is seen even in concentrated acid solution. The excitation for HI is similar to that of KI. However, the HI emission maximizes at \( \approx 400 \text{ nm} \) instead of \( \approx 420 \text{ nm} \) as in KI.

*Full width at half maximum.
Figure 6

Excitation and Emission Spectra of 1.3 M HI. Excitation monitored with emission wavelength of 400 nm. Emission monitored with excitation wavelength of 280 nm.
The iodide and bromide entities are ions which possess absorption bands known as Charge Transfer to Solvent (CTTS). In this type of transition, the ion, upon photolysis, loses an electron to the solvent so that a solvated electron and a free radical are produced. These types of transitions are sensitive not only to the solvent but to the concentration of other species and to the temperature. The similarity of the excitations for HI and KI seem to indicate that the luminescence of these salts and acids are initiated by a CTTS process. We therefore investigated several other known CTTS ions for this luminescence.

In figure 7, the excitation and emission spectra of sodium thiocyanate are presented. The emission spectra, by now familiar, are normal. The excitation spectra show concentration effects. At low concentrations the sample is polycrystalline; the excitation onset is \( \lambda \approx 225 \text{ nm} \), the maximum appears at \( \lambda \approx 260 \text{ nm} \) with a shoulder around 285 nm. The luminescence vanishes for excitation wavelengths above 325 nm. At high concentrations (8 M), the sample is a glass and the excitation onset is \( \lambda \approx 240 \text{ nm} \) with a maximum at 280 nm and total loss of signal around 345 nm. This concentration effect is to be expected if the luminescence truly originates from a CTTS transition.

In figure 8, the spectra of hydroxide and hydrosulfide are compared. The hydrosulfide emission is shifted considerably from that of hydroxide, the onset occurring at \( \lambda \approx 370 \text{ nm} \) and the maximum at \( \lambda \approx 430 \text{ nm} \). The excitation of hydrosulfide is also different from all pre-
Figure 7

Excitation and Emission Spectra of 0.1 M and of 8 M NaSCN.

Excitation monitored with emission wavelengths of 415 and 410 nm, respectively. Emission monitored with excitation wavelengths of 258 and 280 nm, respectively.
Figure 8

Excitation and Emission Spectra of 0.4 M NaSH and of 0.5 M NaOH.

Excitation monitored with emission wavelengths of 430 and 405 nm, respectively. Emission monitored with excitation wavelengths of 300 and 245 nm, respectively.
vious ions. The excitation band originates around 225 nm, rises to a shoulder about 270 nm and peaks at ~305 nm. The FWHM of the 305 nm peak is approximately 40 nm.

**Relationship to CTTS**

All of these ions, including hydroxide ion, are known to possess CTTS transitions. As stated, these absorption bands are quite sensitive to solvent and solvent state, concentration, temperature, and even pressure. For example, the first absorption band of iodide shifts almost 50 nm (10,000 cm⁻¹) when an ammonia solvent is replaced by glycerol. The temperature dependence of the first absorption band of iodide ion in water is on the order of -12 cm⁻¹/degree. This figure was obtained in liquid solution and changes of state would generally not fit this pattern since the sample is now in a "new" solvent. It would be interesting to study the detailed effects of glass formation, for example, on these transitions.

Because of the solid state, we would not presume to see a normal temperature effect on these transitions. Indeed, we would not expect even to see an identical shift for all ions upon going to 77K. However, we might forecast some general trend in the shift from absorption maximum at room temperature to the excitation maximum at 77K. In Table I, this comparison is made. In each case, as expected, the excitation maximum is lower in energy than the

---

†A recent study has been found, see reference 82.
Table I. Shift between absorption maximum of first CTTS transition in water (20°C) and excitation maximum for emission in ice (77K). Units of cm$^{-1} \times 10^3$.

<table>
<thead>
<tr>
<th>Species</th>
<th>Abs. Max.</th>
<th>Ex. Max.</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>I$^-$</td>
<td>44.3</td>
<td>37.0</td>
<td>7.3</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>49.1</td>
<td>41.6</td>
<td>7.5</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>53.5</td>
<td>40.0</td>
<td>13.5</td>
</tr>
<tr>
<td>SH$^-$</td>
<td>43.5</td>
<td>32.7</td>
<td>10.8</td>
</tr>
<tr>
<td>SCN$^-$</td>
<td>45.0</td>
<td>38.5</td>
<td>6.5</td>
</tr>
</tbody>
</table>
absorption maximum in water at room temperature and, for I\(^-\), Br\(^-\), and SCN\(^-\), the shifts are of the same order of magnitude.

The shifts for hydroxide and hydrosulfide, while similar to each other, are larger than the other three systems. Hydrogen bonding to the solvent might be invoked to explain these latter cases. However, evidence has already been presented that, in the case of hydroxide, the hydrogen atom is a likely precursor to the luminescence. If this species is also involved in the luminescence of hydrosulfide, the anomaly becomes understandable. The transfer of a hydrogen atom to solvent, which we term HTTS, would be expected to be more greatly shifted from the CTTS absorption. If the CTTS absorption band involves a state with Rydberg character, as has been suggested,\(^{52}\) a competing reaction of bond dissociation might well occur. This competing reaction might take precedence over electron transfer in some instances (e.g., in strongly hydrogen bonded systems such as aqueous hydroxide at low temperatures).

As stated previously the luminescence of KBr (and, hence, probably all of the CTTS anions* except OH\(^-\) and SH\(^-\)) virtually disappears upon purification. Therefore, the emission, which evidently is initiated by a CTTS transition, must be the result of a recombination of the free electron and some impurity. Based on the evidence that the hydroxide emission has a hydrogen atom precursor and the

*The emission of SCN\(^-\) was not reduced upon extensive purification;\(^{80}\) however, isothiocyanic acid may still have been present.
Figure 9

Excitation and Emission Spectra of 10 M $\text{H}_2\text{SO}_4$ : 1 M KBr and 10 M $\text{H}_2\text{SO}_4$. Excitation monitored with emission wavelengths of 420 and 400 nm, respectively. Emission monitored with wavelengths of 240 and 248 nm, respectively.
10 M H₂SO₄
+ 1 M KBr

10 M H₂SO₄

EX          EM

Wavelength nm
resemblance of the luminescence of ice under ionizing radiation to the luminescences we have observed, the impurity was postulated to be H⁺. Purified KBr was therefore added to acid solution. The results are presented in figures 9-12. Unfortunately, the acids themselves possess a slight self-emission and it becomes necessary to present the spectra of both the acid and the acid:KBr solutions.

In figure 9, the spectrum of 10 M H₂SO₄ is compared to that of 10 M H₂SO₄:1 M KBr. As is evident, a large increase of the excitation peak at ~240 nm is observed. This peak is comparable to the excitation peak observed for concentrated HBr (also at ~240 nm). The probable explanation of the difference between this excitation band and that of figure 4 is a simple concentration shift. The emission maximum lies at ~415-420 nm.

The same phenomenon is also observed for 1 M H₂SO₄:1 M KBr (figure 10). In this sample the sulphuric acid self-emission is somewhat larger and, as a result, the intensification observed is only a factor of two. Again, however, only one band of the "pure" H₂SO₄ excitation spectrum intensifies. The excitation maximum of 1 M-H₂SO₄:1 M KBr shifts slightly to ~245 nm, further evidence of a concentration effect.

Finally, in figure 11 the sulphuric acid is replaced by phosphoric acid. Again, a two-fold intensification is observed. The excitation maximum for 1 M H₃PO₄:1 M KBr lies at ~245 nm as in the previous sample.
A similar experiment was performed with NaI. However, since this compound reacts rapidly with sulfuric acid, hydrofluoric acid was substituted. Both systems emit faintly. Upon joint solution, however, a large increase of intensity was observed (figure 12). The excitation maximum lies at $\approx 275$ nm (i.e., the excitation is identical to that of the previous iodide emissions). A yellow discoloration of the ice at the point of irradiation was noted in this sample probably due to production of $I^*$ or $I_2$.

It is somewhat speculative to assert that the increase of intensity for the acidified solutions is due to charge recombination luminescence of $H_3O^+$ and $e^-$. However, this reaction seems to be the most likely explanation. Certainly, the luminescence is due to charge recombination of some cationic species with a free electron but the identity of the cation, if it is not $H_3O^+$, is yet to be determined. If the hydronium ion is the precursor to emission, as has been suggested previously, it could upon recombination produce luminescence by at least two mechanisms:

$$H_3O^+ + e^- \rightarrow H_3O^\ast \rightarrow H^+ + H_2O^\ast$$

$$H_2O^\ast + H_2O + h\nu_p$$

This mechanism seems improbable in light of our earlier discussion. A second mechanism is:
Figure 10

Excitation and Emission Spectra of 1 M H₂SO₄:1 M KBr and of 1 M H₂SO₄. Excitation monitored with emission wavelengths of 420 and 410 nm, respectively. Emission monitored with excitation wavelengths of 248 and 250 nm, respectively.
1 M H₂SO₄

+ 1 M KBr

EX    EM

Relative Intensity

200  300  400  500  600
Wavelength nm
Figure 11

Excitation and Emission Spectra of 1 M $\text{H}_2\text{PO}_4$ :1 M KBr and of 1 M $\text{H}_3\text{PO}_4$. Excitation monitored at emission wavelengths of 420 and 400 nm, respectively. Emission wavelength monitored at excitation wavelengths of 250 and 246 nm, respectively.
Relative intensity

1 M $\text{H}_3\text{PO}_4$

+ 1 M KBr

1 M $\text{H}_3\text{PO}_4$

EX  EM

Wavelength nm

200  300  400  500  600
Figure 12

Excitation and Emission Spectra of 0.5 M HF:0.5 M NaI, of 0.5 M NaI, and of 0.5 M HF. Excitation monitored at emission wavelengths of 410, 410, and 420 nm, respectively. Emission monitored at 277, 275 and 270 nm, respectively.
Relative Intensity

0.5 M NaI
+ 0.5 M HF

0.5 M NaI

0.5 M HF

EX  EM

Wavelength nm
\[ \begin{align*}
H_3O^+ + e^- &\rightarrow H_2O^* \\
H_2O^* &\rightarrow H_3O^+ + hv \\
H_3O^* &\rightarrow H^+ + H_2O
\end{align*} \]

At the present time the ground state of the hydronium radical appears to be unstable with respect to dissociation to H* and H_2O in the gas phase.\textsuperscript{25} All experiments reported here however, were carried out in an ice matrix at low temperatures, which may or may not give added stability to the ground state.

