Resolution of Individual Component Fluorescence Lifetimes from a Mixture of Trapped Ions by Laser-Induced Fluorescence/Ion Cyclotron Resonance†

Brant Cage,‡ Melinda A. McFarland,‡,§ Christopher L. Hendrickson,‡,§ Naresh S. Dalal,*,§ and Alan G. Marshall*,‡,§

Ion Cyclotron Resonance Program, National High Magnetic Field Laboratory, Florida State University, 1800 East Paul Dirac Drive, Tallahassee, Florida 32310-3706, and Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32306

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We have measured the fluorescence lifetime (τ) of both pure $C_6F_5H^+$ and pure $C_6F_3H_3^+$ confined in an open cylindrical (ICR) Penning trap as 44 ± 2 ns and 51 ± 2 ns, respectively, consistent (∼10%) with prior literature values in the absence of ion trapping and magnetic field. For an equimolar mixture of $C_6F_5H^+$ and $C_6F_3H_3^+$ the effective lifetime, τ_{eff}, was 47 ± 2 ns. Ion cyclotron-resonant azimuthal quadrupolar excitation successfully isolated either $C_6F_5H^+$ or $C_6F_3H_3^+$ ions from the mixture, each with the same fluorescence lifetime as from a pure sample. The signal-to-noise ratio, ∼94:1, demonstrates the feasibility of observing fluorophores of lower quantum yield, such as tryptophan. This work represents the first determination of fluorescence lifetimes of organic ions in a Penning trap, and demonstrates the feasibility of resolving fluorescence from individual species in a chemically heterogeneous mixture by mass-selective ion cyclotron resonance.

Introduction

Fluorescence lifetimes can yield valuable information about the rates of electronic excited-state reactions.[1] Moreover, the three-dimensional structure of a macromolecule and/or its site(s) of ligand binding may be determined by energy transfer and quenching;[1] molecular size and shape are reflected by rotational correlation times determined from fluorescence anisotropy;[1] and chemical components may be distinguished by fluorescence lifetime filtering.[1,2] There is considerable current interest in extending such analyses to unhydrated molecules or ions in the gas phase. For example, the fluorescence lifetimes[3] of electrosprayed plumes of tryptophan and cytochrome *c* were recently obtained by laser-induced fluorescence (LIF)[3] to establish the heme−tryptophan proximity, as well as to enable fluorescence detection under controlled hydration and charge conditions in a *high vacuum environment*. Here, we couple the ion storage and mass selection of a Penning trap with LIF to measure fluorescence lifetimes of individual components of a mixture of gas-phase ions.

Atomic ions, such as Mg^+, Be^+, Hg^+, and Ba^+,[4−9] have been characterized by LIF in a Penning trap (i.e., static magnetic field plus three-dimensional axial quadrupolar electric potential field).[10] The first example of LIF of organic molecular ions in an ICR Penning style trap was the detection of the excitation spectrum of $C_6F_6^+$.[11]

To demonstrate measurement of fluorescence lifetimes of mass-selected trapped ions, we chose fluorobenzenes, because their radical cations, $M^{+\bullet}$, fluoresce at much longer wavelengths than the parent neutrals. Pioneering work on the electronic spectroscopy of fluorobenzene ions ($C_6F_nH_{6-n}^{+\bullet}$)[12] was done by Allan and Maier[13] by use of electron impact ionization to obtain wavelength-resolved emission spectra. Generally,[14] the fluorobenzene cation ground state is obtained by removing an electron from the highest occupied π-orbital of the neutral, resulting in three electronic bound states, all within ∼3 eV, denoted (from lowest to highest energy) as $\tilde{X}$, $\tilde{A}$, and $\tilde{B}$. Emission mainly corresponds to a $\pi-\pi$ transition from the ground vibrational 2nd excited electronic state to the quantum ladders of the various vibrational modes of the electronic ground state, generally denoted $\tilde{B} \rightarrow \tilde{X}$. The fluorescence lifetimes (τ) for members of the series were obtained (at $\sim 10^{-3}-10^{-5}$ Torr sample pressure) by a gated electron impact technique[15] and were found to exhibit single-exponential decay[15] with $\tau \approx 50$ ns and a quantum yield of nearly unity.[15] Later experiments[16−18] reported LIF excitation spectroscopy at millitorr sample pressure, revealing substantial vibrational information, including an interesting Jahn−Teller distortion of the symmetric species, 1,3,5-trifluorobenzene and hexafluorobenzene.

