

External Heavy-Atom Spin—Orbital Coupling Effect. IV. Intersystem Crossing

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acetic acid monomer) has undergone a substantial blue shift upon dimerization. Such a blue shift is sometimes understandable as arising from resonance interaction between transition moments on individual molecules¹²; and the blue shifts in Fig. 4 were carefully studied from this point of view. It was concluded that the single-molecule transition moments are almost surely too small to account for the observed shifts. It is considered most likely that the blue shifts occur mainly because the electrons in the originating orbital are stabilized in the well-known way for $n \rightarrow \pi^*$ transitions. The basicity of these electrons allows them to form hydrogen bonds. This interpretation of the dimer spectra therefore lends support to the assignment of the 58 kK band in acetic acid and its related bands in the other carboxyl spectra as something along the

lines of $n' \rightarrow \pi^*$, just as in the case of the carboxyl absorptions.

In the course of the present investigation the spectra of heavier carboxylic acids (such as propionic acid, isobutyric acid, etc.) were obtained; as well as the spectra of heavier esters (such as ethyl and isopropyl formate, and corresponding acetates).¹³ The various spectra all appear to show the bands we have been describing, though with more or less blurring of the structure. Sometimes several absorptions come in the same place, as with formic acid. The worst example seems to be methyl acetate where the 58-, 62-, and 68-kK bands of acetic acid have apparently merged into one wide absorption band with a peak at around 62 kK. It was not until the spectra of most of the compounds mentioned above had been recorded and examined that the pattern of correlations described in this paper began to reveal itself.

¹² G. S. Levinson, W. T. Simpson, and W. Curtis, *J. Am. Chem. Soc.* **79**, 4314 (1957).

¹³ E. E. Barnes, Ph.D. thesis, University of Washington, 1960.

External Heavy-Atom Spin-Orbital Coupling Effect. IV. Intersystem Crossing*.[†]

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The relative phosphorescence to fluorescence quantum yields and phosphorescence lifetimes of naphthalene have been measured in a number of glassy media, some of which contain perturbing atoms of large atomic number. The intersystem crossing process $S' \rightarrow T$ is very sensitive to external heavy-atom perturbation. It is shown that the order of decreasing sensitivity to this perturbation is: intersystem crossing process ($S' \rightarrow T$) > phosphorescence quenching process ($T \rightarrow S$) > phosphorescence emission process ($T \rightarrow S$). It is strongly suggested by the data contained herein that heavy atom quenching of fluorescence can indeed be attributed primarily, if not entirely, to increase in the probability of the intersystem crossing process. A number of possible uses for the heavy-atom technique are suggested.

INTRODUCTION

IT has been shown previously^{1a} that the *external* heavy-atom effect discovered by Kasha² is of a spin-orbital coupling nature, that it is of a magnitude

comparable to that of the *internal* effect, and that both effects operating simultaneously are linear in the perturbations. It has also been shown^{1a} that the interaction prerequisite to spin mixing is probably donor-acceptor in character. The manifestations of the *external* spin-orbital coupling effect thus far investigated have been the enhancement of singlet \rightarrow triplet ($T \leftarrow S$) absorption probability,^{1a,b} and the lifetime of phosphorescent decay^{1c}; the present work concerns itself with the effect of environmental molecules which contain heavy-atoms on the relative phosphorescence (ϕ_p) and fluorescence (ϕ_f) yields, and phosphorescence decay (τ_p) of the solute naphthalene. It is thought that the data obtained are of some importance to studies of fluorescence quenching and intersystem crossing, that the magnitude of the variations displayed by the ratio ϕ_p/ϕ_f and τ_p lends itself to utilization in analysis and, with optimization of the effects recorded here, that

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[†] Other publications in this series are: (a) S. P. McGlynn, R. Sunseri, and N. Christodouleas, *J. Chem. Phys.* **37**, 1818 (1962); (b) J. Nag-Chaudhuri, L. Stoessell, and S. P. McGlynn, *J. Chem. Phys.* **38**, 2027 (1963); and (c) S. P. McGlynn, M. J. Reynolds, G. W. Daigre, and N. D. Christodouleas, *J. Phys. Chem.* **66**, 2499 (1962).