Many recent studies into excimers have shown that excited state complexes can form even when the ground state complex is unstable. Further discussion of this possibility will be found in Chapter V.
CHAPTER IV
ON THE HYDRONIUM RADICAL

Theoretical Considerations

The possible existence of free radicals of the type HA·, where A is a hydrogen bond acceptor molecule (or ion), was proposed by H. J. Bernstein. He assumed that the bond dissociation energy \( D(H-A) \) is given by

\[
D(H-A) = D(X-H) - D(X-HA) - \Delta H
\]

where

\[
-\Delta H = D(XH-A) = \Delta H_f(A) + \Delta H_f(X-H) - \Delta H_f(XH-A)
\]

is the enthalpy of hydrogen bond formation of A with the donor X-H. This assumption is correct only if \( \Delta H_f(X-HA) = \Delta H_f(XH-A) \); that is, if the hydrogen atom is in a single-well potential between X and A. A Morse potential* was taken as a model potential so that \( D(X-H) \) and \( D(X-HA) \) could be found using IR data for \( \nu(X-H) \) and \( \nu(X-HA) \). For OH bonds, the value obtained in this way was 5-25 Kcal/mole. Since typical hydrogen bond strengths lie in the range 2-8 Kcal/mole, Bernstein estimated that this new type of free radical had a stability of 7-33 Kcal/mole.

Shortly thereafter a letter from T. J. Sworski provided

*\( v(r) = D \left[ 1 - e^{-a(r - r_e)} \right]^2 \) for which: \( v_e = \frac{\sqrt{\pi} D e}{\pi c u} \).
kinetic evidence for the existence of the hydronium radical as a precursor to molecular hydrogen formation in the process of water radiolysis. In a study of the effects of solutes on $G(H_2)^+$ Sworski showed\textsuperscript{55} that the precursor to this process disappeared by a first order kinetic route. Sworski's investigations involved the process $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ in irradiated nitrate solutions hence it was shown that the reduction of cerium was inversely proportional to the concentration of nitrate but independent of pH. The known rate constants,\textsuperscript{56} $8.15 \times 10^9 \text{M}^{-1}\text{s}^{-1}$ and $2.06 \times 10^{10} \text{M}^{-1}\text{s}^{-1}$ for the nitrate and hydronium ions, respectively, for reaction with $\text{e}^-_{\text{aq}}$ were adequate to prove, since the reduction process was independent of pH, that $\text{e}^-_{\text{aq}}$ was not involved in the reaction.

Following these first papers, numerous workers have attempted to assess, quantum chemically, the stability of $\text{H}_3\text{O}^+$ and the related species $\text{NH}_4^+$. A brief discussion of these calculations follows.

The earliest calculations were single-center,\textsuperscript{57,58} that is, combinations of Slater determinants composed of orbitals all centered on the heavy atom were used. All calculations found the $\text{H}_3\text{O}^+$ radical to be stable with respect to autoionization, but thermodynamically unstable because the independent water-hydrogen atom system was of lower energy. Potential energy curves however, were not calculated.

Extended basis set restricted SCF calculations were performed

\begin{equation*}
^4G(H_2) = \text{number of molecules produced per 100 eV incident energy.}
\end{equation*}
by Bader and Gangi.\textsuperscript{25} They used the same basis set as for water, (see reference 45) with an added diffuse s orbital centered on the oxygen, i.e. an (11,5,2/4,1) primitive set contracted to (6,3,2/2,1). The optimal geometry was calculated to be C\textsubscript{3v} with O-H bond lengths of 0.9837\text{Å} and bond angles of 111.77°. The energy for this configuration was found to be -76.496 hartrees. This energy is considerably ( 30 Kcal/mole) above the -76.543 hartrees found* for the separated system. A barrier of 6.6 Kcal/mole to dissociation was found, however, which led the authors to surmise that this radical might be stable in low temperature matrices. These authors also calculated a barrier to inversion of ∼2 Kcal/mole and an ionization potential of 4.6 eV. Finally, the excited states calculated at the minimum energy geometry were found to have vertical excitation energies of 4.4 eV (\(2E^1 + 2A_1\)) and 5.2 eV (\(2A_1 + 2A_1\)).

Several other papers\textsuperscript{59-62} have dealt with the hydronium radical in cursory fashion. Lathan et al.,\textsuperscript{59} using STO-3G and 4-31G basis sets, found a minimum energy for a hydrogen bonded hydroxyl radical-hydrogen molecule system, the dissociation to the free species being endothermic by 0.6 Kcal/mole. This complex was also found to be of lower energy than that of the separated water-

*The calculated energy of water in this basis, -76.043 + 0.5 hartrees (since the energy of the hydrogen atom by definition is 0.5 hartrees).
hydrogen atom system. This erroneous result was attributed to lack of polarization functions (p orbitals) on the hydrogens. Blustin and Linnett,\textsuperscript{60} using the Floating Spherical Gaussian Orbital (FSGO) method (a model, in which orbitals are positioned between atoms, which was developed "not to obtain an accurate solution of the Schrodinger wave equation but rather to develop a relatively simple scheme of calculations and possibly give alternate and perhaps improved concepts for understanding chemical phenomena"	extsuperscript{63}), found both $\text{H}_2\text{O} + \text{H}^*$ and $\text{H}_2 + \text{OH}^*$ complexes to be slightly stable and to exhibit a strong dipole/induced dipole character.

Webster,\textsuperscript{61} in a study of the mechanisms of generation of the hydrated electron, discussed the formation of $\text{H}_3\text{O}^*$ as

$$\text{H}_3\text{O}^+ + e^-_{\text{aq}} \rightarrow \text{H}_3\text{O}^*$$

The radical could either dissociate into $\text{H}_2\text{O} + \text{H}^*$ or lose an electron to reform the starting species. The momentary retention of an electron in this manner, and the supposition that this retention was a significant step in the formation of the solvated electron, was discounted since the relaxation of the solvent cage ($\approx 10^{-10} \text{ s}$) would be much longer than the time of development of the solvated electron spectrum ($\approx 10^{-12} \text{ s}$).

Efskind\textsuperscript{62} used semiempirical INDO techniques to address the question of whether the hydronium radical was stable in aqueous solution. He found, indeed, a stable gas phase radical but all of
the radical complexes with water were predicted to be unstable.

The question of the gas-phase stability of the hydronium radical seems to have been laid to rest by the work of Niblaeus et al. who studied potential energy surfaces using unrestricted Hartree-Fock calculations with configuration interaction (UHF-CI). Of the three basis sets they tried, only the largest showed a potential minimum. This basis was the only one to include polarization functions and these do not appear to have been optimized. The barrier to dissociation was found to be 4.6 Kcal/mole in the UHF step and was reduced to 3.4 Kcal/mole when configuration interaction was included. Therefore, the authors concluded that this species probably would not exist even in a low temperature matrix since the zero point energy, which they calculated to be on the order of 4 Kcal/mole, should be greater than the dissociation barrier.

The most striking aspect of this work appears to be the dependence of the dissociation energy surface on polarization functions. Bader and Gangi used two uncontracted sets of d functions on oxygen and one set of p functions on the hydrogens -- sets which, although not optimized, seem to be better than those used by Niblaeus. Thus, the suggestion that the lower potential barrier found in the latter work was due to spin polarization and a better geometric optimization technique would appear suspect.

To test the possibility that the better d function sets of Bader and Gangi might have been responsible for the larger potential barrier found by them, the problem was reinvestigated using the pre-
viously mentioned water basis in Chapter II. This basis set (I) is
given in Table II, as is another basis set (II) which is also based
on that of Dunning but to which additional diffuse s and p orbitals
sets on oxygen and hydrogen have been added. The basis set I,
although based on Dunning's (9,5,2/4,1) contracted basis set, was
adapted by A. Liakus to a lobe gaussian program for the calcula-
tions presented in Chapter II and was used without readaptation in a
cartesian gaussian program. The small factor* difference involved
showed no evident effect on either the energy or geometry of H$_2$O,
H$_3$O$^+$, or H$_3$O$. The calculations were done using the Gaussian 80
program of J. S. Binkley et al.$^{65}$

The optimal geometry and energy of water calculated with these
two basis sets are compared in Table II to those of Niblaeus and to
the experimental parameters. Several facts are obvious, the most
important of which may be the rather large increase in the cor-
relation energy calculated for the set with the uncontracted oxygen
p and d functions. All other results are quite similar, with the
difference of the bond length and bond angle between sets I and II
apparently due to the diffuse p functions which were added to set II.

*This factor, which was 0.983992 for the p functions and 0.979559
for the d functions, had the effect of changing the effective
Slater coefficient of the d orbital of oxygen from 1.93 to 1.95.
Similarly, this exponent was changed from 2.53 to 2.55 for the
hydrogen p functions.
In every case, the geometry used for the configuration interaction was that obtained with the gradient optimization package of Gaussian 80 ("Berny Optimization") in the UHF approximation. Therefore, only one geometry is shown. The effect of configuration interaction on the optimum geometry in Niblaeus' work was to increase bond lengths considerably. This geometry optimization, however, was not perform for their CI calculations which included polarization functions.

The proton affinities (PA) calculated for water are also given in Table III. These affinities are compared to those of Dierkesen et al. which were found by subtracting the difference of the zero-point energies of water and the hydronium ion from the difference in the calculated energies. The former was estimated to be

$$\Delta E_0 = 18.75 - 13.47 = 5.28 \text{ Kcal/mole}$$

The results of their calculations on $\text{H}_3\text{O}^+$ are given in Table IV. Excellent agreement is found between the results of both basis sets and the calculations of Dierkesen, even though the CI geometry was reoptimized in this last work. The experimental parameters are not known with any degree of accuracy.

Again, a rather large increase of correlation energy is observed for basis set I. The CI energy, for each basis, was 1.5 Kcal/mole less than for the corresponding water system, as reported by Dierkesen. Thus, the change in the correlation energy appears to
be fairly independent of the basis set contraction; however, the
total correlation energy is not. The electron affinities shown in
Table IV are merely the difference between the energies of the
hydronium ion and the hydronium radical for the optimal geometries.
These UHF values are very close to those obtained by placing an
electron in the lowest virtual orbital of $\text{H}_3\text{O}^+$ (which gives energies
0.003 and 0.004 hartrees higher for basis sets I and II,
respectively), indicating close compliance with Koopmans' theorem.
The significant increase in electron affinities observed between the
two basis sets is evidently due to the optimized diffuse p functions
added to set II. A large increase in electron affinity is observed
also between the UHF and CI calculations in both sets. This
increase is greater in the second set even though the total
correlation energy calculated is much less, which indicates that the
diffuse p functions on oxygen and hydrogen improve the CI
calculation as well.

Table V shows the optimal parameters obtained for the hydronium
radical for these two basis sets, as well as those obtained by the
previous workers. Again, basis set II stands out since the geometry
is significantly altered and the energy is lower than in any
previous calculation at the UHF level. The correlation energy, while
less than that of basis set I, has increased relatively compared to
the water calculations. Thus, the thermodynamic instability has
been reduced by the diffuse functions.
The Hartree-Fock limit has been estimated as -76.50207 hartrees. The energies calculated for basis set II indicate that the correct limit must be at least -76.522 hartrees, since the calculation for water is 0.015 hartrees above the limit using this basis (see Table III). This estimate, however, must be considered only as an upper bound.

