The Contribution of Electronically

Excited States to the Radiation

Chemistry of Organic Systems

Progress Report

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Abstract

The effect of n-perfluorohexane to quench both the emission and photo-ionization current of TMPD in isooctane and in tetramethysilane has been shown to be consistent with an interaction of perfluorohexane with some relatively long-lived, coherently excited state of TMPD that is generated at the photoionization threshold and which decays either to the emitting state of TMPD or to a geminate ion-pair.

The 0° and 90° electron impact spectra of the stable isomers of C_3, C_4, and C_5 saturated hydrocarbons are being determined. Preliminary results show large structural effects on the lowest Rydberg singlet-triplet splittings.

Two photon excited emission spectra of decalin, bicyclohexyl, and cyclo-hexane have been been observed in good agreement with previously reported one-photon spectra. A weak emission from propylene has also been detected.

From analysis of the effect of He to shift the NH_3 (3s) $\tilde{A} \leftarrow \tilde{X}$ transition it is concluded that a repulsive interaction sets in when the intermolecular separation is at least 6.5 Å. At pressures sufficiently high for validity of the statistical limit of line broadening theory it is shown that with inclusion of a Boltzmann factor in the perturber distribution function, that $d\tilde{\nu}/dP$ (the differential shift with pressure) becomes approximately independent of pressure and provides a unique value for the repulsive coefficient in a Lennard-Jones potential.

From measurement of the photosensitized singlet emission of p-xylene by bicyclohexyl excited at 1740 Å, it appears that the bicyclohexyl triplet contributes importantly to the sensitization. Also previously reported deviations from Stern-Volmer behavior in the fast-electron-excited process are found too in the photo-excited process (at 1740 Å) and therefore cannot be attributed exclusively to ionic processes.

The much larger ratio of excimer to monomer intensity in polystyrene as compared to neat liquid benzene appears to be due mainly to a reduced entropy of dissociation of the excimer when the phenyls are tied to the polymer backbone. Excimers formed therefore from distant phenyl groups may manifest themselves at high quencher concentrations and thus provide a new technique for probing polymer conformation.

I. Photoionization in Condensed Phases (with Kaidee Lee)

During the past year we have obtained further evidence for the existence of a relatively long-lived neutral excited-state precursor of the geminate ion-pair. This was accomplished by comparing the effects of n-perfluorohexane on both the fluorescence and photoionization quantum yields of TMPD in isooctane and in tetramethylsilane. A manuscript based on the results of this work has been accepted for publication in the International Journal of Radiation Physics and Chemistry (the Magat Memorial Issue) and should appear in print within the next few months. A preprint of this manuscript is separately attached. The abstract accompanying the manuscript is reprinted below.

Both the fluorescence intensity and the photoionization current from TMPD in tetramethylsilane and in isooctane have been studied as a function of the concentration, c_q, of n-perfluorohexane at excitation energies $\sim$1.2 eV above the photoionization threshold and at applied field strengths from 2-6 KV/cm. Over the range of c_q from 0.04-0.2 M, both processes are quenched to almost exactly the same extent implying that they proceed via a common, metastable precursor. The functional dependence of the quenching efficiency on c_q is observed to be of the Stern-Volmer form and therefore quite distinctly different from that which would be predicted were this precursor a geminate ion-pair. Rather, all of the evidence is consistent with an interaction of perfluorohexane with some relatively long-lived, coherently excited state of TMPD that is initially generated at the photoionization threshold and which decays either to the emitting state of TMPD or to a geminate ion-pair. Possible reasons for the absence of any observable effect of the action of the quencher on the ion-pair are discussed. To explain the disparity between these results and those obtained via the action of scavengers in radiation-chemical systems, it is suggested that for ionization processes occurring under high-energy transfer conditions, a geminate ion-pair may be directly produced without passing through a metastable, neutral, excited state.

