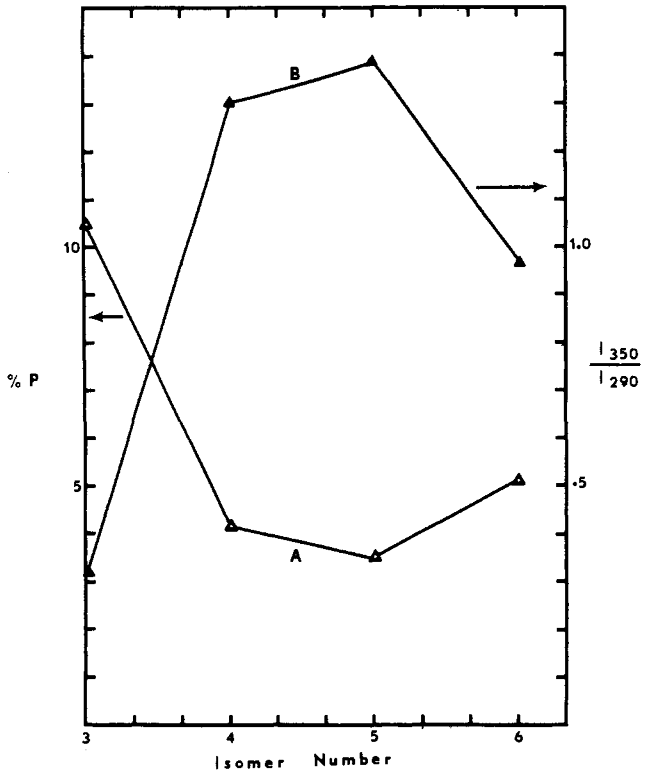

Figure 2. Plots of degree of polarization (left-hand ordinate) and I_{350}/I_{290} (right-hand ordinate) against isomer number for alkyl benzenesulfonate micelles in water at 25.0 ± 0.2 °C.

diffusion of molecules. Thus, the data in Figure 2 show that, in micelles composed of these surfactants, the environment around the benzene moiety resists both translational and rotational diffusion in a similar way. (Similar effects have been found[15] for a series of isomeric C_{16} alkyl benzenesulfonates.) This is the first instance that we know where translational and rotational measurements have been made on the same system.

Why the microviscosity in the vicinity of the fluorescent residue in micellar aggregates should vary in such a manner with isomer composition is not readily apparent. One possibility is that the configuration of the two alkyl chains about the benzene moiety is a determining factor. It is reasonable to expect that the *p*-sulfonate group in all cases lies at the periphery of the micelles at the water interface and that the micellar radius is governed by the length of the longer chain. Along the series $3C_{12}$-$6C_{12}$ the longer chain decreases from 9 to 6 carbon atoms and the short chain increases from 2 to 5 carbon atoms. Thus, as the micelles become smaller in radius, more room has to be found for the increasingly longer short chains. To accommodate this tendency toward crowding, it is possible that the head groups separate to greater distances. Thus, there exists two opposing effects, the interrelationship between which could conceivably result in the observed minimum in local viscosity. These possibilities are being tested using alkyl benzenesulfonate which have been synthesized with long chains of equal length and variable short chains.

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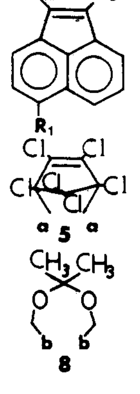
Dual Wavelength Fluorescence from Acenaphthylene and Derivatives in Fluid Media

Sir:

Fluorescence that occurs from upper excited states has been called anti-Kasha fluorescence (AKF) by Birks.[1] Azulene is a well-documented example of AKF,[2] and fluoranthene[3] and 1,12-benzoperylene[1] show similar characteristics. Fluorescence from the second excited singlet state of [18]annulenes was also reported.[4] Acenaphthylene (**1**) is a nonalternate hydrocarbon whose luminescence characteristics are largely unexplored because of extremely low quantum yields of fluorescence.[5] The major absorption bands of **1** recently were characterized by MCD studies.[6] Our interest[7] in the photochemistry of **1** led us to investigate the laser-induced emission from **1** and its derivatives. To our surprise, two well-separated emission maxima are observed,[8] one of which appears to be AKF.