In this paper, we show that fluorescence lifetime may be measured to within ∼10% accuracy from pulsed laser-induced fluorescence decay profile of ions of a single mass-to-charge (*m*/*z*) ratio. Moreover, from a mixture of fluorescent ions of two different *m*/*z* values, mass-selective ejection can eliminate either ion to provide for fluorescence lifetime measurement of the other, making it possible to measure fluorescence lifetimes from a chemically heterogeneous sample.

Experimental Methods

Detection of Penning-trapped ion laser-induced fluorescence in a direction perpendicular to the laser beam has previously been described.[9,11] Here, we provide a brief overview, highlighting recent improvements. The sample (1,3,5-trifluorobenzene and/or pentafluorobenzene, Aldrich Chemical Co., Milwaukee, WI) enters the 3 T FT-ICR MS instrument[9,11] at a pressure of $\sim 8 \times 10^{-9}$ Torr (base pressure, $\sim 2 \times 10^{-9}$ Torr) via a variable leak valve. Ions are produced by impact from a 45 eV beam of electrons (several μA), generated from an off-axis electron gun located in the fringe field of the magnet, and focused by the

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* Corresponding author.

‡ Ion Cyclotron Resonance Program, National High Magnetic Field Laboratory.

§ Department of Chemistry and Biochemistry.

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magnetic field to the central axis of an open-ended cylindrical (Malmberg-Penning)[19−21] ion trap. After 0.5 s of ion accumulation, the filament current is switched off and helium buffer gas is pulsed into the vacuum chamber at $\sim 1 \times 10^{-5}$ Torr for azimuthal quadrupolar excitation (QE).[22−24]

To avoid switching between the dipolar excitation circuitry necessary for detection of the ion image current and the circuitry required for QE, we follow the method of Hendrickson[11,24] et al., in which switching is eliminated by application of the QE waveform to only the excitation electrodes. All excitation waveforms are amplified with a two-channel, TTL selectable amplifier (ENI, 2100LM2, Rochester, NY). A balun transformer (North Hills, type 0902BB, Syosset, NY) generates two waveforms of equal amplitude and phase for QE (by applying the QE waveform to the center-tap of the secondary coil) and 180° out of phase for dipolar excitation (by applying the dipolar waveform to the primary coil input). Trifluorobenzene or pentafluorobenzene was isolated individually by single-frequency QE at 360 kHz, 18.2 V_{p-p} and 293 kHz, 15.4 V_{p-p} (i.e., near[25] the ion cyclotron frequency for $C_6F_3H_3^+$ or $C_6F_5H^+$, respectively). For simultaneous radial confinement of $C_6F_3H_3^+$ and $C_6F_5H^+$, a stored waveform inverse Fourier transform (SWIFT)[26−28] produced QE at two bands, each consisting of a frequency sweep of uniform excitation and amplitude spanning the cyclotron resonance of either of the fluorobenzene ions. All aspects of the ICR experiment were controlled by a MIDAS[29,30] data station.

A (Lambda-Physik Scanmate 1E, Fort Lauderdale, FL) dye laser (with Coumarin 120 dye) was pumped by the third harmonic (355 nm, ∼85 mJ/pulse) of a Surelite I Nd:YAG laser (Continuum, Santa Clara, CA) producing $\lambda_{exc} = 433$ nm (∼1.2 mJ/pulse) at 10 Hz. The laser excitation pulse was guided through a Brewster window into the vacuum chamber through a homemade baffle system (∼25 × 75 mm Vespel rod with ∼6 mm diameter bore hole through its center) into the ICR cell, so as to intercept the axialized (concentrated) ion cloud. Fluorescence in a direction orthogonal to the laser beam was collected by a UV/visible fiber optic bundle, leading either directly to a fast gated (Hamamatsu Co., Bridgewater, NJ) H7680-01 photomultiplier tube (PMT) (in the present experiments) or to a double port PC-controlled 0.5 m monochromator (Chromex, Albuquerque, NM). The monochromator can switch between the PMT and an intensified fast time charge-coupled device (CCD) camera (Andor Technology, South Windsor, CT). The PMT was gated on after the trailing edge of the laser pulse, thus avoiding saturation of the photon detector. The PMT output is amplified and sent (through a snubber network—see below) into a (Tektronix, Beaverton, OR) TDS784D 1 GHz oscilloscope, and the data from 10000 acquisitions are summed (∼20−30 min). Scans are acquired alternately with the electron gun on (providing ions to the trap), and off (background with no ions in the trap), and the reported fluorescence intensity is the difference between those scans.