The minimum potential energy curves for the reaction:

\[ \text{H}_3\text{O}^+ \rightarrow \text{H}_2\text{O} + \text{H}^+ \]

are shown in figures 14 and 15, the data being given in Table VI. In figure 14, the potential barrier for basis set I is found to be 6.0 Kcal/mole, while for basis II it is only 4.1 Kcal/mole. The reduction of the potential barrier found by Niblaeus et al.\textsuperscript{54} was evidently due to the more diffuse hydrogen functions while they used and not to the reasons they cited.

In figure 15, the results for CI calculations are presented. The large barrier in figure 14 for basis set I is seen to be reduced to 3.6 Kcal/mole, in excellent agreement with the findings of Niblaeus. This barrier is somewhat further reduced in basis set II. The correlation energy difference between these two curves is almost constant from the point of minimum geometry out to infinite separation.

It is now evident that the differences of the earlier workers are totally due to the basis sets employed. Indeed, the effect of
Figure 13

Illustration of parameters used in calculations of the hydronium radical.
Figure 14

UHF potential curves for $\text{H}_3\text{O}^+ + \text{H}_2\text{O} + \text{H}^+$. 
Figure 15

Configuration Interaction (with all double excitations excluding core orbitals) potential curves for $\text{H}_3\text{O}^+ + \text{H}_2\text{O} + \text{H}^+$. 
diffuse hydrogen $p$ functions indicates that an electron added to $\text{H}_2\text{O}^+$ increases the charge density on the hydrogens and that it is not completely centered on the oxygen, as had been suggested.

The Hartree-Fock limit estimated here is probably accurate, in which case the hydronium radical is definitely thermodynamically unstable in the gas phase by $\approx 11.8$ Kcal/mole. Nevertheless, a resonance between $\text{H}_2\text{O}$ and $\text{H}^-$ may exist with an activation energy of 15-20 Kcal/mole. The recent study of Walch and Dunning$^{57}$ showed a potential barrier to the reaction of $\text{OH}^-$ and $\text{H}_2$ to form $\text{H}_2\text{O}^+ + \text{H}^-$ of $\approx 6$ Kcal/mole. Since the barrier for $\text{H}_3\text{O}^+$ dissociation is on the order of 3-4 Kcal/mole, an excess energy of only 2-3 Kcal/mole above the estimated resonance energy would be needed to overcome this second barrier and produce $\text{OH}^- + \text{H}_2$. This supposition is being investigated. This species might then be the first transition state complex studied at this level of calculational accuracy.

**Experimental Considerations**

Direct observation as well as indirect evidence for the existence of the hydronium radical has been claimed by numerous authors. These claims have been refuted in some cases, rendered questionable in others and sometimes ignored. A brief survey of these papers follows.

One of the first papers in which direct evidence for $\text{H}_3\text{O}^+$ was given was that by Melton and Joy,$^{58}$ who also did single center calculations on the molecule. In the experimental portion of this paper, water vapor was irradiated by 100 eV electrons. The neutral
products (and negative ions) of this reaction were allowed to pass through a slit into an ionizing chamber and then through a mass spectrometer. A significant increase in signal was observed for mass number 19, indicating possible production of H$_3$O$^*$. The appearance potential for the H$_3$O$^+$ signal (which was what was actually detected) was found to be 10.9 eV (thus, an ionization potential was also established). An alternate method of production, placing the water vapor in contact with hot platinum (which procedure, when applied to ammonia vapor, produced a significant increase in the NH$_4^+$ signal) failed to produce any increase in the H$_3$O$^+$ signal, which was taken as indicating an I.P. greater than 9 eV for H$_3$O$^*$. These results have not been refuted although it has been noted that the observed increase was relative, and possibly ascribable to other causes.

An E.S.R. signal thought to be that of H$_3$O$^*$ was reported shortly thereafter by Martin and Swift in a Ce$^{4+}$:HClO$_4$ aqueous glass at 77K. Photolysis of the glass produced an H$_2$O$^+$ signal which was transformed, upon warming, into a 1:3:3:1 quartet with hyperfine splitting constant of 22.84 Gauss. Addition of NaN$_3$ was found to quench this signal but not that of CH$_3$ obtained upon addition of acetic acid. This quartet was assigned to H$_3$O$^*$, even though it was very similar to that observed for CH$_3$*. This conclusion was dismissed by several later authors$^{68-71}$ who showed that i), the hyperfine splitting, g factor and line shape matched those of CH$_3$* within experimental error,$^{68-69}$ ii), that the calculated hyperfine
splitting (in the INDO approximation) was on the order of 131-150 Gauss,\textsuperscript{70} in disagreement with that observed; and iii), Claxton et al.\textsuperscript{71} did observe an E.S.R. signal from a water-hydrogen atom system, not in the form of H\textsubscript{3}O\textsuperscript{+}, but of a weakly "hydrogen bonded" complex. (An earlier work by two of these authors\textsuperscript{72} explained the observed absorption of hydrogen atoms in water by a weakly "hydrogen bonded" system as well.)

Evidence for the hydronium radical as an intermediate in the radiolysis of water vapor was given by Boyd et al.\textsuperscript{73} The yield of HD in this system exhibited a marked deuteration effect (3-6 fold) which could not be explained other than by invoking a complex between hydrogen atoms and water. This same conclusion was reached by Kongshang et al.\textsuperscript{74} who measured the pH dependence of Br\textsuperscript{-} produced by radiolysis of aqueous solutions of bromophenol. They concluded that the hydrogen atom is not the primary product of the reaction of solvated electrons and hydronium ions since H\textsuperscript{+} is as efficient in producing Br\textsuperscript{-} as e\textsubscript{aq}\textsuperscript{-}. They postulated that H\textsubscript{3}O\textsuperscript{+} must be the primary product in this reaction.

Negative evidence for H\textsubscript{2}O was presented by Bassi et al.\textsuperscript{75} who measured the cross-sections of H-atom scattering from water at H-atom velocities of 1300-4400 m/s. They found no evidence of any resonance in this energy region (0.2-2.3 Kcal/mole)*, although they

\*Since E = 1/2 mv\textsuperscript{2} = 1/2 (1.008 amu x 1.66 x 10\textsuperscript{-27} Kg/amu) (1300 m/s)\textsuperscript{2}. Thus, E = 1.4 x 10\textsuperscript{-21} J x 1 eV/1.6 x 10\textsuperscript{-19} J = 0.00884 eV = 0.205 Kcal/mole.
suggested that a resonance (or "glory structure") might be seen at lower energies. In light of the calculations presented, this suggestion is incorrect since at least 15 Kcal/mole is required to reach resonance.

The recent work of Williams and Porter,76 in which neutral fragments were produced by electron capture reaction by H\textsubscript{3}O\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{+}, and CH\textsubscript{5}\textsuperscript{+} for Na\textsuperscript{*} or K\textsuperscript{*} vapors, also makes the existence of this species suspect in the gas phase. The electron affinity for H\textsubscript{3}O\textsuperscript{+} was found to be 5.1 ± 0.3 eV (0.1875 hartrees) and the fragmentation energy was given as -1.12 ± 0.07 eV (25.94 Kcal/mole) for the reaction:

\[ \text{H}_3\text{O}^* \rightarrow \text{H}_2\text{O} + \text{H}^* \]

This latter value is not in good agreement, however, with the value estimated from the calculations (i.e. ~15 Kcal/mole). This question will be discussed in the next section. Finally, it is interesting that ND\textsubscript{4}\textsuperscript{*} was found to be metastable, even at the elevated temperatures used in this experiment, thus fulfilling, in part, Bernstein's original proposal.
Table II. Gaussian basis sets for oxygen and hydrogen.

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a) The gaussian orbitals are given by:

\[
\chi(x,y,z) = N' (x,y,z) \sum_p A_p \exp(-\alpha_p r^2)
\]

where \(N'\) is a normalization factor. The symbol \(\chi(x,y,z)\) is 1 for s orbitals; it is \(x, y,\) or \(z\) or \(p\) orbitals; and \(3z^2-r^2, x^2-y^2, xy, xz\) or \(yz\) for d orbitals. The quantities \(A_p\) are the coefficients and the \(\alpha_p\) are the exponents appearing in the table. See D. Neumann and J. W. Moskowitz, J. Chem. Phys., 49, 2056 (1968).

Table III. Optimized parameters and energies for water (energies in hartrees).

<table>
<thead>
<tr>
<th></th>
<th>Basis Set I</th>
<th>Basis Set II</th>
<th>Niblaeus et al.\textsuperscript{a)}</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R(O-H) (\AA) )</td>
<td>0.9412</td>
<td>0.9439</td>
<td>0.948</td>
<td>0.957</td>
</tr>
<tr>
<td>( (HOH) ) (degrees)</td>
<td>105.98</td>
<td>106.17</td>
<td>105.3</td>
<td>104.5</td>
</tr>
<tr>
<td>Energy (UHF)</td>
<td>-76.051115</td>
<td>-76.053484</td>
<td>-76.046823</td>
<td>---</td>
</tr>
<tr>
<td>Energy (CI)</td>
<td>-76.286839</td>
<td>-76.269014</td>
<td>-76.247967</td>
<td>-76.431</td>
</tr>
<tr>
<td>Correlation Energy</td>
<td>0.235724</td>
<td>0.2155</td>
<td>0.201144</td>
<td>0.363\textsuperscript{c)}</td>
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<tr>
<td>Proton Affinity (P.A.)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(UHF)</td>
<td>0.2818</td>
<td>0.2790</td>
<td>0.2683\textsuperscript{b)}</td>
<td>0.261\textsuperscript{d)}</td>
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<tr>
<td>(CI)</td>
<td>0.2794</td>
<td>0.2755</td>
<td>0.2659\textsuperscript{b)}</td>
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</tbody>
</table>

\textsuperscript{a)} Reference 64.
\textsuperscript{b)} Reference 66.
\textsuperscript{c)} Based on Hartree-Fock limit of -76.068.
\textsuperscript{d)} Experimental value reference 56.
**Table IV. Optimized parameters and energies for the hydronium ion.**

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<th></th>
<th>Basis Set I</th>
<th>Basis Set II</th>
<th>Dierksen et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td>R(O-H)(Å)</td>
<td>0.962</td>
<td>0.963</td>
<td>0.959</td>
</tr>
<tr>
<td>8(HOH)(degrees)</td>
<td>112.9</td>
<td>112.9</td>
<td>113.5</td>
</tr>
<tr>
<td>Dihedral Angle (degrees)</td>
<td>129.7</td>
<td>129.6</td>
<td>---</td>
</tr>
<tr>
<td>Energy (RHF)</td>
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<td>-76.329776</td>
</tr>
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<td>Energy (CI)</td>
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<td>Correlation Energy</td>
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<td>Electron Affinity</td>
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<tr>
<td>(UHF)</td>
<td>0.1687</td>
<td>0.1747</td>
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<td>(CI)</td>
<td>0.1841</td>
<td>0.1931</td>
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</table>

a) r(O-H) = 0.972, 8(HOH) = 111.6

b) Experimental value reference 76.
Table V. Optimized parameters and energies for the hydronium radical.

