COO-2192-22

ELECTRONIC RELAXATION PROCESSES IN POLYATOMIC MOLECULES

Progress Report
for period October 1, 1975-September 30, 1976

E. C. Lim

Wayne State University
Detroit, Michigan 48202

September 1976

Prepared For

THE U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
UNDER CONTRACT NO. E(11-1)-2192

DISCLAIMER

Abstract

Excitation energy dependence of radiationless decay rate under collision-free conditions was utilized as a probe of intramolecular vibrational relaxation in tetracene and pentacene. The results give evidence of vibrational relaxation which competes with electronic relaxation. The substitution dependence of $T_1(n\pi^*)\rightarrow S_0$ radiationless transition in monocyclic diazines and the temperature dependence of S_1 non-radiative decay rate in alcoholic solutions of polycyclic monoazines indicate that the vibronic interaction between the lowest energy $n\pi^*$ and $\pi\pi^*$ states leads to a rapid radiationless deactivation of the lower of the two electronic states. Finally, a photon-counting spectrofluorometer of very high sensitivity was constructed, and it was used to record $T_2\rightarrow T_1$ fluorescence in bromoanthracenes and $S_2\rightarrow S_1$ fluorescence in azulene. These spectra represent the first bona-fide, or the most convincing, observation of fluorescence between excited electronic states.

A. Electronic and Vibrational Relaxations in Dilute Aromatic Vapors

The major purpose of this program has been to explore and utilize the energy dependence of radiationless transition as a probe of intramolecular vibrational relaxation.

We studied the excess energy dependence of radiationless decay rate in dilute vapors of tetracene and pentacene, under collision-free conditions, by monitoring the quantum yield and the lifetime of the fluorescence as a function of excitation energy. These molecules represent the largest of the aromatic compounds which have been studied under collision-free conditions. It was found that there is no change in S_1(the lowest excited singlet state) non-radiative decay rate at the S_3 optical threshold. Furthermore, the radiationless decay rate in pentacene, which reflects the decay rate of $S_1 \rightarrow S_0$ internal conversion, decreases with the increasing excitation of C-C stretching mode. The lack of the dependence of the rates on the modes of preparation of S_1 (i.e., direct optical excitation of S_1 versus indirect excitation of S_1 via internal conversion from S_3) can be taken as an indicative of the loss of memory of the initially prepared states and, consequently, of the occurence of substantial intramolecular vibrational relaxation on the time scale of S_1 lifetime. Similarly, the observation that the excitation of C-C stretching modes, which are good accepting modes for $S_1 \rightarrow S_0$ internal conversion, leads to a decrease, rather than an increase, in the non-radiative decay rate can be taken to imply that the full population of the initially excited C-C stretch is not maintained during the excited state lifetime. These results, although subject to interpretation, imply that intramolecular vibrational energy redistribution can be a fast process compared with electronic relaxation for large aromatic molecules with small to moderate excess vibrational energies or, more generally, for aromatic molecules with large excess energies. The assumption of rapid vibrational redistribution is consistent with two other observations relating to the energy dependence of radiationless decay rate in molecules with large excess vibrational energies, namely: (1) a linear relationship between the excess vibrational energy (E_{vib}) dependence of $S_1 \rightarrow S_0$ internal conversion rate (k_{IC}), as measured by $\alpha = d \ln k_{IC} / d E_{vib}$, and the S_1-S_0 electronic energy gap of the molecule, and (2) excellent agreement between the $S_1 \rightarrow S_0$ internal conversion rate in solution and the value obtained by extrapolation of the experimental energy dependence of the gas phase rate to zero excess energy. Theoretical considerations indicate that the statistical average rate constant from random distribution of vibrational levels is a simple exponential function of the excess vibrational energy and of the S_1-S_0 electronic energy gap.

Publication: S. Okajima and I. C. Lim, "Intramolecular Vibrational Relaxation and Excitation Energy Dependence of Fluorescence in Dilute Vapors of Tetracene and Pentacene", Chem. Phys. Lett. 37, 403 (1976).