The compounds under study are displayed in Chart I.[9] Dilute solutions (10^{-4}-10^{-5} M) of each compound in different solvents were subjected to laser excitation while being maintained in an oxygen-free atmosphere by continuous nitrogen sparging in the cuvette. Emission output was plotted by aver-

Chart I



	R_1	R_2	R_3
1	H	H	H
2	Ac	H	H
3	CN	H	H
4	H	D	D
5	H	a	a
6	H	CH_2OH	CH_2OH
7	H	CH_2OAc	CH_2OAc
8	H	b	b
9	H	CH_3	CH_2Cl
10	H	CH_2Br	CH_2Cl
11	H	Br	Br

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Table I. Emission Maxima and Approximate Lifetimes for Acenaphthylene Derivatives in Various Solvents

compd	λ_1, nm	τ_1, ns	λ_2, nm	τ_2, ns	solvent
1	400	0.9	550	0.2	heptane
1	410		550		2-propanol
1	410		550		1-bromobutane
2	400	0.7	570	0.3	hexane
3	390		570		hexane
4	410	0.8	540	0.2	hexane
5	390	0.4	600	0.4	heptane
6	390		570		2-propanol
7	410		540		heptane
8	400		570		heptane
9	400	44	550 (w)		heptane
10	400	45(7)[a]	no peak		heptane
11	410	<0.2	540	<0.1	hexane

[a] The curve was best fitted by two exponential decay curves with the second half-time shown in parentheses.

aging the raw data. Lifetimes were recovered by deconvolution on the laser pulse. Lifetimes of <1 ns must be assumed to be approximations since the decay of the excited state is concomitant with the laser pulse.[10]

In Table I the wavelength maxima and representative lifetimes are shown for compounds **1–11**. A tendency for the half-time of the 400-nm emission to be slightly longer than the 560-nm emission was generally observed. Substances **9** and **10** show enigmatic luminescence behavior compared with the rest of the compounds. All compounds produced similar absorption spectra. Compound **5** shows a bathochromic shift[9b] of the $S_0 \rightarrow S_1$ band whose onset occurs near 470 nm[6] in the parent compound **1**. This band is called the K-band by Michl[6] and is characterized as a charge-transfer band from the ethylene bridge to the ring. The second $S_0 \rightarrow S_2$ band, or so-called L-band, occurs near 344 nm for all compounds **1–11**. It is apparent that a nitrogen laser is directly populating the S_n states where $n > 1$.

A typical emission spectrum for **5** is plotted in Figure 1. A simulation of the absorption spectrum is added to the direct plot from the computer. The relative intensity of the 400-nm emission to that of the 560-nm emission was found to vary with the nature of the compound. Compound **5** shows a more intense 400-nm emission, while other simpler compounds in the series produced maxima of similar magnitude.[5d] The absorption of these yellow substances is significant in the region of 400 nm and this can be expected to have an influence on the apparent lifetime and the wavelength maximum since the so-called inner filter effect must occur for this emission. The inner filter effect is known to enhance the apparent half-time compared with that of the intrinsic lifetime.[11]

The unusual double fluorescence observed is apparently a characteristic property of acenaphthylene and its derivatives. The Stokes shifted fluorescence for **1** was reported by only one group of investigators[5b] and the quantum yield must be extremely low ($\phi_F < 10^{-4}$) since most studies under low-intensity stimulation detect no emission.[5a] Our data corroborate the validity of a very weak emission near 560 nm.

We believe that the 400-nm emission is probably $S_n \rightarrow S_0$ or an AKF. Since the $S_0 \rightarrow S_2$ absorption band is near 337 nm, the most likely event is $S_2 \rightarrow S_0$ fluorescence. Two notable exceptions are compounds **9** and **10**. The emission lifetime of 44 ns for each is surprisingly long for the AKF band compared with those of the other compounds. The Stokes shifted band is so weak for these two substances that any accurate half-time estimate is precluded. The $S_0 \rightarrow S_1$ band is longitudinal in polarization,[6] while higher excited states are transverse and/or longitudinal. The scission of carbon–halogen bonds is a process that is known to occur under photostimulation.[12] If halogen atom dissociation into a radical-cage combination occurred for substances **9** and **10**, then the transverse polarization of $S_2 \rightarrow S_0$ may be enhanced through additional conjugation with incipient radicaloid centers and the lifetime of the state prolonged. Such a process might interfere with the population of S_1 since the "structure" for S_1 is temporarily absent and $S_1 \rightarrow S_0$ emission is thereby inhibited. A definitive answer to the dilemma posed by the unusual spectroscopic behavior of **9** and **10** must await detailed experimentation.