The raw fluorescence-vs-time profile exhibited a ringdown oscillation, which was effectively eliminated, without significant attenuation of the fluorescence signal, by installation of a "snubber" system. The snubber consists of a short piece of 50 Ω coaxial cable whose length is chosen such that the round trip transit time through the cable is equal to the period of the observed oscillation. Termination by a <50 Ω resistor sets up an inverted reflection that effectively cancels the oscillation signal. We found that elimination of the resistor (open circuit) also canceled out the ringing, with no significant attenuation of the PMT signal. In that case, one inserts a coaxial cable slightly longer than needed (i.e., ∼16 cm length to attenuate an oscillation of ∼3.5 ns period) by use of a BNC T adaptor between the output of the amplifier and the input of the oscilloscope, and trims its length while observing the signal on the oscilloscope until maximum suppression of ringing is achieved.

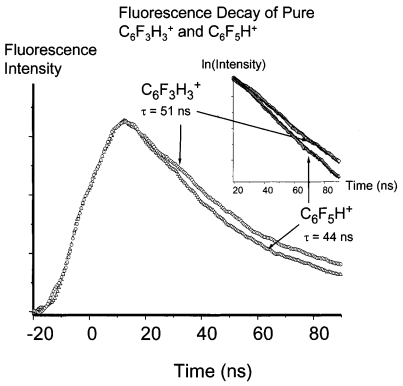

Figure 1. Fluorescence relative intensity of a pure sample of either $C_6F_5H^+$ or $C_6F_3H_3^+$ as a function of time following a 433 nm laser pulse. The intensity profiles are scaled to the same maximum value and superimposed. The inset shows the natural log of fluorescence relative intensity as a function of time; the fluorescence decay lifetime is the negative reciprocal slope of each line.

Results and Discussion

Fluorescence Lifetimes of $C_6F_3H_3^+$ and $C_6F_5H^+$ in a Penning Trap. Figure 1 shows fluorescence intensity (NOTE: $C_6F_3H_3^+$ was normalized to $C_6F_5H^+$ for easier visual comparison) as a function of time, *t*, following pulsed laser excitation ($\lambda_{exc} = 433$ nm) of $C_6F_3H_3^+$ (o) and $C_6F_5H^+$ (△). The time-resolved exponential decay of the fluorescence intensity, $F(t)$, for a single fluorophore is described by[1]

$$F(t) = F(0)\, e^{-t/\tau} \qquad (1)$$

in which $F(0)$ is the fluorescence intensity at $t = 0$, and τ is the fluorescence lifetime. The inset in Figure 1 shows the natural log of the intensity decay over the region from which each lifetime was obtained (see eq 1) by a least squares linear fit, with a correlation coefficient > 0.998 in each case. The fluorescence lifetimes (averaged over multiple experiments) were $\tau = 44 \pm 2$ ns for $C_6F_5H^+$ and $\tau = 51 \pm 2$ ns for $C_6F_3H_3^+$. The value for $C_6F_5H^+$ agrees to within experimental error with a prior measurement,[15] 47 ± 2 ns, obtained by gated electron beam excitation. However, the value for $C_6F_3H_3^+$ is somewhat smaller than the literature value,[15] 57 ± 2 ns. The sample pressures for the prior measurements were $\sim 10^{-3}-10^{-5}$ Torr, whereas our sample pressure is $\sim 8 \times 10^{-9}$ Torr and our experimental (collision gas) pressure is $\sim 1 \times 10^{-5}$ Torr. Our lower experimental pressure would be expected to yield a longer lifetime, so it is not clear why our value is slightly shorter. It is possible that the magnetic field affects intersystem crossing.[31] In any case, our data are self-consistent and reproducible, and show that fluorescence lifetimes of Penning-trapped organic molecular ions differing by 15% are readily differentiated.

Photons Detected and Signal-to-Noise Ratio. The number of fluorescence photons detected (P_{det}) may be approximated[32] as $P_{det} = A_s/A_p$ where A_s is the integrated area of the fluorescence signal (Figure 1, $C_6F_5H^+$) and A_p is the integrated area of a single photon (as determined from the average integrated area of multiple single spikes in low-level light/dark count conditions). Utilizing this method, we estimate that the time profile