This work has been continued using two other solvents, cyclohexane and n-hexane. Preliminary results have been extremely surprising. For both of these solvents we find that n-perfluorohexane now quenches the photocurrent to a significantly smaller extent than the fluorescence.

For example with isooctane, the photocurrent and fluorescence quenching parameters are 10.6 M^{-1} and 11.0 M^{-1} respectively whereas for n-hexane these parameters are 2.9 M^{-1} and 8.8 M^{-1} respectively. The full implication of these results are not yet understood. One possible conclusion is that whereas in isooctane (and in TMS) the product of the quenching of the metastable precursor is a nonionic species, in hexane (and cyclohexane) ionic products are _sometimes_ generated and these products continue to carry the photocurrent. The further consequences of this proposal remain to be examined and indeed too the origin of such differences between isooctane and TMS on one hand and hexane and cyclohexane on the other hand remains to be rationalized. Alternatively, of course, these new results may be a first signal that our model of a metastable neutral precursor to the ion-pair which is viable to quenching by n-perfluorohexane may be somewhat too simplistic and we have begun therefore to consider alternative schemes to explain at least the quenching of photocurrent - such as a scavenging action of the quencher on epithermal electrons. Some of our theoretical results with this new model are discussed in the proposal for continued support of this project for 1978-1979. To date, however, we have been unsuccessful in accomodating all of our results (and those of others) with this "epithermal" model - but approximations have been made and these still remain to be relaxed. Also other solvent systems and of course other quenchers remain to be studied.

II. Electron-Impact Spectroscopy (with D. C. Johnston and D. B. Johnston)

Three manuscripts prepared towards the end of last year were published

early this year. These are

1. "Electron Impact Spectra of Methane, Ethane, and Neopentane"
K. E. Johnson, K. Kim, D. B. Johnston, and S. Lipsky, J. Chem.
Phys. 70, 2189 (1979).

2. "A Re-Examination of the Intensity Distribution in the Electron
Energy-Loss Spectrum of Ethylene", K. E. Johnson, D. B. Johnston,
and S. Lipsky, J. Chem. Phys. 70, 3144 (1979).

3. "The Electron Impact Spectra of Some Mono-Olefinic Hydrocarbons",
K. E. Johnson, D. B. Johnston, and S. Lipsky, J. Chem. Phys. 70,
3844 (1979).

Reprints are separately attached. The abstracts of reprints 1 and 3

are duplicated below. Reprint 2 is a note, with no abstract, but essentially

demonstrates that previously observed discrepancies between optical and

electron-impact spectra of ethylene are simply manifestations of difference

in spectral resolution. The significance of this is that the many theore-

tical studies that had implicitly accepted the reality of this discrepancy

as evidence for a quadrupole transition in ethylene at ≈8.35 – 8.65 eV must

now be reconsidered.

Abstract 1.

Electron impact spectra of methane, ethane, and neopentane
have been obtained at scattering angles of 0° and 90° and at impact
energies from ≈30 to 250 eV. The data are consistent with the
lowest excitation in all of these systems to involve promotion
of an electron to a 3s Rydberg-like orbital. Differences between
0° and 90° onsets are attributed to large-angle intensity enhance-
ments of transitions to the 3s Rydberg triplets. At 90° all of
the spectra exhibit very similar intensity redistributions with
strong enhancement of transitions in the 12-15 eV region as compared
to lower-lying transitions. Assignments of the spectra and possible
origins of the angular dependence are discussed.

Abstract 3.

Electron impact spectra of ethylene, propylene, isobutene, trans-butene, cis-butene, trimethylethylene, and tetramethylethylene have been obtained at scattering angles of 0° and 90° and at impact energies from ≈20 to 150 eV. The spectra scan an energy-loss region from 2.5-15 eV. All of the observed Rydberg transitions of the methyl derivatives are correlated to corresponding Rydberg transitions of ethylene. The missing $\pi \rightarrow 3p$ transitions of ethylene are tentatively located via this correlation. Evidence is also presented for assigning the $N \rightarrow 3R'$ system of ethylene (at 8.26 eV) to a $\pi \rightarrow 3p_x$ transition. Possible assignments of some broad continua above ≈8-9 eV as a $\sigma \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions are considered. In agreement with other reported large-angle electron impact spectra, no evidence is obtained for transitions that could be assigned to triplet Rydberg states. However the $\pi \rightarrow \pi^*$ triplet transitions are all clearly located with transition energies in good agreement with those obtained by a variety of other techniques.