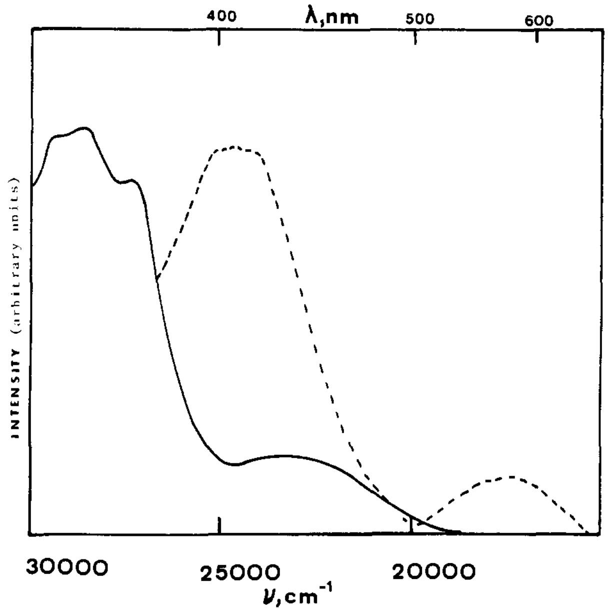

Figure 1. The absorption and laser excited emission spectrum of 7,10-methano-7,8,9,10,11,11-hexachloro-7,10-dihydrofluoranthene showing Stokes and anti-Stokes emission: absorption (——); emission (- - -).

The propensity for compounds **1–11** to exhibit AKF under laser excitation is certainly a rare observation although not unprecedented.[1-4] We suggest that the higher electronic states of **1–11** are severely distorted from ground-state geometry. We suspect that poor Franck–Condon factors for relaxation into S_1 from S_2 are also significant. The high input of energy by laser excitation creates a population of S_n whose emission $S_n \rightarrow S_0$ competes with internal conversion $S_n \rightarrow S_1$.

We anticipate that other derivatives of acenaphthylene can be found that show double fluorescence and we are currently attempting the syntheses of some novel analogues for further study.

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(10) A nitrogen-laser-emitting pulses of 337-nm light of 8 ns fwhm and delivering 2–3 mJ of photon energy was used as the excitation source. A Tektronix R 7912 transient digitizer and a 4010 video graphics terminal were interfaced to a PDP11 T34 computer system and programs written to allow recovery of half-times and to plot in a point-by-point fashion the emission spectrum from each compound: Rodgers, M. A. J.; Foyt, D. C.; Zimek, Z. *Radiat. Res.*, in press.

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Selected Fragment Scans of Mass Spectrometers in Direct Mixture Analysis

Sir:

The analytical applications of mass spectrometry derive largely from information on fragmentation reactions of the general type

$$m_1^+ \rightarrow m_2^+ + m_3 \qquad (1)$$

Conventional mass spectra, whatever the ionization method, present abundances integrated over all those reactions which yield each individual product ion. The importance of metastable ions is that particular reactions are examined.[1] When two independent analyzers are employed to study metastable ions (or the analogous collision-induced dissociations), then two quantities in eq 1 can be specified uniquely. Methods are available which allow scans to be made for fixed m_1^+ (detection of all fragments m_2^+ from a selected parent ion)[2] and for fixed m_2^+ (detection of all precursors m_1^+ of a selected fragment ion).[3,4] Selection for either m_1^+ or m_2^+ can be achieved by scanning a single analyzing field given an instrument of appropriate (reversed) geometry.[5]

We now report the first examples[6] of a new method of scanning mass spectrometers such that the neutral fragment mass, m_3, is constant. This procedure allows compounds with particular functional groups to be directly detected in complex mixtures. As such, it should prove complementary to mass-analyzed ion kinetic energy (MIKE) scans which allow individual compounds to be determined.[7] The new procedure maximizes the *chemical* information by selecting only ions which undergo a specified reaction. For example, all anions which undergo the loss of a neutral fragment of 44 mass units can be detected in a single scan (Figure 1); since this reaction is characteristic of carboxylic acids,[9] one has an immediate indication of the presence and molecular weights of any carboxylic acids in a sample.