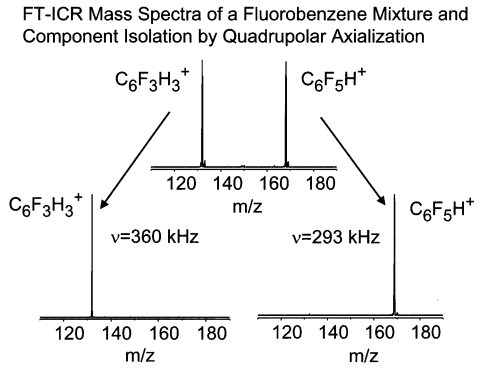

Figure 2. Fourier transform ion cyclotron resonance (FT-ICR) mass spectra of an equimolar mixture of $C_6F_5H^+$ and $C_6F_3H_3^+$. Top: spectrum following quadrupolar axialization encompassing both ICR resonant frequencies. Note that both species are observed after a trapping period of ~20 s. Bottom: FT-ICR mass spectrum after application of quadrupolar axialization at the cyclotron frequency of $C_6F_3H_3^+$ (left) or $C_6F_5H^+$ (right). Note that either component may be isolated from the other component.

in Figure 1 represents an average of ~75 photons/laser pulse. Although the present detection efficiency is still low, it is significantly improved above our prior level of ~2 photons/pulse.[11]

Signal-to-noise is here defined as the maximum time-domain signal divided by the standard deviation of the baseline noise. The standard deviation of the baseline was determined by least-squares fit to the difference between two fluorescence intensity-vs-time traces in the absence of ions. The signal-to-noise ratio for the data in Figure 1 was 94:1.

Mass Selection by Azimuthal Quadrupolar Excitation. The three-dimensional axial quadrupolar electrostatic potential required to confine ions along the magnetic field axis of a Penning trap necessarily introduces a radially outward-directed force that results in ion radial diffusion (and ultimate loss). To confine ions of mass *m*, and charge *q*, in a magnetic field, B, for tens of seconds for exposure to multiple laser shots, it is necessary to introduce an additional azimuthal quadrupolar electric excitation (QE) at the unperturbed ion cyclotron resonance frequency,

$$\omega_c = qB/m \text{ (SI units)} \qquad (2)$$

in the presence of a collision gas (in this case, helium). The QE interconverts ion cyclotron and magnetron motion, and the collisions rapidly dampen the cyclotron radius to zero. The net effect is to shrink the ion packet, leaving the ions centered ("axialized") along the magnetic field direction in a packet ~1 mm in diameter.[22−25,33,34,36] Nonresonant ions diffuse rapidly to the side electrodes of the trap and are removed. Thus, QE acts to select ions of a given *m*/*z* from a mixture of ions of multiple *m*/*z* values.

Simultaneous and separate isolation of $C_6F_3H_3^+$ and $C_6F_5H^+$ from a 1:1 molar mixture are shown in Figure 2. The upper trace shows the mass spectrum of the mixture following a 20 s SWIFT QE excitation spanning a small frequency band near the ICR frequency of each ion; both species are clearly observed by subsequent broadband dipolar excitation. The lower left and lower right mass spectra were acquired after application of single-frequency[25] 20 s QE at 360 kHz (to retain only the trifluorobenzene) or 293 kHz (to retain only pentafluorobenzene). These data show that either or both fluorobenzene ions can be mass-selected and confined for 20 s, to allow for repeated LIF analysis.

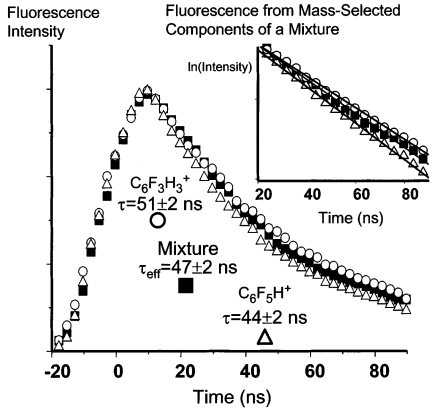

Figure 3. Superimposed plots (as in Figure 1) of fluorescence intensity (scaled to a common maximum value) or natural log of relative intensity vs time for an equimolar mixture of $C_6F_5H^+$ and $C_6F_3H_3^+$. The topmost and lowermost traces in each case are acquired during application of quadrupolar axialization near[25] the cyclotron frequency of $C_6F_3H_3^+$ or $C_6F_5H^+$, respectively, and the middle trace is acquired during simultaneous quadrupolar axialization at the cyclotron frequencies of both $C_6F_3H_3^+$ and $C_6F_5H^+$ (see text). For clarity in display, some data points have been omitted—the experimental time resolution is 0.5 ns.