B. Vibronic Interactions and Radiationless Transitions in Aromatic Molecules with Non-bonding Electrons

The thrust of this program has been to investigate the effect of $n\pi^*$-$\pi\pi^*$ vibronic interaction on radiationless transitions of aromatic molecules with non-bonding electrons. More specifically, it is intended to test the so-called "proximity rule" which states that the proximity, or the near degeneracy, of the lowest energy $n\pi^*$ and $\pi\pi^*$ states leads to a rapid non-radiative deactivation of the lowest excited state.

The electronic energy gap between $n\pi^*$ and $\pi\pi^*$ states, and therefore the extent of vibronic interaction between them, can be modified by several different methods. The first is through the use of hydrogen bonding solvents, which decreases the energy of a $\pi\pi^*$ state while increasing the energy of an $n\pi^*$ state. The second is through the chemical substitution by a conjugating group which shifts the energies of $n\pi^*$ and $\pi\pi^*$ states to the opposite direction. Finally, the third involves thermal dissociation of the hydrogen bond in protic solvents which affects the relative energies of $n\pi^*$ states. While the first of these methods has been utilized before, the latter two have not been applied in connection with the proximity effects in radiationless transitions.

We have therefore studied the substitution dependence of $T_1(n\pi^*) \rightarrow S_0$ radiationless transition in monocyclic diazines with the view to test the validity of the proximity rule. The lowest triplet state of monocyclic diazines (pyrazine, pyrimidine, and pyridazine) is $^3n\pi^*$. Upon methyl substitution (or substitution by a conjugating group) the $^3\pi\pi^*$ state shifts to the red, while the $^3n\pi^*$ state shifts to the blue, so that the $^3\pi\pi^*$-$^3n\pi^*$ energy gap in methylated diazines. As the energy gap between thise two states decreases both the quantum yield and the lifetime of the $^3n\pi^*$ phosphorescence decreases dramatically, indicating that the $T_1 \rightarrow S_0$ radiationless decay rate increases sharply.

We also studied the temperature dependence of S_1 non-radiative decay rate in alcoholic solutions of several polycyclic monoazines (quinoline, isoquinoline and acridine). It was found that both the fluorescence yield and the fluorescence lifetime decrease dramatically as the temperature of the system is raised. Since the temperature dependence of the quantum yield is nearly identical to that of the fluorescence lifetime, it is the temperature dependence of nonradiative processes which is responsible for the thermal quenching of fluorescence. In sharp contrast to this temperature sensitivity of fluorescence, the quantum yield of $S_1 \rightarrow T_1$ intersystem crossing remains relatively independent of temperature. The only reasonable mechanism whereby heat can greatly quench fluorescence without much affecting $S_1 \rightarrow T_1$ intersystem crossing is the one in which both $S_1 \rightarrow S_0$ internal conversion and $S_1 \rightarrow T_1$ intersystem crossing increase with increasing temperature. For isoquinoline, the observed temperature dependence of the combined radiationless decay rates can be fitted by $k_{nr}(T) \sim k_{nr}(77\ K) + 6 \times 10^{12}\ e^{1600\ cm^{-1}/RT}$, in which the rates are expressed in units of s^{-1}. Both the magnitude of the preexponential factor and the magnitude of the activation energy suggest that it is the proximity of the $n\pi^*$ and $\pi\pi^*$ singlet states, caused by the breaking of hydrogen bonds by heating, which leads to the ultrafast radiationless processes at higher temperatures.

The proximity effect in radiationless transitions of N-heterocyclics can be traced to the vibronic interaction between the lowest energy $n\pi^*$ and $\pi\pi^*$ singlet states. If the energy gap between these states is relatively small, the lower state will be strongly distorted ($\Delta\omega \neq 0$), and it may even be displaced($\Delta Q \neq 0$), along out-of-plane vibrational coordinates. This distortion and displacement can lead to a large increase in the vibrational factor for radiationless transition, which is known to depend on the relative frequency shifts and displacements of the accepting modes.