Following the acceptance of these manuscripts by J. Chem. Phys. we began a modification of the spectrometer to permit simultaneous 0° and 90° measurements. The major advantage of this being an economy of operation both in time and expense. The 90° leg in the new modification is the same as had previously been used for both 0° and 90° measurements. A new 0° leg however was put together from previously unused lenses and a newly fabricated analyzing sphere. Due to a very early suggestion by Dr. H. H. Brongersma, the surface of this new analyzing sphere was sand-blasted rather than carbonized, as had been our usual practice, (and, indeed, all other elements remained carbonized). After many unsuccessful attempts to generate a zero-degree beam with resolution close to theoretical (of ≈60 mv), we concluded that the problem had to reside in the nature of the sphere surface. With a new sphere fabricated and now carbonized, a 65 mv beam was easily achived. All of this however had taken many more months than we had anticipated. David C. Johnston is now in the process of surveying the 0° and 90° impact spectra of some 16 compounds that span almost all of the stable isomers of C_3, C_4, and C_5 saturated hydrocarbons. About 5 of these compounds are now finished and exhibit rather large differences in Rydberg singlet-triplet splittings. The origin of this is not yet understood.

III. Two Photon Laser Excitation of Saturated and Mono-Olefinic Hydrocarbons

   (with Larry Wilson and D. B. Johnston)

   <u>Emission spectra of decalin, bicyclohexyl, and cyclohexane were obtained</u> during the Winter of 1979 <u>that are in good agreement with spectra previously measured using a single photon excitation technique</u> [Rothman, Hirayama, and Lipsky, J. Chem. Phys. <u>58</u>, 1300 (1973)]. With the equipment working so well, it was then decided to start searching for the ethylene emission (with quantum yield estimated at $\sim 10^{-7}$) rather than continuing at this time with the saturated hydrocarbons. Propylene, with emission yield of 5×10^{-7} [Hirayama and Lipsky, J. Chem. Phys. <u>62</u>, 576 (1975)] was examined first, but strong Raman scattering obscured the weak emission. By cleaning the grating of the analyzing monochrometer and recoating its mirrors and with the addition of Br_2 gas filters and repositioning of the pin-diode and the propylene cell, a very weak signal was finally detected from the propylene. At about this time, however, Larry Wilson left Minnesota to take a position at Dow Chemical in Midland, Michigan and we began to solicit post-doctoral applications to continue the work. We expect to have someone here by the end of Fall, 1979. In the meanwhile David B. Johnston has been improving the intensity of the propylene emission. However, rather severe fluctuations in the intensity of the laser beam due largely to an inadequacy of our present pump to handle the large volume of N_2 that flows through the laser cavity has made difficult quantitative measurements of weak signals. The signal from the pin diode (channel A) is processed with an analog multi-function converter, exponentiated to the n power (n = 1.5 − 2) and divided into the photomultiplier signal (channel B) from the propylene cell but fluctuations in this ratio still remain. Funds are being requested for

a larger capacity pump (8 cubic ft/min). Also a signal averager that we are requesting for our photon counting spectrometer can be used advantageously in this experiment as well.