<table>
<thead>
<tr>
<th></th>
<th>Basis Set I</th>
<th>Basis Set II</th>
<th>Niblaeus et al.</th>
<th>Bader &amp; Gangi</th>
</tr>
</thead>
<tbody>
<tr>
<td>R(O-H) (Å)</td>
<td>0.9823</td>
<td>0.9866</td>
<td>0.989</td>
<td>0.984</td>
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<tr>
<td>θ(HOH) (degrees)</td>
<td>110.96</td>
<td>107.82</td>
<td>109.5</td>
<td>111.77°</td>
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<tr>
<td>Dihedral Angle</td>
<td>123.85</td>
<td>116.17</td>
<td>125.4</td>
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<tr>
<td></td>
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</tr>
<tr>
<td>Inversion Barrier (Kcal/mole)</td>
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</tr>
<tr>
<td>(UHF)</td>
<td>2.44</td>
<td>---</td>
<td>2.8</td>
<td>2.0</td>
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<tr>
<td>(Cl)</td>
<td>3.3</td>
<td>---</td>
<td>4.5</td>
<td>---</td>
</tr>
<tr>
<td>Energy (HF)</td>
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<tr>
<td>Energy (Cl)</td>
<td>-76.7503331</td>
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</tr>
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<td>Correlation Energy (C.E.)</td>
<td>0.24871</td>
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<tr>
<td>C.E.(H₃O)-C.E.(H₂O)</td>
<td>0.01299</td>
<td>0.01517</td>
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<tr>
<td>E (UHF)(Kcal/mole)</td>
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<td>29.30</td>
<td>29.49</td>
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</tr>
<tr>
<td>E (Cl)(Kcal/mole)</td>
<td>23.00</td>
<td>19.74</td>
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a) Energy difference between H₃O⁺ and H₂O + H⁺.
Table VI. Calculated points along the H O + H reaction path.

a) Basis Set I  

<table>
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<tr>
<th>R(Å)</th>
<th>R(au)</th>
<th>r(au)</th>
<th>θ(degrees)</th>
<th>ϕ(degrees)</th>
<th>ΔE(UHF)</th>
<th>ΔE(CI)</th>
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<tr>
<td>0.9500</td>
<td>1.795</td>
<td>1.859</td>
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<td>55.61</td>
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<tr>
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<td>1.856</td>
<td>110.96</td>
<td>56.15</td>
<td>31.20</td>
<td>23.00</td>
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<tr>
<td>0.9991</td>
<td>1.888</td>
<td>1.855</td>
<td>110.84</td>
<td>56.43</td>
<td>31.32</td>
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<tr>
<td>1.0391</td>
<td>1.964</td>
<td>1.850</td>
<td>110.60</td>
<td>56.90</td>
<td>32.33</td>
<td>22.89</td>
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<td>1.1091</td>
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<td>1.838</td>
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<td>57.79</td>
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Table VI (continued)

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<th>r₂(au)</th>
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<td>19.39</td>
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<tr>
<td>1.100</td>
<td>2.079</td>
<td>1.840</td>
<td>1.840</td>
<td>107.66</td>
<td>107.07</td>
<td>65.25</td>
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<td>2.173</td>
<td>1.826</td>
<td>1.826</td>
<td>107.75</td>
<td>106.97</td>
<td>65.36</td>
<td>33.35</td>
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<tr>
<td>1.200</td>
<td>2.268</td>
<td>1.814</td>
<td>1.814</td>
<td>107.68</td>
<td>106.90</td>
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<td>33.37</td>
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<td>1.806</td>
<td>1.806</td>
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<td>1.800</td>
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<td>65.52</td>
<td>30.41</td>
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<td>1.500</td>
<td>2.835</td>
<td>1.790</td>
<td>1.790</td>
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<td>106.70</td>
<td>65.52</td>
<td>20.95</td>
<td>14.75</td>
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<td>1.783</td>
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<td>106.52</td>
<td>65.47</td>
<td>0.74</td>
<td>0.57</td>
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<tr>
<td>---</td>
<td>---</td>
<td>1.784</td>
<td>1.784</td>
<td>106.17</td>
<td></td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Luminescence Work and the Existence of an Stable Excited State of H$_3$O$^*$_

Although the calculations suggest that the hydronium radical is unstable in the gas phase, comparison with the fragmentation energy of Williams and Porter indicates a discrepancy. The reason for this discrepancy is not clear. One possibility is the omission of geometry reoptimization in the configuration interaction step, an omission which may have caused the correlation energy at the equilibrium geometry to be underestimated relative to correlation energies for geometries in the vicinity of the barrier. The minimum at 1.03Å in the CI potential curve for basis I hints at this possibility. However, other possibilities exist. The zero point energy, for example, may be much higher than estimated; alternatively, the experimental results may be artificially high because the molecule following electron capture dissociates before attaining the equilibrium geometry.

Luminescence results indicate that the responsible species is in a spin forbidden excited state. The simplest species seems to be some type of hydrogen atom - water system, which may be stable only as an excited state complex (i.e., an exciplex). This idea has not been elaborated in the literature, although Melton and Joy$^{58}$ do suggest that their results could be attributed to an excited state of H$_3$O$^*$, as well as the ground state. The possibility
that the hydronium radical exists as an excited species and that it might be responsible for the emission of low temperature ice was discussed by Bernas and Truong. However, they did not repeat this assertion in any of their later works. Preliminary calculations on the quartet state of H$_3$O$^+$ add support for this suggestion as seen in Table VII. A stationary point was found on the excited state surface with basis set II for a planar D$_3h$ configuration with bond lengths of 1.3969Å. This configuration lies 3.51 eV above the ground state of the same geometry, in fairly good agreement with the 3.33-3.0 eV found for the emission of ice. Unfortunately, electron correlation effects would tend to increase this energy gap. The species is also found to be stable by 7.2 eV with respect to autoionization. That is, the excited state is more stable in this regard than the ground state. This number, though, is still a great deal lower than the 10.9 eV appearance potential for the H$_3$O$^+$ signal found by Melton and Joy. Furthermore, it is also seen that the quartet state, as the ground state, is not thermodynamically stable; nor can any physical reasons be cited for the possession by this state of large dissociation barriers. Indeed, this state apparently dissociates readily, since no local minimum has been found in later calculations. The calculations presented, then, merely indicate that this sort of complex, if it exists, could explain the experimental results.

The actual potential barrier dissociation of the emitting species may be estimated by reference to the work of Maria and
McGlynn who found an activation energy of 500-600 cm\(^{-1}\) (or \(\sim 1.4-1.7\) Kcal/mole). This quantity could represent the barrier height above the zero point energy for the luminophore in an ice matrix.

While it seems clear that the emission of the acidic solution is due to the recombination of \(\text{H}_3\text{O}^+\) and \(\text{e}^-\), even this assertion is problematic since the CTTS transition of iodide should move to higher energies at lower temperatures.\(^8\) This problem may be resolved by assuming that the iodide and bromide are closely associated with \(\text{H}_3\text{O}^+\), thus lowering the energy of the CTTS transition as well as that of the emission.

The possible production of an exciplex of \(\text{H}_2\text{O}\) and \(\text{H}^+\) in the photolysis of hydroxide is also difficult to explain. The two excitation peaks in the hydroxide spectrum correlate well to the hydrogen atom affinities of \(\text{OH}^-\) and \(\text{OH}^+\).\(^\dagger\) Thus, the production of hydrogen atoms should not generate enough energy to form an excited state complex. Perhaps hydrogen bonding could lower the energy required to transfer a hydrogen atom into a close association with water

\[
\text{OH}^-_{\text{aq}} \xrightarrow{\text{hv}} 0^-_{\text{aq}} + \text{H(}\text{H}_2\text{O})^+_{\text{aq}}
\]

enough energy might then be available, by rearrangement of this system, to allow population of an excited state.

\(^\dagger\)4.77 and 4.34 eV, respectively (see reference 77 and 78).
This difficulty with hydroxide luminescence is also encountered in the mechanism postulated by Maria and McGlynn\textsuperscript{11}: the low-energy tail of the excitation cannot provide sufficient energy to both cause photodetachment of an electron from OH\textsuperscript{−} and simultaneously excite the quartet state of OH\textsuperscript{*}.\textsuperscript{12} The absence of the hydroxyl emission at \(\sim\)306 nm in aqueous systems at low temperatures also makes this interpretation questionable since this state should also be populated. Finally, the quartet state of hydroxyl, although weakly attractive, is dissociative — no barrier to dissociation exists in the gas phase. A barrier may arise however, upon solvation of this species, although this barrier would have to be on the order of 6 Kcal/mole in order for the quartet state of hydroxyl to provide an adequate explanation of this emission*.

The difficulties with the hydroxyl emission mechanism prompted Merkel and Hamill\textsuperscript{12} to suggest that the luminescence of hydroxide arose from the triplet state of hydroxide populated by recombination of hydroxyl radical and e\textsuperscript{−}\textsubscript{aq}.

\[
\text{OH}^* + \text{e}^-\textsubscript{aq} \rightarrow (\text{OH}^*)^* \rightarrow \text{OH}^- + \text{hv}\textsubscript{p}
\]

*The vibrational frequency of the first excited state (\(2\text{L}^+\)) is 3180.5 cm\(^{-1}\). The zero point energy is approximately half of this or 1590.25 cm\(^{-1}\) which is equal to \(\sim\)4.6 Kcal/mole. We assume the zero point energy for the quartet state to be similar since only one vibrational mode exists and its frequency would not be expected to vary by more than 10\%. 


Quenching of the chloride-complexed thallous ion luminescence was cited as proof that such a triplet state exists for the hydroxide ion. However, this quenching may arise by other mechanisms than triplet-triplet annihilation. Since the electron affinity of the hydroxyl radical is only 1.8 eV in the gas phase, the proposed triplet at 3.1 eV should be quite unstable to electron detachment. Stabilization of the triplet by solvation was suggested,¹² a supposition strengthened by comparison with the thiocyanate ion whose luminescence has been assigned⁸⁰ to a triplet state existing above the electron affinity of the gas phase neutral radical. Since this assignment must be called into question by the results in Chapter III, this argument loses some luster.

The attribution of the luminescence of concentrated acidic solutions by a $T_1$ state of hydroxide does not appear reasonable because proton diffusion through ice, even at 77K⁺, is quite rapid. Luminescence from an excited state of hydroxide would thus be expected to be quenched by recombination of this species with $H^+$. Therefore, the measured life-times of 1-1.5 s gainsay this assignment. The resemblance between the luminescence for acid and base solutions suggests that the same emitter is being observed.

The second excitation peak for the luminescence of hydroxide may be due to a build-up of hydroxyl radicals as mentioned previously. This mechanism rationalizes the deuteration effect as well.