In addition to the above work we have also examined the matrix elements of $T_1(\pi\pi^*) \rightarrow S_0$ radiationless transitions in aromatic molecules with non-bonding electrons in order to deduce the relative importance of various mechanisms of the intersystem crossing. The study indicates that, unless forbidden by symmetry, the mechanisms involving $n\pi^*$-$\pi\pi^*$ vibronic coupling in the triplet manifold are much more important than those involving vibronic coupling in the singlet manifold. Unlike in aromatic hydrocarbons, the mechanisms induced by nonadiabatic coupling can be competitive when compared to those induced by adiabatic coupling.

The study of the position-dependent isotope effects in radiationless transitions, which represents one of the major goals of this phase of the research (see the previous renewal proposal), did not progress as rapidly as we expected, the major stumbling block being the unexpected non-exponential decay of phosphorescence in naphthaldehydes and napthyl methyl ketones. We are presently trying to uncover the origin of this unexpected observation.

> Publications: S. L. Madej, S. Okajima, and E. C. Lim, "Proximity Effects in Radiationless Transitions of Aromatic Molecules with Nonbonding Electrons: Substituent and Temperature Dependences of Luminescence in Some N-heterocyclics", J. Chem. Phys. 65, 1219 (1976); N. Kanamaru and E. C. Lim, "$T_1(\pi\pi^*) \rightarrow S_0$ Radiationless Transitions in Aromatic Molecules with Nonbonding Electrons", J. Chem. Phys., in press.

C. Fluorescence Between Excited Electronic States of Aromatic Molecules

With very few exceptions, the study of fluorescence in polyatomic molecules has been limited to the radiative transition between the lowest excited singlet state and the ground state. This practice is dictated by the high efficiency of $S_n(n>1) \rightarrow S_m(m>1)$ internal conversion which leads to a very low quantum yield of fluorescence from S_n. Thus, much of the additional information on excited states that can be gained from emission studies remains unexplored. With the advent of the photon-counting technique, it is now possible to measure fluorescence quantum yield as low as 10^{-6}, so that the observation of fluorescence between excited electronic states is technically feasible in some favorable cases. Accordingly, we have constructed a photon-counting spectrofluorometer of very high sensitivity, and used it to record $T_2 \rightarrow T_1$ fluorescence in azulene. The observation of $T_2 \rightarrow T_1$ fluorescence in anthracene derivatives is important since it has been proposed, but not proven, that the intersystem crossing in meso-substituted (9- and 9,10-) anthracenes proceeds through the second triplet state (T_2) lying slightly above S_1. The observation of $T_2 \rightarrow T_1$ fluorescence, as well as the measured energy of T_2, provides compelling proof for the correctness of this supposition. The appearance of non-totally symmetric vibrations in highly resolved $S_2 \rightarrow S_1$ fluorescence of azulene indicates that a substantial portion of the total oscillator strength is vibronically induced. Significant new information on vibronic coupling pathways in azulene is expected to emerge when a detailed vibrational analysis of the fluorescence spectrum is completed.

Publications: G. D. Gillispie and E. C. Lim, "$T_2 \rightarrow T_1$ Fluorescence in Subsitiuted Anthracenes", J. Chem. Phys., in press; G. D. Gillispie and E. C. Lim, "$S_2 \rightarrow S_1$ Fluorescence of Azulene in a Schpolskii Matrix", submitted to J. Chem. Phys.

Research Participants

Gregory D. Gillispie, post-doctoral research associate

Suzanne Lyle Madej, predoctoral research assistant

Shigeo Okajima, predoctoral research assistant

Edward C. Lim, principal investigator

The principal investigator devoted 2/3 of his time to the project during three summer months and at least 1/3 of his time during the remaining nine months.