IV. Foreign Gas Perturbation of Molecular Rydberg States (with L. Wilson,

D. Merritt, and D. B. Johnston)

Although the major results on this project were obtained last year

and form the basis of L. Wilson's Ph.D. dissertation, it was discovered

during the course of preparing the ammonia results for publication that

in two rather crucial pressure regions there were an inadequate number

of points to extract the Lennard-Jones parameters. For $NH_3(\tilde{A})$ + He, below

≈ 20 atm, the impact limit of line-broadening theories [see Hindmarsh and

Farr, Progress in Quantum Electronics $\underline{2}$, 141 (1972)] appears to be an

adequate approximation and predicts that the maximum of the spectral distri-

bution should shift linearly with pressure, with slope $d\tilde{\nu}/dP$ (cm^{-1}/atm)

given by

$$\frac{d\tilde{\nu}}{dP} = \left(\frac{3\pi}{8}\right)^{2/5} \left(\frac{L^1}{RTc}\right) v^{3/5} \beta_6^{2/5} S(\alpha)$$

where $L^1 = 6.02 \times 10^{20}$, R = .082 liter atm, $c = 3 \times 10^{10}$ cm/sec, v is the

relative velocity of the NH_3 + He system, β_6 is the attractive parameter

in the Lennard-Jones interaction, i.e.,

$$\frac{\Delta E}{\hbar} = -\beta_6/R^6 + \beta_{12}/R^{12}$$

and

$$S(\alpha) = \int_0^\infty x\, dx\, \sin(\alpha/x^{11} - 1/x^5)$$

where

$$\alpha = (\gamma_{12}/\gamma_6^{11/5}) v^{6/5}$$

with

$$\gamma_6 = \pi\Gamma(5)\beta_6/2^4\Gamma^2(3)$$

and

$$\gamma_{12} = \pi\Gamma(11)\beta_{12}/2^{10}\Gamma^2(6) \quad .$$

Thus with β_6 obtained via Unsöld's relation [A. Unsöld, Physik der Sternatmosphären (2nd Ed.), 1955] $= 3.19 \times 10^{-32}$ cm^{6}sec^{-1} (using the NH$_3$ 3s quantum defect of 1.24 to provide an effective radial quantum number of 1.76), an accurate determination of $d\tilde{\nu}/dP$ at low pressure determines a unique value of β_{12}. Most of our previous data were obtained at He pressures too high for the validity of the impact limit and thus only a lower bound on β_{12} could be established (from the fact that $d\tilde{\nu}/dP > 0$ for He) of 2.3×10^{-75} cm^{12}sec^{-1}. Thus, a repulsive interaction is experienced when the intermolecular separation is at least 6.5 Å.

For argon, $d\tilde{\nu}/dP$ starts out negative at low P but at $\approx$100-200 atm approaches zero and then becomes positive. In this pressure region the statistical limit of line-broadening theories is an adequate representation and we have found that with inclusion of a Boltzmann factor in the perturber distribution function that at pressures slightly greater than required to make $d\tilde{\nu}/dP$ positive, this positive slope becomes approximately independent of pressure, with slope (for a Lennard-Jones potential) given by

$$\frac{d\tilde{\nu}}{dP} = (\frac{1}{6})\Gamma(3/4)(\frac{kT}{\hbar})^{3/4}(\frac{L^1}{RTc})\beta_{12}^{1/4}$$

where k is the Boltzmann constant and all other constants are as previously defined. Thus with an accurate slope in this region, β_{12} can be uniquely determined. Unfortunately our original Ar data did not go sufficiently to high pressures to establish accurately this slope.

Don Merritt began making the necessary additional measurements early this year but left before their conclusion to take a position with Medtronics Corporation in Minneapolis. David B. Johnston is currently completing these measurements. Larry Wilson will return from Dow the weekend of September 7 to discuss the first draft of our manuscript on this work.