¹⁺The diffusion rate is equal to $10^{13}$-10$^{14}$ m mole$^{-1}$ sec$^{-1}$. See reference 79.
as the "will o' the wisp" nature of the second peak. Additional evidence is found in the work of Bernas and Truong who found an emission peak in photolyzed H$_2$O$_2$ aqueous solutions at ~280 nm. This emission was attributed to the 0-0 emission band of a hydrogen bonded hydroxyl radical in support of the work of Merkel and Hamill. Thus, the 0-0 absorption of hydroxyl would also be shifted to this position upon hydrogen bonding to water.

4.5 eV Absorption in Water and the Existence of a Stable Excited State of H$_3$O$^+$

The experimental evidence for the existence of H$_3$O$^+$ can be rationalized, and the luminescence of low temperature ices can be explained by the postulated stability of an excited state complex of atomic hydrogen and water. Moreover, all the evidence presumptive for a low-lying triplet state of water can be rationalized along the same lines. The possible detection of the H$_3$O$^+$ complex by Melton and Joy was performed by scattering electrons in water vapor. Furthermore, the experiments of Edmonson et al. showed that the 4.5 eV signal required not only electron excitation but water adsorption onto the walls of the sample chamber. The active species then, is produced by reaction of thermalized electrons with water adsorbed onto the sample chamber walls followed by diffusion of the new species from the walls into the scattering zone. The species is

---

†Since the 0-0 absorption and emission bands of OH$^+$ shows no Stokke's shift in neon matrices at 4.2K (see reference 48).
not a negative ion.\textsuperscript{33} Since water is well known to produce H-atoms upon reaction with electrons,\textsuperscript{24} the production of such a complex is a possibility. A higher quartet state of H\textsubscript{2}O\textsuperscript{+}, found by accident\textsuperscript{\dagger}, lies \textasciitilde3.3 eV higher in energy (at the given geometry) than the one given in Table VII (-76.1194 hartrees). Thus, the species responsible for the signal increase observed by Melton and Joy may also be responsible for the electron scattering and electron impact results on water as well.

Finally, the optical absorption results of Larzul \textit{et al.},\textsuperscript{36} results which are impurity conditioned,\textsuperscript{37} may not have arisen from organic impurities. As noted in Chapter II the sample cell used by these scientists was made of nickel, a good hydrogenating catalyst. While this fact may have had nothing to do with the observed absorption, equally well it could have had a great deal to do with it. This supposition may explain the fact that the deuterated sample, even though 99.76\% isotopically pure (and hence chemically pure), had a higher absorptivity.

The 4.5 eV absorption in water systems may thus constitute experimental evidence for the existence of the hydronium radical. As a result, the existence of an excited state complex of H\textsubscript{2}O and H\textsuperscript{+}.

\textsuperscript{\dagger}The extended Huckel symmetry guess gives the wrong orbital order and the direct minimization routine does not allow the order to change. Using Guess = Core and the regular SCF routine permits convergence to lower state.
with its ability to explain the results becomes very important indeed. Nevertheless, the gas phase and low temperature condensed phase, for which most of the anomalous results for water arise, are two very different environments and the connection between the experimental results remains tenuous.

Summary

The luminescence of aqueous acidic solutions and that of ice excited by ionizing radiation is evidently due to the recombination of an electron with a hydronium ion. The exponential lifetime of the observed emission, however, is contrary to that expected for a recombination luminescence and tends to indicate a spin-forbidden transition. However, a fast lifetime component has been reported by several authors\textsuperscript{11,13,14}, and this component may be related to the recombination diffusion time. The emission of hydroxide solutions is difficult to assign but apparently originates in the same species as the water and acid luminescences.

In conclusion, it is seen that numerous anomalous experimental results are related and suggest the existence of an exciplex of water with a hydrogen atom. The most feasible form of this postulated exciplex is between the $^3\text{B}_1$ state of water and a (ground state) hydrogen atom.
Table VII. Partly optimized parameters for the quartet state of \( \text{H}_3\text{O}^- \) and its possible dissociation products.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Basis Set II</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R(\text{O-H})(\text{Å}) )</td>
<td>1.3969</td>
</tr>
<tr>
<td>( \theta(\text{HOH})(\text{degrees}) )</td>
<td>120.0°</td>
</tr>
<tr>
<td>( \phi(\text{H} \cdots \text{HOH})(\text{degrees}) )</td>
<td>180.0°</td>
</tr>
<tr>
<td>Energy (UHF)</td>
<td>-76.242524 hartrees</td>
</tr>
<tr>
<td>Ground state energy at optimized quartet geometry (UHF)</td>
<td>-76.371579 hartrees</td>
</tr>
<tr>
<td>( \Delta E(\text{UHF}) )</td>
<td>0.129055 hartrees</td>
</tr>
<tr>
<td>Triplet energy ( \text{H}_3\text{O}^+ ) for given geometry</td>
<td>-75.9780</td>
</tr>
<tr>
<td>Energy quartet ( \text{OH}^- + \text{H}_2 ) (^a)</td>
<td>-76.33</td>
</tr>
<tr>
<td>Energy triplet ( \text{H}_2 + \text{OH}^- ) (^a)</td>
<td>-76.10</td>
</tr>
<tr>
<td>Energy triplet ( \text{H}_2\text{O} + \text{H}^- ) (^a)</td>
<td>-76.29</td>
</tr>
<tr>
<td>Energy ( \text{OH}^- + 2\text{H}^- ) (^a)</td>
<td>-76.41</td>
</tr>
</tbody>
</table>

\(^a\) After Gangi and Bader, reference 25.
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65. J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, D. J. DeFrees, H. B. Schlegel, S. Topiol, L. R. Kahn, and J. A. Popli, Gaussian 80, QCPE 1981, 10, 416.
LUMINESCENCE STUDIES

PART II

THE TEMPERATURE DEPENDENCE OF THE PHOSPHORESCENCE OF PHENANTHRENE IN ETHANOL - EFFECTS OF GASES
CHAPTER I
INTRODUCTION

Shift Observed Upon Degassing of Sample

Stolzle\(^1\) observed the effects of degassing on the phosphorescence of phenanthrene in isopropanol. It had been reported previously by von Foerster\(^2\) that the phosphorescent intensities and lifetimes of polyaromatic hydrocarbons were fairly constant upon warming from 77K until a certain temperature, which varied for each solvent, was reached. Upon reaching this temperature a rapid decline in both the intensities and the lifetimes of the luminesphores was observed. For heptane this temperature corresponded to the melting point. However, for isopropanol, this temperature was much lower than the crystal melting point.

Stolzle also observed this low-temperature quenching in isopropanol, but discovered, upon further heating, that the phosphorescence reappeared. This reappearance had been reported previously although Stolzle, apparently, was unaware of it. Schmillen and Tschampa\(^3\) had already shown that the low-temperature, rapid-change region of phosphorescence intensity (and lifetime) in alcoholic solvents occurred in the glass transformation region and that the second (or reappearance) region corresponded to crystal formation. The temperatures observed in ethanol, for example, are in good correspondence with the formation temperatures of these "states" as measured by Differential Thermal Analysis\(^4\) (DTA).

\(^1\) Stolzle
\(^2\) von Foerster
\(^3\) Schmillen and Tschampa
\(^4\) Differential Thermal Analysis
Luminescence, therefore, is a useful tool for monitoring changes of state.

Finally, Stolzle observed that degassing the sample produced little effect on the temperature dependence of the phosphorescence intensity but considerable effects on the lifetime dependency. Stolzle suggested that the intensity of the luminescence of phenanthrene was inhibited by formation of a complex of the excited state with the solvent and thus only the phosphorescent lifetime was affected by degassing.

In light of the work of Schmillen and Tschampa, however, this degassing effect requires better explanation. For this reason, the effects of gases (Oxygen, Nitrogen, Argon, and Ethane) upon the temperature dependence of the phosphorescence of phenanthrene in ethanol have been studied.* The effect of degassing on the intensity and lifetime of this luminescence is shown in figure 1. This effect in glassy ethanol had been observed previously by Martinez et al., who attributed the shift in intensity and lifetime to quenching by oxygen as it diffused through the softened glass. Two areas of rather general interest converge in this one problem: the properties of glasses, and oxygen-quenching of phosphorescence.

Relationship to Glass Theory

The study of glasses is at once one of the oldest and yet

*With G. Schoeffler.
newest fields in science. Many empirical facts about glasses are known but quantitative theories to explain them are rare. Glasses are known, however, to be prone to relaxation effects. That is, the observed properties arise by the inability of the molecules to adjust themselves with sufficient rapidity to different stimuli. The properties observed for a glass, therefore, are dependent upon its past history, e.g., the cooling rate during glass formation and the extent of annealing.

While relaxation effects are important in glass theory, a paradox, first discussed by Kauzmann, arises if the glass formation is assumed to be of completely kinetic origin. Kauzmann showed, assuming kinetic effects are avoided by infinitely slow measurements, that the extrapolated curves for entropy, heat content, specific volume, etc. of the supercooled liquid would go to zero above absolute zero, thus giving rise to negative zero point values for these quantities. Therefore, Kauzmann proposed the existence of a point (not observed) at which spontaneous crystallization would take place.

A different solution to this paradox was proposed in the highly limited yet successful theory of Gibbs and Dimarzio who assumed that a second-order phase transition underlies the glassy state and would be found if experiments were done infinitely slowly. This assumption has not and evidently can not be verified experimentally. Consequently, any further discussion of glasses will be postponed until after the presentation of results.
Figure 1

The relative intensities and absolute lifetimes measured for the phosphorescence of phenanthrene in ethanol as a function of temperature nondegassed sample (circles), and degassed sample (squares).
The figure illustrates the relationship between temperature (in degrees K) and two different parameters:

1. **Relative Intensity**: This parameter is represented on the vertical axis. The graph shows a decrease in relative intensity as temperature increases, with distinct peaks and troughs indicating changes in intensity at certain temperature intervals.

2. **Lifetime (seconds)**: Represented on the bottom graph, the lifetime shows a similar trend, decreasing as temperature increases, with specific points of interest highlighted.

The graphs suggest that there are significant changes in both relative intensity and lifetime at specific temperature ranges, indicating possible phase transitions or other temperature-dependent phenomena.
Thesis - O₂ and N₂ Can Break H-Bonds

The mechanism suggested by Martinez et al.⁵ to explain the shift in the glass region observed in figure 1 is certainly reasonable in view of the fact that phosphorescence quenching by oxygen is well known.¹⁰ This quenching results from triplet-triplet annihilation, in which energy and spin are exchanged between two triplet states, so that one is degraded to a ground-state singlet, and the other raised to a higher-singlet state. Since molecular oxygen has a triplet ground state and a low-lying, excited singlet state, it is a highly efficient quencher.

