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DEUTERIUM ISOTOPE EFFECTS IN ELECTRONIC RELAXATION OF LARGE POLYATOMIC MOLECULES

Progress Report

Edward C. Lim

Wayne State University
Detroit, Michigan 48202

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Abstract

Isotope and energy dependences of radiationless decay rate, combined with energy dependence of sensitized phosphorescence in biacetyl, show that internal conversion to the ground state is generally a dominant photophysical process for molecules with large vibrational excitation. The energy dependence of decay rate gives evidence of slow vibrational relaxation (compared to electronic relaxation) for molecules with small to moderate excess energies, but vibrational relaxation faster than electronic relaxation for high vibrational relaxation. A new theoretical account of the isotope effects on radiative transitions and a theoretical analysis of the position-dependent isotope effects in radiationless transitions of aromatic molecules with non-bonding electrons have been presented.

PROGRESS REPORT

I. Energy and Isotope Dependence of Electronic Relaxation in Isolated Organic Molecules

The study of the excitation energy and isotope dependence of fluorescence (quantum yield and lifetime) in dilute organic vapors has been extended to include a number of additional aromatic hydrocarbons and their derivatives. The results of these investigations lead to the following general conclusions and observations:

(1) Intramolecular vibrational redistribution appears to be a slow process compared to electronic relaxation for smaller aromatic molecules with low excess vibrational energies, but it appears to be faster than the electronic relaxation when the excess vibrational energies are large,

(2) The greater excess energy dependence of $S_1 \rightarrow S_0$ internal conversion (the dominant photophysical process for large excess energies) in deuterated compounds leads, for large excess vibrational energies, to a larger absolute decay rate for these molecules than the corresponding protonated compounds, although the converse is the case for low vibrational excitation.

(3) The excess vibrational energy dependence of $S_1 \rightarrow S_0$ internal conversion rate is nearly an exponentially increasing function of the $S_1 - S_0$ electronic energy gap.

The experimental evidence leading to the assumption of rapid vibrational energy redistribution are (a) the lack of change in the electronic relaxation rate as the threshold for excitation of S_3 is crossed, (b) the close correspondence between the estimated $S_1 \rightarrow S_0$ internal conversion rates of naphthalene and anthracene in solution and the values obtained by extrapolation of the exponential energy dependence of the gas phase internal conversion rates to zero excess energy, and (c) the observation (3), which has been theoretically predicted for cases in which vibrational relaxation is faster than the electronic relaxation.

We have also carried out a calculation of the excess energy dependence of $S_1 \rightarrow S_0$ internal conversion in gas phase aliphatic ketones through a quasi-diatomic molecule model calculation which treats the optically excited carbonyl stretching vibration as the only important accepting mode. Comparison of the result with experiments indicates that the sharp decrease in the fluorescence lifetime with increasing excitation energy in certain halogenated ketones can be rationalized in terms of a rapidly increasing rate of internal conversion as the vibrational energy content of S_1 is increased. This has serious implications on the interpretation of gas phase photochemistry of these compounds since the result points to the probable importance of the ground state dissociation following internal conversion.

The following papers are in print or submitted for publication:

C.-S. Huang and E. C. Lim, "An Energy Gap Law for Radiationless Excitation of Aromatic Molecules with Excess Vibrational Energies: $S_1 \rightarrow S_0$ Internal Conversion Following Excitation of S_2 and S_0," J. Chem. Phys., 62, 3826 (1975).

S. Okajima and E. C. Lim, "Intramolecular Vibrational Relaxation and Excitation Energy Dependence of Fluorescence in Dilute Vapors of Tetracene and Pentacene," submitted to Chem. Phys. Letters.

G. D. Gillispie and E. C. Lim, "The Role of Internal Conversion in the Gas Phase Photochemistry of Aliphatic Ketones," Chem. Phys. Letters (in press).

C.-S. Huang and E. C. Lim, "The Energy and Isotope Dependence of Electronic Relaxation in Dilute Vapors of Fluorene and β-Naphthylamine," submitted to Chem. Phys. Letters.

