COO-913-53

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The Contribution of Electronically Excited States to the Radiation Chemistry of Organic Systems

Progress Report

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Abstract

Fluorescence spectra and fluorescence quantum yields have been obtained from upper excited states of benzene, toluene, p-xylene, naphthalene and pyrene. Measurements have been made both in the vapor and liquid phases. Non-radiative rate constants of the order of 10^{14} sec^{-1} have been calculated from the quantum yields and absorption strengths.

Emission from cyclohexane and bicyclohexyl solids has been found to critically depend on their crystalline structure. For cyclohexane the emission spectrum suddenly blue-shifts on cooling below its solid-solid phase transition temperature. For bicyclohexyl there is a sharp discontinuity in its emission quantum yield and blue shift in its spectrum on cooling below a heretofore unreported phase transition at ~0°C. The results are consistent with a partial Rydberg nature of the excited cycloalkane state.

Weak fluorescence has been observed from a number of simple olefins in the region from 230-260 nm, both in vapor and solution phases. Quantum yields and spectra are being determined. The transitions are tentatively assigned as originating from the lowest singlet Rydberg state.

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~~To Government Agencies and Their Contractors~~

During the Spring of 1972 we concluded an extensive project to collect and correlate emission spectral characteristics of a wide variety of saturated hydrocarbons. Although there remained still a host of unexplained observations, all of which we very much wanted to explore further, nevertheless, we decided to postpone this for a while. Our vacuum uv spectrometer had been tied up now for about 3 years looking at saturated hydrocarbon emissions. It was time for a change and we felt it would be interesting to attempt to utilize our experience in measuring low emission yields to search for fluorescence from highly excited states of aromatic molecules. Since the lifetimes of the higher states cannot be less than $\simeq 10^{-15}$ sec and allowed radiative transitions occur with rates of the order of 10^9 sec^{-1}, we estimated that measurement of an emission quantum yield at the 10^{-6} level would be adequate for our purpose. Already, with saturated hydrocarbons, we had managed to achieve the 10^{-5} level for excitation at 1650 Å. Using the more intense Hg 1849 Å and 2537 Å lines together with appropriate chemical filters and somewhat more careful optical baffeling we were confident 10^{-6} could be achieved.

The advantages of being able to observe an upper state emission were quite obvious. From the emission quantum yield and the radiative rate constant (obtained from the absorption strength) the rate of non-radiative depletion of the excited state could be determined. In view of the intense theoretical activity on internal conversion and the paucity of pertinent experimental data, any information on such rates would be significant. Additionally, no other technique could achieve a measurement of these rates, since 10^{14} - 10^{15} sec^{-1} is far out of the reach of current real time methods and line broadening technique would require for the upper excited states of most large molecules impossibly high resolutions.

From the emission quantum yields of the states S_n, S_{n-1}, etc. for excitation at each of the wavelengths λ_n, λ_{n-1}, etc. the internal conversion efficiencies from S_n to S_{n-1} would be determined. Again there is theoretical interest in these numbers. Also such data would finally give the answer to the question of whether non-radiative transition from S_n to S_1 involves cascade through intermediate states.

Once emission quantum yields are known, it is a short step to G values and thus would be available to the radiation chemist for the first time yields of highly excited neutral states. Since these states carry most of the oscillator strength below the ionization potential, it is likely that they are produced, in large part, directly and therefore their yields would be primary ones. Also primary G values for a number of neutral electronic states of a single molecule would provide more stringent requirements for the theory of the electron degradation spectrum.

Our first experiments were begun in the Spring of 1972. By the Summer we began to see emissions which seemed real and by the Fall of 1972 we submitted to the AEC two Progress Reports on our results, one dealing with S_n emission from liquids, the other with S_n emission from vapors. From then until the end of January measurements were refined and extended. Finally on January 30 we submitted two manuscripts to J. Chem. Phys. These have now been published and reprints are attached.