It is observed (cf. figure 1) that degassing affects not only the glass region but, apparently, the crystal region as well. The depression of the crystal region onset to lower temperatures, the depression of the temperature at which the maximum occurs, and the depression of the temperature of final disappearance for this upper region is characteristic of systems containing oxygen or nitrogen. This phenomenon has not been reported. It seems to be attributable to an effect of the dissolved gases on the physical properties of the ethanol. Since the dominant intermolecular force in ethanol is hydrogen bonding,¹¹ the dissolved oxygen or nitrogen is evidently influencing this property.

Relationship to Hydrogen Bond Breaking Studies

Many compounds of oxygen and nitrogen are well-known hydrogen bond acceptors. This ability has not been studied extensively for O₂ and N₂; however, an infrared absorption shift was reported¹² for
these compounds, as well as for nitrous oxide, when these gases were adsorbed onto silica. This shift was attributed to hydrogen bonding between the gases and hydroxyl groups on the surface of the silica. Semiempirical quantum mechanical calculations appeared to support this assertion.\textsuperscript{13} The various shifts observed for ethanol, then, are probably due to oxygen-quenching of the phosphorescence in the glass region as well as hydrogen bond breaking by \( O_2 \) and \( N_2 \) (evidently by competitive complexation).

Hydrogen bond breaking by anesthetics was discovered by the Montreal group.\textsuperscript{14–17} A direct proportionality of this property and anesthetic potency was observed. Since both nitrous oxide and nitrogen are known to have anesthetic properties, the idea of hydrogen bond breaking by \( N_2 \) and \( NO \) is feasible. It is not known whether \( O_2 \) has anesthetic properties or not since it is toxic at high pressures. Nevertheless, this work suggests that it can break hydrogen bonds as well.

Both of these areas, hydrogen bond breaking and oxygen effects, are of fundamental importance to biology. For example, anesthetics are known to have deleterious effects upon mitosis,\textsuperscript{18,19} evidently affecting the DNA of the microorganisms of interest. Similarly, oxygen is the basis of most metabolic systems. Interaction between oxygen (or nitrogen) and DNA is a startling conjecture; nevertheless, it has been substantiated by the observation that the melting curve of DNA shifts upon degassing. Hydrogen bonding has also recently been found to be important in the
complexation of oxygen by oxymoglobin\textsuperscript{27}; this hydrogen bond, on the basis of our work, may not be a unique as supposed.
CHAPTER II

EXPERIMENTAL WORK AND RESULTS THEREOF

The experimental arrangement, somewhat modified, is that provided in the general introduction. A large phosphorescope was employed in order to permit use of a larger, (1l) dewar. The greater coolant volumes possible with 1l containment improved the temperature stability of the system. Temperatures between 77 and 160K were obtained by flowing chilled nitrogen vapors into the dewar. These vapors were generated (following a suggestion by J. Scott) by metering nitrogen gas through a copper coil immersed in liquid nitrogen. Temperature control was reproducible within ± 2K.

Temperature measurement was effected by taping a copper-constantan thermocouple to the outside of the sample tube (8 mm O.D. suprasil). The thermocouple was connected in parallel to a potentiometer (Leeds and Northrup #8690) and a rolling chart recorder (Sargent). A reference potential was provided by immersing the second junction in an ice-water bath. The inherent error in temperature measurement was less than ± 0.5K.

The samples were cooled quickly (~20K/min) to the annealing point (~106K) and held at this temperature for approximately ten minutes. Annealing prevented the fluctuations of intensity associ-able with cracked samples. After annealing, the sample was cooled further to 77K. Upon equilibration (~3-5 minutes), a measurement was taken and the nitrogen flow reduced. After reequilibration,
the process was repeated. Upon passage through the glass region, an incremented emissivity caused by the formation of crystals was observed. The initial temperature, in this region was maintained for 30-45 minutes to permit further crystal growth. Some samples evidenced considerable hesitation in the crystal formation process. This hesitation was characteristic of those systems containing oxygen and nitrogen; some samples of this type had to be recooled below 110K, and rewarmed, before crystal growth was observed to initiate. Samples not containing oxygen or nitrogen exhibited rapid crystal growth in almost all cases.

Phenanthrene was zone refined (more than 100 passes). Ethanol was distilled twice from bulk, once with CaO and once with Mg (under nitrogen atmosphere). Fresh solutions were prepared for each experimental run. Sample concentrations varied within the range 7-13 mg/ml (i.e., $10^{-3}$-$10^{-4}$ M). These solutions were placed in the emission tubes and degassed by 20 (or more) freeze-thaw cycles to a final pressure less than 1µ at 77K. The various gases (all 99.99% Matheson grade) were then added and the tubes scaled. Samples in which the pressure was greater than atmospheric were closed with a built-in stopcock. The only samples not treated in this manner were the "non-degassed" and "saturated" samples which were closed with a stopcock.

Lifetime measurements were made by abrupt shuttering of the excitation light. The decay curves were displayed on an x-y
recorder operated in the time sweep mode. The phototube, electrometer and x-y recorder had a measured response time of 0.75s; therefore lifetimes less than 1s were not considered reliable. The measured intensity was sensitive to minor changes in alignment which necessitated the design of a new dewar holder. The intensities obtained with this holder were subject to \( \pm 10\% \) variations.

Results for a degassed sample are compared in figure 2 to those for degassed samples pressurized under 500T Ethane and 1000T Ar. The observed variations are slightly larger than the experimental error, the major deviations occurring in the higher temperature portion of the glass transition regime. The differences are apparently due to pressure effects on the glass, although traces of contaminants may have been responsible. The crystal regions show excellent correspondence, although the intensities do vary somewhat. This variation may be a result of the difficulty of crystal formation caused by the presence of the gases. Thus, the sample containing ethane exhibited the highest degree of variation.

The relative absorption coefficients for relevant gases are shown in Table II. All show comparable solubilities, the smallest being that of \( \text{N}_2 \) which is less by a factor of two. Although these absorption coefficients were measured at room temperature and atmospheric pressure, the rapid cooling rate used in proceeding from room temperature to the glass annealing point is expected to
Figure 2

Phosphorescence intensities and lifetimes for phenanthrene in ethanol - Degassed (squares), Degassed + 1000T Ar (open circles), and Degassed + 500T Ethane (triangles).
make these data pertinent.

In figure 3, the results obtained for several pressures of oxygen are shown. A large shift is evident at higher concentrations of oxygen. Indeed, the loss of intensity in the oxygen "saturated" sample is immediate and is reflected in the decrease of the lifetime curve as well. This rapid decline occurs twelve degrees below the accepted glass transition temperature for ethanol\(^8,12\) (95-100K for nondegassed samples). While an effect attributable to the phosphorescence quenching ability of oxygen is expected to appear in the glass transition region, such an effect is not expected in the crystal region. The onset of crystallization \(T_o\) in the oxygen "saturated" sample was shifted approximately twenty degrees relative to the degassed sample, and both the maximum and disappearance temperatures for this region \(T_m, T_d\) were fifteen degrees lower. These shifts are difficult to explain in terms of an "annealing of the crystal."

That there is a thermal shift of the decay curves due to oxygen diffusion through a glass in the annealing region is confirmed in figure 4, which shows the curves obtained for nondegassed and degassed samples of phenanthrene in 2,3-dimethyl pentane. Thus, it can not be confirmed that the effect of \(O_2\) in the glass region is caused by hydrogen bond breaking. Nevertheless, some such effect may be indicated by the significant lowering of the onset of quenching in the oxygen "saturated" sample below the accepted glass transition temperature.
Figure 3

Phosphorescence intensities and lifetimes for phenanthrene in ethanol - Degassed + 500 mT O₂ (open triangles), Degassed + 500T O₂ (open squares), and O₂ saturated (760 mm, circles).
Figure 4

Phosphorescence intensities and lifetimes for phenanthrene in 2,3-dimethyl pentane – nondegassed sample (circles) and degassed samples (triangles).
The interpretation of the crystal region, however, is a different matter. Here all temperatures (onset, maximum, and disappearance) are affected and it is difficult to imagine any effect besides hydrogen bond breaking which could account for this shift.

Further evidence for this supposition is given in figure 5 where a similar shift is observed both in the glass and crystal regions. The differences of intensities of the N$_2$ - "saturated" and 1000T N$_2$ samples in the glass transition onset region may be due to incomplete removal of oxygen by nitrogen bubbling or to some other experimental artifact. Again, however, there exists a significant shift in both regions for both samples. Thus, nitrogen unmistakably causes a shift similar to that generated by oxygen.

This shift in the 1000T N$_2$ sample is not caused by oxygen impurity, which is, at most, 30 ppm (i.e., <30 mT O$_2$). The results for the 500 mT O$_2$ sample, which is an order of magnitude higher in O$_2$ content, mimic the degassed sample, indicating that 30 mT is an insignificant impurity addition. This shift is also not due to pressure effects, as shown by comparison of the 1000T Ar with 1000T N$_2$ sample (cf. figure 6). Similarly, since argon is roughly twice as soluble as nitrogen the shift shown in the crystal region cannot be due to simple impurity effects (i.e., freezing point depression).
Figure 5

Phosphorescence intensities and lifetimes of phenanthrene in ethanol
degassed sample (filled squares), degassed + 1000 T N$_2$ (circles), and
N$_2$ saturated (≈760 nm N$_2$) (open squares).
Figure 6

Phosphorescence intensities and lifetimes for phenanthrene in ethanol - Degassed + 1000T Ar (open circles), and Degassed + 1000T N₂ (filled circles).
Table I. Relative solubilities of the various gases used in ethanol.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$B$, Bunsen absorption coefficient a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>0.237 (at 25°C)</td>
</tr>
<tr>
<td>$C_2H_6$</td>
<td>0.2098 (at 25°C)</td>
</tr>
<tr>
<td>N</td>
<td>0.1198 (at 24°C)</td>
</tr>
<tr>
<td>O</td>
<td>0.2177 (at 24°C)</td>
</tr>
</tbody>
</table>

a) Defined as the milliliters of gas (corrected to STP) absorbed by 1 cc of liquid. When the partial pressure of the gas is 1 atmosphere. See references 25 and 26.
Table II. Apparent glass transition temperatures (in degrees Kelvin) and crystal region data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$</th>
<th>$T_n$</th>
<th>$T_m$</th>
<th>$T_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degassed</td>
<td>107-117</td>
<td>133</td>
<td>144</td>
<td>154</td>
</tr>
<tr>
<td>1000T Ar</td>
<td>104-111</td>
<td>135</td>
<td>140</td>
<td>152</td>
</tr>
<tr>
<td>500T Ethane</td>
<td>104-109</td>
<td>135</td>
<td>144</td>
<td>156</td>
</tr>
<tr>
<td>Nondegassed</td>
<td>90-100</td>
<td>124</td>
<td>129</td>
<td>145</td>
</tr>
<tr>
<td>O$_2$ Saturated</td>
<td>83-93K</td>
<td>113</td>
<td>130</td>
<td>139</td>
</tr>
<tr>
<td>500T O$_2$</td>
<td>94-103K</td>
<td>129</td>
<td>140</td>
<td>150</td>
</tr>
<tr>
<td>500 mT O$_2$</td>
<td>106-115K</td>
<td>133</td>
<td>139</td>
<td>153</td>
</tr>
<tr>
<td>N$_2$ Saturated</td>
<td>90-95</td>
<td>127</td>
<td>135</td>
<td>147</td>
</tr>
<tr>
<td>1000T N$_2$</td>
<td>93-98K</td>
<td>128</td>
<td>134</td>
<td>143</td>
</tr>
</tbody>
</table>
CHAPTER III
ON THE GLASS TRANSITION

