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Radiative electronic energy transfer-time studies of naphthalene–biacetyl system by one and two-photon excitation, and optical antenna mechanism

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Abstract

In principle, the optical energy absorbed by a complex molecule raises that molecule to one of its excited states, and afterwards this excitation energy decays through the relaxation channels. Initially, electronically excited naphthalene emits photons and these emitted photons are absorbed by the acceptor molecule biacetyl, then excited biacetyl fluoresces. In this investigation radiative energy transfer-time is measured in cyclohexane by one and two-photon excitations. The UV–vis spectrum of biacetyl vapor at room temperature conditions was broad and structureless.
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1. Introduction

The absorption spectrum of naphthalene vapor from 5 to 30 eV has been measured using synchrotron radiation. Above the bands at 5.89 and 7.7 eV which are assigned to π–π^* transitions, there is a steep increase to a broad continuum with a maximum at about 16 eV, attributable to sigma electronic excitation superimposed on this continuum. There is a complex sequence of bands, which are analysed as Rydberg series. The analysis is aided by complementary data from photoelectron spectroscopy. The absorption spectra of naphthalene in rare gas matrices have been observed from 333 to 125 nm, [1–4]. The experimental and theoretical values of the transition energies and oscillator strengths of the six transitions assigned to π-electronic states. It is of interest that all the assigned transitions are parity allowed, and it is not necessary to postulate any parity forbidden transitions. The peculiar line-shapes of certain absorption transitions in naphthalene have been interpreted, in terms of interference between Rydberg

states and isoenergetic π^* vibronic states, leading to antiresonances in the absorption spectrum. Symmetry properties of the first two excited singlet states and triplet lifetime are also reported [5–17]. The compound 2,3-butanedione, commonly called biacetyl, has been the subject of considerable study in optical spectroscopy. Biacetyl is one of the products in the photolysis of acetone, and biacetyl itself undergoes photophysical and photochemical reactions. The electronic states of biacetyl have been discussed in terms of the LCAO-MO theory [18–20]. The absorption and emission spectra of the biacetyl crystal at low temperatures show considerable sharp vibrational structure [21]. The visible absorption of biacetyl vapor is discrete but extremely complex owing to the thermal distribution of molecules over many levels of low-lying torsional modes. The principle absorption bands belong to the n–π^* electronic transitions, the 0–0 bands occurring near 437 and 490 nm in the solid at low temperatures [21–24]. Biacetyl is the simplest molecule among a wide variety of α-dicarbonyl compounds, which are of great interest from the photophysics and photochemistry point of view. Raman-active and IR-active frequencies in the solid, liquid and gas phase are known for the ground state of biacetyl.

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2. Experimental

Spectroscopically pure naphthalene and biacetyl were obtained from Aldrich and used as received. All other chemicals used also were spectroscopically pure. Naphthalene and biacetyl in the vapor phase mixed in a high vacuum line at the concentrations of 1 mm mercury pressures. The steady state absorption spectra were measured in a Cary-219 Spectrophotometer using 1 nm bandpass. An SLM-8000-S, Spectrofluorimeter was used to obtain steady state fluorescence spectra. Fluorescence lifetimes were determined with a PRA single photon counting nanosecond fluorescence spectrophotometer interfaced to a Terak-8510 graphic system for data analysis, storage, and display. Three pulsed Laser sources were used for Laser flash photolysis: Lambda-physics EMG-101, MSC-Excimer (XeCl, 308 nm, approximately 8 ns, 10–100 mJ pulse^{-1}) and Excimer pumped dye Laser operating at 250–750 nm band, and optical filters were used to select 300 and 600 nm lines for one and two-photon excitations, Molectron UV-400 nitrogen (337.1 nm, approximately 8 ns, 2–3 mJ pulse^{-1}), and Quanta-Ray DCR-1 Nd: YAG coupled with PDL-1 dye-laser operating at 266, 335, 485, 532 and 1064 nm. Approximately 6 ns, 10–100 mJ pulse^{-1}. The lasers were attenuated and/or adjusted properly or defocused so that their intensities as absorbed by the solutions or vapor mixtures were comparable when the three laser systems were used to generate excitation pulses at various wavelengths. A kinetic spectrophotometer with nanosecond response (pulsed 500 W-Xenon lamp, Bausch and Lomb, UV–vis high intensity monochrometer and RCA-4840 photomultiplier tube with output signal terminated into 93 Ω), a Tektronix-7912 digitizer and an LSI-11 microprocessor unit controlled the experiments and processed the data at the initial stage. The data from LSI-11 were finally transferred to a time shared PDP-11/55 computer system for storage and further analysis. All of the three laser flash experiments in the study used front-face geometry, with angles of 20°–30° between the direction of using a flow cell; the kinetic experiments, which required a small number of laser shots (from 1 to 99 shots), were performed in static cell. The pathlengths of the cells were 2–3 mm along the direction of the analyzing light. The flash and laser flash photolysis experiments for the vapor phase were carried out on oxygen-free (degassed in the vacuum line, background pressure was 10^{-7} Torr), solutions contained in $1 \times 0.2 \, cm^2$ quartz cells, with the absorbed light passing along the 0.2 cm pathlength. The exciting laser beam intersected the cell at angles ranging from 20°–90°, and the flash duration time was short enough (6–20 ns), to follow the decays of the excited states.