The equipment that had been used for these studies was the same as that used for the saturated hydrocarbon work. It consisted of a 1/2 meter vacuum UV analyzing monochromater and a 1/3 meter vacuum UV analyzer. Since we wished to continue with both upper state and saturated hydrocarbon emission studies, we decided to split the machine. Dr. Gregory took the 1/3 meter and Dr. Hirayama the 1/2 meter both to be used as exciting monochromaters in conjunction with 1/2 meter Bausch and Lomb monochromaters as analyzers (obtained from the Chemistry Department). Dr. Hirayama retained most of the original optical system whereas Dr. Gregory began construction of essentially a new apparatus. His equipment is now almost finished and will soon be available for further studies on saturated hydrocarbons.

Dr. Hirayama was back in operation in a short while but we decided before continuing with upper state emission to first finish off a problem that had been begun about two years ago concerning changes in the emission characteristics of some cycloalkanes at their solid-solid phase transitions. We had developed in the interim some new ideas about this problem and after about 3 months of additional experiments prepared a manuscript which was submitted May 31 to Chem. Phys. Letters. This has been accepted now and will appear in a forthcoming issue of that journal. A preprint is attached.

The observed changes in spectra at the phase transitions we explain in terms of a Rydberg nature of the first transition in the cycloalkanes and an effect of change in density at the solid-solid transition on the position of this Rydberg state. Environmental effects on Rydberg transitions have been a subject of increasing interest to spectroscopists during the past four years. Since electron ejection processes in condensed phases are, in a sense, reactions of Rydberg states and the large reaction rate constants of excited cyclohexane and decalin with benzene and CCl_4 that have been discovered through pulse radiolysis techniques may be connected with the Rydberg nature of the cycloalkane state the subject is clearly not without pertinence to radiation chemistry. We therefore decided to pursue the subject further.

With the possible exception of ethylene, the lowest excited singlet state of many simple alkanes is believed to be a Rydberg state. In the vapor phase, the Rydberg state usually appears quite distinctly in absorption on the long wavelength side of the strongly allowed $V \leftarrow N$ transition. In condensed phases, however, the Rydberg transition is broadened and apparently blue-shifted into the envelope of the $V \leftarrow N$ transition and is therefore difficult to study. Although simple olefins have never before been observed to emit, it is clear that were an emission observed from the Rydberg state, an excellent tool would be made available for studying its interaction with various environments. With this in mind we decided to postpone for a while our study of upper state emissions in order to have a try at finding the Rydberg fluorescence of simple olefins. This work began about the middle of May, and,although our results are still preliminary, we have now observed what we believe to be the Rydberg fluorescence from several olefins. A brief report of progress is attached.

We proposed last year to study a number of additional problems such as photoionization of alkane liquids and energy migration within these liquids and to determine G values of the lowest excited alkane states. For the reasons listed above, other problems engaged our interest and we have not had the time to pursue the original proposal as closely as planned. However, the G value work has just begun and since this is not too difficult a problem, we anticipate results within the next few months. The photoionization and energy transfer experiments we still very much want to do and are again proposing them for study next year.

Our work on the electron-impact spectrometer has continued actively during the past 9 months but progress has been slower than anticipated and we are still in the process of tuning the spectrometer along the input leg of the monochromater. Our most recent problem is that the beam current at the entrance to the monochromater sphere is an order of magnitude too low. We expect about 1 μamp and are at a level of about 0.1 μamp. The diode current is space charge limited and with 56V between anode and cathode is about 10 μamp. The beam is supposed to pass the condenser lens aperture without appreciable loss, which it does, and then to overfill slightly the first aperture of the 10:1 decelerator lens. However, we find the beam much too spread out at this aperture with almost the entire 10 μamp caught on its surface. The entire leg has by now been disassembled, aligned and reassembled many times and all of the elements seen by the beam coated with aquadag to reduce the level of stray electrons. Most recently we discovered a slight error in the computer program for the electron-optical design which resulted in our high voltage decelerator lens being too long by 0.675 mm. This is now being corrected in the Shop and hopefully will prove to be the origin of our difficulty.