TABLE 1: Lifetimes of the Fluorobenzenes, Both Pure and QE-Selected

	fluorescence decay lifetime, τ	
	$C_6F_3H_3^+$	$C_6F_5H^+$
pure sample, LIF (this work)	51 ± 2 ns	44 ± 2 ns
mixture	47 ± 2 ns	
QE-selected	51 ± 2 ns	44 ± 2 ns
pure sample, electron ionization[15]	57 ± 2 ns	47 ± 2 ns

Resolution of Heterogeneous Fluorescence. Fluorescence intensity and ln(intensity) as a function of time are shown in Figure 3 for a fluorobenzene mixture (■) in which SWIFT QE traps both $C_6F_3H_3^+$ and $C_6F_5H^+$. (For clearer display, only every fifth data point is shown in the main figure, and only every eighth data point in the inset.) Least-squares analysis (see inset in Figure 3) yields an effective lifetime, $\tau_{eff} = 47 \pm 2$ ns. Also shown are similar plots for the same mixture subjected to QE at the slightly off-resonant[25] ICR frequency (360 kHz) of $C_6F_3H_3^+$ (○) or (293 kHz) for $C_6F_5H^+$ **(△)**. The respective fluorescence lifetimes (see inset) were 51 ± 2 ns and 44 ± 2 ns, in good agreement with the values we obtained for pure $C_6F_3H_3^+$ and $C_6F_5H^+$. Table 1 summarizes the fluorescence lifetimes for each pure fluorobenzene ion, their mixture, and for each fluorobenzene ion isolated in the Penning trap from an initial mixture, along with prior literature values.[15] These data demonstrate that a two-component mixture can be resolved to yield the same fluorescence lifetime for each component in the mixture as for either component presented as a pure compound.

Conclusion

This work has, for the first time, shown that fluorescence lifetimes are readily obtainable at acceptable precision (~10%) from organic ions in a Penning trap. We are also able to resolve the fluorescence decays for two gas-phase ions of very similar lifetime (44 vs 51 ns) by mass selection based on quadrupolar excitation near[25] the ion cyclotron resonance frequency. Because the ions are distinguished by their masses rather than their fluorescence lifetimes, the present method (unlike methods based on phase-sensitive detection[1]) can distinguish ions of similar or even identical fluorescence lifetimes. An interesting extension of this research would be to examine the magnetic field

dependence, if any, of the fluorescence lifetimes and emission intensity to explain the small discrepancy between the present values and the prior[15] literature values.

We further project the feasibility of analysis of gas-phase macromolecule (e.g., protein) ion conformation based on fluorescence energy transfer measurements based in turn on fluorescence lifetime measurements, because the present signal-to-noise ratio (94:1) bodes well for successful analysis of fluorophores of lower quantum yield (Φ), such as tryptophan ($\Phi = 20\%$).[35] For example, a common donor−acceptor fluorescent labeling combination for proteins[36] is dansyl chloride (acceptor) and α-naphthyl-isocyanate (donor), with a donor quantum yield[36] of $\Phi = 60\%$. One obvious interest in such experiments would be to compare the conformations of the solution-phase protein with the completely unhydrated gas-phase protein, to assess the effect of solvation on protein conformation. Similarly, one could examine fluorescence quenching and/or frequency shift on binding of a ligand to the active site of an enzyme or receptor ion in the gas phase.

Finally, fluorescence of mass-selected components of mixtures could be extended to optically detected high-field magnetic resonance (ODMR) of large organic ions, as already achieved for atomic ions[8] and small organics at lower field (~0.34 T).[37] Experiments at a Zeeman field of 3 T could generate highly accurate quantum parameters, such as the Landé *g*-values (for both the ground and excited states), zero field splittings, and hyperfine fields of organic molecular and/or inorganic transition metal complex ions.

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(12) Footnote 1. In general, *n* equal to or greater than three provides an energy level diagram (the state originating from σ-ionization is shifted above the π-ionized states) favorable for fluorescence.

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(25) Footnote 2. The ion orbital frequency, ν_c, is found by $\nu_c = \omega_c/2\pi = 1.535611 \times 10^7 B_0/(m/z)$, in which ν_c is in Hz, B_0 in Tesla, *m* in u, and *z* in multiples of elementary charge. For a review of FT-ICR MS, see Marshall, A. G.; Hendrickson, C. L.; Jackson, G. S. *Mass Spectrom. Rev.* **1998**, *17*, 1−35. In practice, it has been found that a QE frequency that is slightly off-resonant produces superior results. The frequencies actually used are the ones given in the text; the true resonance frequencies for our magnet are 354 kHz and 278 kHz for $C_6F_3H_3^+$ and $C_6F_5H^+$, respectively.

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