3. Results and discussion

The vapor sensitization of biacetyl fluorescence or phosphorescence by several aromatic donors has been investigated in detail, in an attempt to validate the biacetyl method. A brief description of the biacetyl methods are as follows. An aromatic donor will be raised to its first excited singlet by absorption of ultraviolet radiation. Among other processes which will subsequently occur, the triplet state of the donor molecules will also be populated. If a suitable acceptor molecule, (i.e. biacetyl), is present, the electronic energy of the donor, naphthalene, can be transferred to the biacetyl, producing a biacetyl molecule in its first singlet state. Excited singlet biacetyl molecules so produced will emit fluorescence lights as well as phosphorescence lights, this behavior are labeled as sensitized fluorescence and sensitized phosphorescence, since emissions occurs without the emitting molecule initially absorbing light. Comparing the quantum yield of the sensitized fluorescence or sensitized phosphorescence with that produced in a separate experiment were biacetyl itself is excited affords a determination of the triplet yield of aromatic donor. The triplet yield is, in essence a measure of the number of singlet donor molecules which eventually cross over into the triplet manifold. The following reaction mechanism is typical for optical energy transfer from donor to acceptor molecules (Scheme 1).

In this study, donor molecule was naphthalene in the vapor phase and acceptor molecule was biacetyl in the vapor phase, therefore naphthalene emits light as fluorescence and this fluorescence light will be absorbed by the acceptor molecule biacetyl, then excess energy in the biacetyl will be released as light at different frequencies, which is sensitized fluorescence. Naphthalene emits light as an optical transmitter and biacetyl absorbs this light as an optical receiver, therefore the mechanism is called an optical antenna at the nano-Hertz time domain (Scheme 2).

However, if for example, the sensitization process produces not ^{3}BiA but an exciplex (excited state complex between triplet donor and the ground state of biacetyl), then phosphorescence quantum yields and lifetimes will almost certainly be quite different. Also in the sensitized process vibrational energy will also be imported to the biacetyl, for in general triplet aromatic states lie higher energies than triplet biacetyl. It is possible that triplet biacetyl could decompose under these conditions and thus change the phosphorescence quantum yield markedly from that obtained in the direct process. Any of the above complications would completely vitiate the biacetyl method for the determination of triplet yields. Normally, molecules with extinction coefficients of the order of 10^{+4} mol^{-1} l cm^{-1}, can be photographed at a concentration of 10^{-6} to 10^{-7} M. The excitation light was passed through a 1 cm quartz cell containing the gaseous sample. Emission was detected at right angles via a photomultiplier and recorded photographically on a storage oscilloscope. Experiments were then done on detecting the sensitized fluorescence and sensitized phosphorescence of biacetyl using a variety of aromatic donors. Here, excitation wavelengths were in the ultraviolet where absorption of biacetyl was either zero or less than 5%. However, the slight absorption by biacetyl at these wavelengths, if no consequence, since biacetyl under these conditions was excited to its second