Theoretical Compendium

The transformation of a supercooled liquid into a glass is a general characteristic of matter. Glass transitions have been observed for hydrocarbons, highly-polar compounds, inorganics, polymers, even elementary materials. As mentioned previously, a great deal of work is being done on glassy systems by scientists in many different disciplines.* The largest current areas of research on this subject, both theoretical and experimental, are probably those concerning amorphous semiconductors and glassy polymers. This extensive work promises new insights into this rather chaotic area. For example, topological approaches seem to show great promise of penetrating to the heart of this maze.7 Nevertheless, the most successful glass theory21 is perhaps that of Gibbs and Dimarzio.9 This theory, which incorporates a lattice model for linear polymers, successfully predicts the dependence of glass transition temperatures and specific volumes on molecular weights. In it, monomers in a chain (of length x) are allowed to occupy either high-energy or low-energy conformations on a lattice. The lattice may have a number of unoccupied sites, the number of which is denoted \( n_0 \). Furthermore, since many different

*Recently a glassy state of stainless steel has been achieved.20

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conformations give equivalent energies, a degeneracy or weighting factor must be incorporated in the Boltzmann Sum. This degeneracy is denoted $W(f,n_o)$, where $f$ is the fraction of bonds in the "flexed" or high-energy conformation. This factor is defined as the number of ways in which $n_x$ polymers (containing $x$ monomers) can be packed on the lattice of $(xn + n_o)$ sites when the total number of "flexed" bonds is $f(x-3)n_o$ (since the number of bonds in a polymer of length $x$ is $x-1$ and the two end bonds are inflexible). The minimum value of the degeneracy $W(f,n_o)$ is unity. Since $W(f,n_o)$ is a monotonic increasing function of temperature, a temperature ($T_2$) exists below which the polymer system cannot become less degenerate. This point (below which $W = 1$) is termed the "amorphous ground state." The partition function for this model suggests the presence of discontinuous derivatives of the internal energy, entropy, free energy and specific volume (with respect to temperature). Thus, a second-order phase transition is indicated. This result differs somewhat from Kauzmann's original proposal of spontaneous crystallization which requires a first-order phase transition. It must be observed, however, that $W(f,n_o)$ is unity for a system of polymers with all bonds unflexed, as well as for the "amorphous ground state." This unflexed system may be considered to be crystalline. Thus, some relationship between Kauzmann's proposal and Gibbs and DiMarzio's theory must exist.

The G-D theory is highly successful in predicting glass transition temperatures for linear polymers of given molecular
weights. It is not easily extensible to other systems, however, and such extensions as have been made are not firmly based in intuitive concepts: There does not appear to be any strong similarity between glassy polymers and amorphous semiconductors, for instance.

**Experimental Review**

Experimental measurements on glasses are numerous, the most pertinent to alcohol glass being those of Lesikar and Martine et al. Lesikar studied the effects of organic halide content on glass formation temperatures \( T_g \) of normal alcohols, as well as the effects of Lewis bases on the same alcohols. The normal alcohols were chosen because hydrogen bonding is evidently more important as a determinant of \( T_g \) for these than for branched alcohols. Martinez and coworkers studied the effects of heating and cooling rates on \( T_g \) in ethanol using fluorescence depolarization and delayed fluorescence measurements. A discussion of these measurements will now be presented.

Lesikar used differential thermal analysis (DTA) to study mixtures of the lower normal alcohols with organic halides* and Lewis bases.† In the former study, the measured glass transition

*CCl\textsubscript{4}, CHCl\textsubscript{3}, CH\textsubscript{2}Cl\textsubscript{2}, C\textsubscript{2}HCl\textsubscript{3}, C\textsubscript{2}Cl\textsubscript{4}, CH\textsubscript{2}Cl-CH\textsubscript{2}Cl. See reference 1.
†Pyridine, triethyl amine, diethyl ether, isopropyl ether, dioxane, acetone, methyl ethyl ketone, methylisobutyl ketone, cyclohexanone benzaldehyde, acetophenone, EtAc, DMSO, DMAA, toluene and benzene. See reference 22.
properties, namely the excess glass temperature \( T_e \), (the increase in \( T_g \) above that expected for an ideal mixture based upon a presumed linear variation between the \( T_g \)'s for pure alcohol and pure organic halide) and the initial molar slope (IMS) (the rate of change of \( T_g \) with composition at low concentrations of organic halide) were found to be dependent upon the hydrogen bonding properties of the organic halide. Carbon tetrachloride, for example, which does not hydrogen bond to any large extent, showed a very large IMS and a very small \( T_e \) (less than 2°C). Chloroform, on the other hand, which is a strong hydrogen bond donor (and also a good anesthetic!), showed the smallest values of IMS and also very large values of \( T_e \). Lesikar therefore concluded that alcohol-organic halide clusters were forming in the alcohol-rich mixtures and that this clustering raised the value of \( T_e \).

The various Lewis bases did not give similar results; therefore, the bases were conjectured to coordinate, by dipolar forces, to the pre-existing alcohol association chains. Lesikar did not find, to his surprise, that these hydrogen-bond acceptors utilized this capability in low-temperature solutions.

Steric effects, then, can dominate hydrogen bonding effects in glass formation. Lesikar's work may be interpreted intuitively by supposing that normal alcohols below their freezing point, can incorporate hydrogen-bond donors into the "clan," but that hydrogen-bond acceptors are rejected, evidently because of some precrystalline order imposed on the chains. \( O_2 \) and \( N_2 \) being small
are not so sterically constrained.

The work of Martinez et al. is of significance to any understanding of the glass properties of ethanol. Their work also utilized luminescence techniques. Three regions of fluorescence depolarization were observed to occur in glassy ethanol: 90-100, 106 and 121K (the last two numbers indicating maximal value temperatures). The delayed fluorescence exhibited only two regions, with maxima at 108 and 121K. The interpretation given these regions, based on the established $T_g$ for ethanol of 95-100K and the observation by radiowave absorption$^{24}$ of microcrystal formation in ethanol at 120K, was that the first region, that at 90-100K, corresponded to the glass transition, the second to "relaxation" of the glass and the third (maximum at 121K) to formation of microcrystals. They also observed that, for slow cooling and heating rates (i.e., rates less than 0.2K per second), the region maximizing at 108K in the delayed fluorescence disappears, and that the increase in delayed fluorescence for the 121K region corresponds to the decrease observed in phosphorescence intensity. (All of this work was carried out in degassed ethanol and the curve obtained for phosphorescence decline in slowly-cooled and heated ethanol corresponds to that observed in our degassed samples.)

Since we have shown that the crystal region (and, hence, microcrystallization of ethanol) is affected by dissolved $N_2$ and $O_2$, and since the delayed fluorescence (DF) of concentrated solutions ($\nu 10^{-1}$
M phenanthrene) showed no DF increase in the 90-100K region, a reinterpretation of the work of Martinez et al. is apparently required. The intense DF peak at 121K may be assigned as the glass transition because in this transition viscosity varies between $10^{13}$-$10^7$ poise, thus allowing greater mobility of the phenanthrene. The first DF peak at 108K, which disappears upon slow cooling, is, as stated, a "relaxation" of the glass or, more simply, the annealing point. Finally, the region at 90-100K observed in the depolarization of fluorescence experiment but not in DF may be a "breathing" of the glass, that is, a second annealing point.

With this interpretation, it may be seen that, in the rapidly cooled glass, at least three different configurations are apparently "frozen in." Two of these "frozen in" configurations allow diffusion of the impurity molecules (i.e., those configurations frozen in at ~108 and 121K), while one does not (that at 90-100K). (The term "configuration" is being used somewhat loosely because several different types of concerted molecular motions may be lost in each temperature region.) This interpretation also explains the repolarization of the fluorescence which occurs upon passing through the first two regions at 90-100 and 106K. The decline of the intense DF peak at 121K which occurs at higher temperatures, however, cannot be explained in terms of solvent crystallization since this was observed to occur (cf. figure 1) at ~135K. The continued decrease of the viscosity of the solvent may allow collisional quenching to compete with triplet-triplet
annihilation in depleting the triplet state in this region.

Further work is evidently demanded.
CHAPTER IV
ON HYDROGEN BOND BREAKING

Overview

Hydrogen bonding has been studied for quite some time, the first successful theory being that of Pauling who treated the interaction as electrostatic. Correct energy magnitudes for hydrogen bonds were predicted by treating the effect as a dipole-dipole interaction. However, the model failed to explain the charge redistribution evidenced by the IR shift of hydrogen-bonded species. This redistribution, in turn, is satisfactorily explained by molecular orbital theory. Although H-bonding is quite weak, it appears to be adequately treated by ab initio quantum mechanical molecular orbital treatments. Semiempirical methods, while less reliable, are frequently used because many of the systems of interest are quite large.

Hydrogen bonding affects the physical properties of systems containing these bonds. Direct observations of hydrogen bonding are limited to IR, and NMR spectroscopy, although hydrogen bonding can be inferred from x-ray crystallography and optical absorption spectroscopy. The methods of IR and NMR spectroscopy permit an evaluation of H-bond strengths.

On the Hydrogen Bond Breaking Ability of Anesthetics

During the study of the anharmonicity of H-bond shifted vibrations, di Paolo and Sandorfy observed that the formation of
hydrogen bonds was inhibited by bromine containing fluorocarbons. Since these compounds are known anesthetics a series of studies was initiated to examine this effect.

The systems studied were self-bonded water, alcohols, amines and amides as well as some heterogeneous systems (e.g., water-dioxane). IR bands which could be ascribed to "free" and H-bond entities were observed. A significant shift in the relative proportions of these bands was found upon addition of anesthetics to the system. This effect was greatly increased by lowering the temperature, so that the associated (or H-bonded) band virtually disappeared upon addition of the anesthetics. The order for HBB was given as $F < Cl < Br < I$ and was found to increase for system containing acidic hydrogens. This order and the effect of acidic hydrogens mimics the effect of substitution on anesthetic power.

The mechanism by which HBB takes place is simply competitive complexation of the H-bond donors by the anesthetics (or O$_2$ and N$_2$). This competition is enhanced when the anesthetic has the joint ability to accept and to donate H-bonds, as in the case for species containing acidic hydrogens.