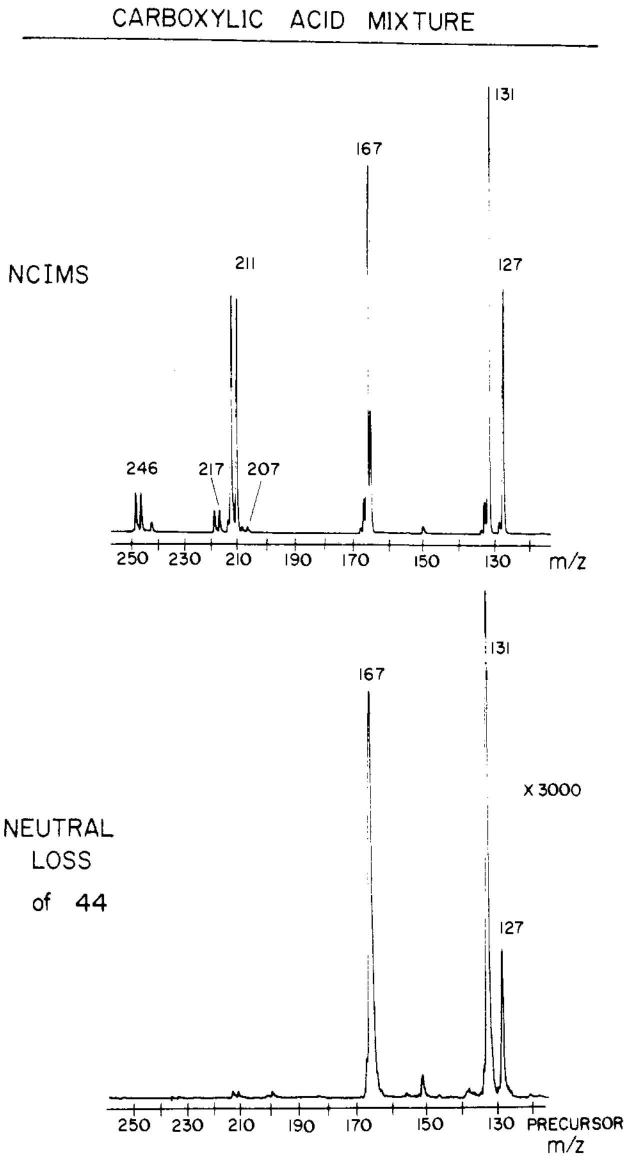

Figure 1. Comparison of the chemical ionization mass spectrum (CIMS) (isobutane, negative ions) with a scan which selects ions which undergo the reaction $m_1^- \rightarrow m_2^- + 44$. The sample consisted of a mixture containing barbituric acid ($(M - H)^-$ 127), glutaric acid ($(M - H)^-$ 131), and *p*-nitrobenzoic acid ($M^{-\cdot}$ 167).

The experiment consists of operating a dual analyzer mass spectrometer—in our work a reversed sector instrument, magnetic sector followed by electric sector—under computer control so that the two sectors are scanned in concert. In a typical analysis two spectra are acquired. The first is a normal mass spectrum of the mixture. The second, a selected fragment scan, employs active computer monitoring and control of the instrument. In the selected fragment scan mode the computer monitors the magnetic field as it is scanned, calculates the mass of the ion being transmitted by the magnet, and continuously sets the electric sector voltage to pass the appropriate m_2^+. Either m_2^+ can be held constant (selected fragment ion)[10] or m_3 can be held constant, $m_2^+ = m_1^+ -$ constant (selected *neutral* loss).

Mass spectra are most easily interpreted by examination of the neutrals lost from the molecular ion or quasi-molecular ion ($(M + H)^+$, $(M - H)^-$, etc.), hence the usefulness of the present method of scanning at fixed m_3 in the identification of functional groups. Figure 2 shows a neutral loss scan for another mixture containing carboxylic acids. Note that, in both the negative (Figure 1) and the positive ion spectra (Figure 2),

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