We had expected the tuning to take not more than a few months and for the spectrometer to be fully operational by now. We had not, however, appreciated either the number or level of difficulties that can develop with a low energy electron beam and we are therefore now considerably more cautious in estimating the date of operation. However, a conservative guess at this time is that the 0° beam will be operating by the end of this year.

Time Devoted to Project by Principal Investigator:

a)	November 1, 1972 - June 15, 1973	50%
b)	June 15, 1972 - September 15, 1973	100%
c)	September 15, 1973 - October 31, 1973	50%

Meetings Attended by Scientific Personnel:

1. "Processes and Intermediates in the Radiation Chemistry of Condensed Phases". U.S.-Japan seminar, two Harbors, Catalina Island, California February 5-9, 1973. S. Lipsky presented lecture on "Properties of Highly Excited States".

2. "Gordon Conference on Radiation Chemistry", New Hampton, New Hampshire, July 23-27, 1973. T. Gregory,participant.

3. "Chemical Spectroscopy and Photochemistry in the Vacuum Ultraviolet" NATO Advanced Study Institute, Val Morin, Quebec, Canada, August 5-17. S. Lipsky, to present lectures on "Fluorescence in the Liquid State". F. Hirayama, participant.

Ph.D. Dissertations Completed:

1. Craig W. Lawson, Emission of Liquid Benzene: Comparison of 1849 and 2537 A Excitation, June 1973.
2. William C. Rothman, The Fluorescence of Saturated Hydrocarbons, August 1973.

Supplement to Technical Progress Report

for Contract No. AT (11-1)-913

for the period November 1, 1972 - October 31, 1973

1. Report Number COO-913-46

Title: Fluorescence of Saturated Hydrocarbons III. Effect of Molecular Structure

Authors: William Rothman, Fumio Hirayama and Sanford Lipsky

A preprint of this manuscript was attached to last year's progress report. With only slight alterations in footnote 23, it was accepted for publication and appears now in J. Chem. Phys. 58, 1300 (1973). A reprint is attached.

2. Report Number COO-913-49

Title: Fluorescence from Highly Excited States of Some Aromatic Molecules in Solution

Authors: Fumio Hirayama, T. A. Gregory and Sanford Lipsky

A preprint of this manuscript was attached to last year's progress report. However, some data were subsequently refined and the manuscript rewritten and submitted on January 30, 1973 as a Communication to J. Chem. Phys. It appears now in J. Chem. Phys. 58, 4696 (1973). A reprint is attached.

3. Report Number COO-913-50

Title: Fluorescence from Highly Excited States of Some Aromatic Molecules in the Vapor Phase

Authors: T. A. Gregory, Fumio Hirayama and Sanford Lipsky

Work on this manuscript was begun last year and a progress report (COO-913-48) was submitted in October, 1972. Further work was done on the system (toluene and p-xylene S_3 vapor emissions were found) and the progress report was extensively rewritten and submitted as a Communication to J. Chem. Phys. on January 30, 1973. It appears now in J. Chem. Phys. 58, 4697 (1973). A reprint is attached.

4. Report Number COO-913-51

Title: The Effect of Crystalline Phase on the Fluorescence Characteristics of Solid Cyclohexane and Bicyclohexyl

Authors: Fumio Hirayama and Sanford Lipsky

A preliminary report on this work was submitted May, 1971 (COO-913-44). The project was discontinued until recently when new experiments indicated a possible explanation for the observations. A manuscript was submitted to Chem. Phys. Letters May 31, 1973 and accepted on June 13. It is scheduled to appear in one of the forthcoming issues. A preprint is attached.

5. Report Number COO-913-52

Title: Fluorescence of Simple Olefins

Authors: Fumio Hirayama and Sanford Lipsky

This report is a preliminary one and is not intended in its present form for publication. However, the results will be discussed in a lecture at the NATO Advanced Study Institute on "Chemical Spectroscopy and Photochemistry in the Vacuum Ultraviolet", Val Morin, Quebec, Canada, August 5-17.