II. Isotope Effects on Radiative Electronic Transitions

Isotope effects on $T_1 \rightarrow S_0$ radiative transitions of aromatic hydrocarbons and isotope effects on $S_0 \rightarrow S_1$ absorption have been subjected to further experimental studies. The most unusual new finding is the observation of significant deuterium isotope effect ($I_D/I_H \simeq 1.2$) on the 0,0 band of $S_0 \rightarrow S_1$ absorption in pyrazine. Comparison of the $T_1 \rightarrow S_0$ decay rates in $^{12}C_6D_6$, $^{12}C_6D_6$, and $^{13}C_6H_6$ shows that $^{13}C_6H_6$, with nuclear spin on carbon, does not decay faster than the other two compounds. This effectively proves that the nuclear hyperfine interaction is not the source of the deuterium isotope effect on $T_1 \rightarrow S_0$ radiative decay. That leaves the nuclear coordinate

dependence of the transition moment as the only logical source of the isotope effect. Since it is the 0, 0 band of the spectra which is affected by deuteration, the conventional theory requires that the nuclear coordinate dependence of the transition moment come from the higher-order mechanisms involving non-Condon or non-BO Herzberg-Teller coupling. However, the magnitude of the observed isotope effect on $T_1 \rightarrow S_0$ radiative transition, as well as that on $S_0 \rightarrow S_1$ absorption of pyrazine, is too large to be accounted for by these higher-order mechanisms. Because of these difficulties we have carried out a theoretical investigation of the nuclear coordinate dependence of electronic transition moment from a non-conventional approach. By using "AO following nuclei" wavefunctions as the building block for the electronic wavefunction in the adiabatic BO vibronic wavefunction, the spin-free Hamiltonian is diagonalized to generate eigenfunctions and eigenergies. It was found that the electronic transition moments based on these eigenfunctions show dependences upon the vibrational modes which are not directly involved in vibronic coupling. This leads to interpretations of deuterium isotope effects in radiative transitions which are not based on the convertional Herzberg-Teller description.

The same theoretical analysis has also been shown to be capable of predicting relative intensity of the vibronically induced band in absorption relative to that in emission for both pyrene and pyrazine.

Two papers on these subjects are in press. These are:

N. Kanamaru and E. C. Lim, "Nuclear Coordinate Dependence of Electronic Transition Moments in Orbitally Forbidden Transitions: A New Interpretation of Deuterium Isotope Effects," Chem. Phys. Letters (in press).

N. Kanamaru and E. C. Lim, "Vibronic Coupling and Polyatomic Spectra," Chem. Phys. Letters (in press).

III. Position-Dependent Isotope Effects in Radiationless Transitions of Aromatic Molecules with Non-bonding Electrons

A theoretical analysis of radiationless transition from an electronic state, which is vibronically coupled to a higher-lying state, has been carried out. The result indicates that, by virtue of large distortion (frequency change) and displacement along the normal coordinate, the vibronically active out-of-plane bending vibrations may be important accepting modes for the radiationless transition. This provides a theoretical basis for understanding the previously observed position-dependent isotope effects in dibenzoquinoxaline. We have also carried out synthesis of various position isomers of deuterated quinoxaline, phthalazine, β-naphthaldehyde and β-naphthylmethyl ketone, for the purpose of extending these studies.

The following paper on this subject has been published:

N. Kanamaru and E. C. Lim, "Radiationless Transitions in Aromatic Molecules with Non-bonding Electrons: Role of Vibronically Active Out-of-Plane Modes," J. Chem. Phys., 62, 3252 (1975).

Participants in the research during this period were:

1. E. C. Lim, principal investigator
2. N. Kanamaru, post-doctoral research associate
3. G. D. Gillispie, post-doctoral research associate
4. S. Okajima, predoctoral research assistant
5. C.-S. Huang, pre-doctoral research assistant, not receiving compensation from the grant.

Dr. Kanamaru is presently with the Institute of Physical and Chemical Research in Wako-Shi, Japan.

The principal investigator devotes full time to the project during 3 summer months and at least 1/3 of his time during the remaining 9 months.