V. Other Projects (with L. Walter)

Lee has spent the last year using our low-level emission spectrometer to conclude various parts of his experimental research. His thesis is now being written and a complete report of his results will be presented next year. Additional experiments that were concluded this year include a) Measurement of the emission quantum yield of the ND_3 $\tilde{A} \rightarrow \tilde{X}$ transition when excited into the $\nu_2^1 = 1$ level of the $\tilde{A}$ state using the Cd 2144 $\overset{\circ}{A}$ line. The purpose of this measurement was to compare the ratio of the quantum yields origining in $\nu_2^1 = 1$ and $\nu_2^1 = 0$ [see T. A. Gregory and S. Lipsky, J. Chem. Phys. $\underline{65}$, 5469 (1976)] with that predicted from the ratio of spectral widths of the absorptive transitions to these states [A. E. Douglas, Discuss. Far. Soc. $\underline{35}$, 158 (1963)]. b) Measurement of the quenching of the emission of bicyclohexyl by p-xylene and measurement of the intensity of the bicyclo-hexyl sensitized emission of p-xylene. This was done for excitation at 1740 $\overset{\circ}{A}$ to compare with previous measurements made using fast electrons as excitation source. Qualitatively similar dependencies of both "donor" and "acceptor" intensities on p-xylene concentration have been found suggesting that previously observed deviations from Stern-Volmer behavior $\underline{cannot}$ be attri-buted to ionic reactions. Although the data are still being analyzed, our qualitative conclusion thus far is that $\underline{the\ lowest\ triplet\ levels\ of\ saturated}$ $\underline{hydrocarbons\ play\ an\ important\ role\ in\ sensitization\ processes.}$

In doing some of these experiments Lee employed the photon counting equip-ment that the University purchased for us last year. Signal averaging was accomplished with apparatus borrowed from our electron-impact spectrometer. However this impact spectrometer now operates full time and we are therefore requesting funds for the purchase of another signal averager for use with our emission spectrometer and our laser experiment (see Section III).

VI. Collaborative Projects

1. Determination of Organic Chlorine in River Water by Photohydrolysis

    (with Professor Larry Conroy)

    This project was reported in our last years progress report. The work
remains in progress. Our only function here has been to provide some lab-
oratory space and some equipment.

2. The Effect of Molecular Weight on Polymer Conformations in Various
    Organic Solvents (with Professor Matt Tirrell)

    Our collaboration with Professor Tirrell on this project has become
much more extensive during the past year. We previously reported that
Professor Tirrell was interested in utilizing the ratio of monomer to excimer
fluorescence intensity to determine certain features of polystyrene conforma-
tions in organic solvents and that we made available to him and his student
a spectrophotofluorimeter that we had constructed and were no longer using.
During the past year I became intrigued with the anomolously
large excimer to monomer ratio exhibited by polystyrene as compared to
neat liquid benzene. After a number of experiments we were able to conclude
that this enhancement of excimer intensity is due almost exclusively to a
reduced entropy of dissociation of the excimer when tied to the polystyrene
backbone and this suggested new ways of probing the conformation. A pre-
liminary portion of this work was presented at the March APS meeting and
the abstract (from Bull. Am. Phys. Soc. 24, #3 March 1979) is reprinted
below.

> The fluorescence spectra of a series of dilute solutions of
> ten very narrow molecular weight distribution polystyrenes ($\overline{M}_n$: 700
> to $12 \cdot 10^6$) have been determined as a function of concentration sol-
> vent and molecular weight. The ratio of excimer to monomer fluores-
> cence intensity, I_E/I_M, shows no concentration dependence over the

concentration range 0.0025 to 0.05 g/cm^3, as would be expected for intramolecular excimer formation. This is contrary to certain previously published work. The spectra vary with solvent power in a manner consistent with a dependence of I_E/I_M on segment density within the polymer coil. However, I_E/I_M is found experimentally to depend on $(\overline{M}_n)^{1/2}$, and not on $(\overline{M}_n)^{-1/2}$ as does segment density. This dependence is shown to be consistent with the molecular weight dependence of the number of intramolecular segment-segment contacts for a randomly coiling polymer chain.

A manuscript based on this is currently being prepared.

VII. Time Devoted to Project by Principal Investigator

a) Academic year: 50%

b) Summer: 75%

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