A semi-quantitative relationship was established in a recent paper by the Montreal group$^{17}$ between HBB and anesthetic ability. In this study solutions containing water-dioxane, n-ethylacetamide, and t-butanol were compared to similar solutions containing equal molar quantities of several anesthetics. The change in the IR band areas of the "free" and associated bands
was found to correlate well with the inverse of the "effective anesthetic pressure." This latter quantity was defined as the pressure of the anesthetic required to suppress the righting instinct in fifty percent of the experimental animals.\textsuperscript{31}

By virtue of the above correspondence, an anesthetic effect of oxygen and nitrogen should be expected. Such an effect is known in the case of nitrogen (i.e., "nitrogen narcosis"). This property, mainly observed in scuba diving, is governed by a rule of thumb, known as Martini's rule, which states that the degree of narcosis is equivalent to one martini on an empty stomach for every fifty feet in depth.\textsuperscript{32} This effect is not well understood at present. Physiological studies have been made but no mechanism has been suggested. Some portion of this effect may be due to HBB. However, since other inert gases show similar tendencies,\textsuperscript{33} the total effect cannot be ascribed to HBB. The narcosis by the noble gases is puzzling since argon showed no HBB tendency. It must be noted, however, that the study\textsuperscript{33} which showed argon to have significant narcotic properties was carried out at high partial pressures of oxygen. Narcosis studies might be improved by maintaining a constant partial pressure of oxygen. While the narcosis property may be due, to some extent, to solubility effects, qualitative differences between nitrogen and other inert gases are to be expected.
Hydrogen Bonding by O\textsubscript{2} and N\textsubscript{2}

The mechanism of HBB, presumably competitive complexation, implies the ability of O\textsubscript{2} and N\textsubscript{2} to accept hydrogen bonds. The work of McDonald\textsuperscript{31} is corroborative since he observed an IR absorption band to shift upon adsorption of N\textsubscript{2}, O\textsubscript{2}, and NO on silica. These shifts were ascribed to complexation between the gas molecules and hydroxyl groups attached to the surface. Support for this assignment was given by Lygin et al.\textsuperscript{35} who investigated mode of these complexes using the CNDO approximation. Both linear and T shaped complexes were investigated, the former being found to be the more stable. The calculated energies of the O\textsubscript{2} and N\textsubscript{2} complexes, 3.6 and 6.2 Kcal/mole respectively, are in the general range of H-bond energies, and are in qualitative agreement with the heat of reaction determined from IR shift (12 and 24 cm\textsuperscript{-1}, respectively). Apparently, then, weak hydrogen bond complexes of N\textsubscript{2} and O\textsubscript{2} with ROH are to be expected.

This conclusion is borne out by the ab initio MO work of Cherry\textsuperscript{36} who studied the O\textsubscript{2}-H\textsubscript{2}O system both in the ground (\textsuperscript{3}Σ\textsubscript{g}) and the excited states (\textsuperscript{1}Ω\textsubscript{g}). A very weak H-bond (∼1 Kcal/mole) was found for the ground state complex with both the STO-3G\textsuperscript{37} and 4-31G\textsuperscript{38} basis sets. It must be noted, however, that the results of Part I of this dissertation suggest that the use of polarization functions would increase the calculated H-bond energy of such a complex.
Extension of Work to DNA

Given the importance of H-bonding in biological molecules, especially DNA, it seemed natural to extend this work by testing this HBB hypothesis on this entity. Therefore, a solution of calf thymus Na DNA (Sigma) was prepared (0.0518 mg/ml in H$_2$O) which gave an absorbance of $\approx 0.9$ @ 260 nm. The change in the absorbance was monitored as a function of temperature, the heating rate being $\approx 1-2^\circ\text{C/min}$, and the saturating gas (O$_2$ was bubbled into the chilled solution for 1 hr., as was Argon). The temperature dependence is presented in figure 7. The total change in absorbance was $\approx 10\%$.

These "melting" curves are well known for DNA and result from the "unstacking" of the aromatic rings of the bases during the denaturation process.\textsuperscript{39} The process of denaturation of DNA is a dynamic equilibrium and it is rate-independent for slow rates. The DNA will renature rapidly upon cooling if the process has not been carried to completion (in which case, the renaturation is extremely slow because the DNA strands have separated completely). Information related to the relative number of G-C and A-T base pairs contained in the DNA\textsuperscript{39} can be obtained from the slope of the curve.

The temperature at which the denaturation process occurs is dependent upon the added solutes, being greatly increased by salts\textsuperscript{39} (KCl) and decreased by HBB systems (e.g., urea). This latter solute was found to decrease the temperature of melting by 3-5$^\circ\text{C/mole.}$\textsuperscript{41} The shift observed in figure 7 seems anomalously
Figure 7

The temperature dependence of the absorbance of calf thymus NaDNA (0.0518 mg/ml in H₂O) - O₂ saturated (triangles), nondegassed (squares), and Ar saturated (circles).
large compared to that found for urea. The rapid diffusion of the gases and the rather weak, rapidly broken complexes which form, may account for this large effect. The shift observed is consistent, however, when it is recalled that oxygen is roughly twice as soluble as nitrogen in water.25

These experiments, while certainly not conclusive tend to substantiate the explanation for the observed ethanol shift. They also re-enforce the possible biological importance of the HBB of O₂ and N₂ gases.
CHAPTER V
SUMMARY AND CONCLUSIONS

A good deal of evidence seems to indicate the formation of weak hydrogen-bonded complexes of molecular nitrogen and oxygen. Some of this evidence is inferential; however, the effect observed in Chapter II on ethanol is quite real. In particular, the argon saturation procedure (which was used to remove dissolved air from the DNA sample in figure 7), also produced a shift which was very similar to that for the degassed sample pressurized under 1000T argon. The removal of O₂ and N₂ by helium saturation was much less effective. The "freeze-thaw" method of degassing was in general the most efficacious; therefore, samples treated in this manner are emphasized in this work.

The shift observed in the glass region, for the sample with 1000T N₂ added, is difficult to explain without invoking HBB, particularly since argon addition at similar pressures produced no observable shifts. Thus, pressure effects, to which glasses are sensitive, and solubility effects, (argon being considerably more soluble than nitrogen) can not be invoked. Rate effects could produce such shifts in the glass region; consequently, every effort was made to use the same temperature variation rates. (The crystal region, however, should not be strongly rate dependent.) Oxygen is present as impurity in N₂; however, the maximum O₂ contamination (<30 ppm thus <30 mT) is too small to cause the observed shift.
This point becomes clear by comparison with the sample containing 500 mT O₂, which mimics the degassed curve.

The quenching of phosphorescence by O₂ diffusion in the soft glass is certainly present, as suggested by Martinez et al.⁵ The large shift in the crystal region cannot be ascribed to such effects since both the apparent melting point and the crystal onset region shift similarly. Indeed, the phosphorescence lifetimes in the crystal region indicate no quenching attributable to oxygen diffusion in that the lifetimes remain long and exponential. A good deal of scatter in the life-time data in the crystal region, reported by Schmillen and Tschampa, was also observed in this work. The cause of these variations is unknown to us.

Some discrepancy exists between our observed crystal melting points and those of Schmillen and Tschampa.³ However, as can be seen in figures 1-6 the melting points are reproducible and fall into the two categories previously mentioned — shifted and unshifted. Since the previous authors did not describe the experimental procedure in great detail no explanations for this discrepancy can be offered.

The shift in the crystal melting point is too large to be caused by a colligative effect. Indeed, given the limited solubility of the gases studied and a cryoscopic constant of 2.86°C/mole, colligative effects should be negligible. Furthermore, argon and ethane are just as soluble as oxygen. Finally, crystal size effects, which also have an influence on the melting point, are of a magnitude much too small to explain the observed magnitudes
(see Kauzmann). Therefore, this effect must be attributed to an alteration of the physical properties of ethanol by dissolved O and N₂. The most feasible mechanism is hydrogen bond breaking.

As seen in Chapter 3, this work leads naturally to a discussion of the theory of glasses. Rapid progress may be expected in this area. Extensions of the Gibbs-Dimarzio theory can be expected and novel topological approaches are surely predictable. Glass technology will undoubtedly experience a great improvement as soon as theory becomes capable of predicting glass preparation routes leading to desired properties. Indeed, predictions of glass formation abilities in new materials (e.g., the successful formation of graphite glass and the multitude of applications thus engendered) may well become the norm. The possible correspondence between the spontaneous crystallization theory of Kauzmann and the amorphous ground state ideas of Gibbs-Dimarzio should be investigated further.

The work on the hydrogen bond breaking of anesthetics, discussed in Chapter 4, is seemingly of great significance and obvious extensions to NMR studies on biologically important molecules should be pursued. DNA replication mechanisms have been studied extensively in recent years and several of the enzymes involved in the process have been discovered (e.g., the "unwinding" enzyme of Albert). The initial step, that of hydrogen-bond breaking, however, has remained a mystery. The build-up of some metabolite, with HBB abilities may be responsible, in view of the
work presented here, for the initiation of the entire replication sequence.

In conclusion, several somewhat rash suggestions have been made. These surmises have been made in the hope that they will suggest new experiments which will either prove or disprove them. Nothing more is intended. The effects of oxygen and the importance of hydrogen bonding require no significant coupling to give rise to concepts of far-reaching significance.
REFERENCES

ADDENDUM

GENERAL CONCLUSIONS OF LUMINESCENCE STUDIES

When this work was initiated, the suggestion was made that spectroscopy, while often an end in itself, can also be considered a tool for investigating chemical systems. The work presented was pursued in the spirit of this remark. Luminescence spectroscopy was indeed found to be a valuable tool in understanding physical and chemical phenomena.

The resolution of the original questions has required, however, familiarity with numerous techniques not only in spectroscopy but quantum mechanics, statistical physics, biochemical analysis, etc. Truly, most questions in science today cannot be restricted to a single field without losing many of the important implications. Thus, the trend towards specialization requires that collaboration with workers in other disciplines be sought. Given the wide applicability of the techniques of luminescence spectroscopy, interaction with almost all fields may be expected.
VITA

Terrence Lenoir Mathers was born at the Fort McArthur Army Hospital, San Pedro, California on December 13, 1952 to William Chester and Geri Magdalena Mathers (née Gertrude Magdalena Wagner). He attended Westwood Elementary School in Westwood, California, El Rodeo Junior High School and Beverly Hills High School in Beverly Hills, California, graduating in June, 1970. He attended Mississippi State University from January, 1971 through May, 1975 finishing with a B.S. degree in Chemistry. From August, 1975 until this writing he has been pursuing a Ph.D. in Physical Chemistry at Louisiana State University. He is not married.
EXAMINATION AND THESIS REPORT

Candidate: Terrence Lenoir Mathers

Major Field: Physical Chemistry

Title of Thesis: Luminescence Studies: Luminescence Of Aqueous Ionic Solutions; Temperature Dependence Of Phosphorescence Of Phenanthrene In Ethanol - Effects Of Gases

Approved:

Dean P. McGovern
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Date of Examination:

April 29, 1982