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¹ Other publications in this series are: (a) S. P. McGlynn, R. Sunseri, and N. Christodouleas, *J. Chem. Phys.* **37**, 1818 (1962); (b) J. Nag-Chaudhuri, L. Stoessell, and S. P. McGlynn, *J. Chem. Phys.* **38**, 2027 (1963); and (c) S. P. McGlynn, M. J. Reynolds, G. W. Daigre, and N. D. Christodouleas, *J. Phys. Chem.* **66**, 2499 (1962).

² M. Kasha, *J. Chem. Phys.* **20**, 71 (1952).

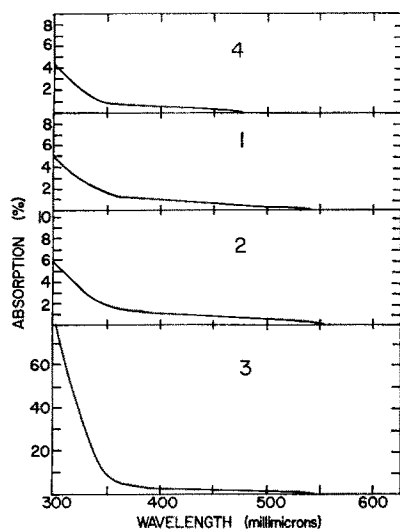


FIG. 1. Absorption spectra of halide solvents at room temperature; 4- (4-ethanol, 1-methanol), 1-propyl halide, by volume: (1) propyl chloride alcoholic solvent, (2) propyl bromide alcoholic solvent, (3) propyl iodide alcoholic solvent, (4) alcoholic solvent.

the chances of stimulated emission from the triplet state of an organic molecule may be increased somewhat.

It must be noted that external heavy-atom effects on ϕ_p/ϕ_f have been observed by Robinson *et al.*,³ the matrix being xenon, and by Graham-Bryce and Corkhill,⁴ who used a glass containing ethyl iodide as the perturbing medium. The present experiments differ from those of the authors mentioned^{3,4} in that they are quantitative, but are otherwise very similar to those of Graham-Bryce and Corkhill.⁴

EXPERIMENTAL

All quantum yield and lifetime measurements were performed on an Aminco-Keirs spectrophosphorimeter (SPM). The excitation source was a xenon XBO-150 W lamp (Osram) and the detector was an RCA 1P21 photomultiplier tube connected to an Electro-Instruments X-Y recorder. The wavelength error was approximately ± 2 m μ . All the lifetimes reported are "first observable life-times," a term defined elsewhere.¹⁰ The most probable error in any group of half-life measurements was 0.11 sec, while the average error was 0.09 sec.

The better-resolved phosphorescence spectra were obtained using a Becquerel phosphoroscope and a Steinheil spectrograph: the dispersion of this instrument was 80 Å/mm at 5800 Å and 20 Å/mm at 4250 Å. A Beckmann DK spectrophotometer was used to monitor all solvent and solute purifications.

All solvents, unless otherwise indicated, formed clear

glasses at 77°K. In most previous work²⁰ on external heavy-atom effects the main problem has been to compound halide solvents which show no adverse strain-effects at 77°K. Graham-Bryce and Corkhill⁴ used ethyl iodide in a mixed alcoholic medium with much success. In the present work, the heavy-atom solvent composition was $\frac{1}{5}$ EtOH: $\frac{4}{5}$ MeOH:1 propyl halide by volume. Absorption spectra of these solvents were run at 22°C, and are compared with EPA in Fig. 1; only the iodide solvent absorbs appreciably at 330 m μ , the wavelength of maximum fluorescence intensity of naphthalene. It is indicated, then, that the fluorescence is selectively absorbed (compared to phosphorescence) by the medium and that an increase of the ratio ϕ_p/ϕ_f results for this reason alone. Correction for this spurious increase is not readily effected; however, it is simple to over-correct: one merely presumes that the volume of the medium has contracted at 77°K to $\frac{1}{2}$ of its volume at 295°K, the extinction remaining the same as in Fig. 1, and that all of the luminesced light must traverse the total internal width of the sample tube (2 mm) and, therefore, made to experience absorption along a 2-mm path. It is known from low-temperature absorption measurements that the first statement above is an exaggeration, while the fact that emission and excitation beams are at

TABLE I. Mean lifetimes and relative quantum yields of naphthalene in various solvents at 77°K.

Solvent	Concentration (mg/ml)	Mean lifetime (sec)	Relative quantum yield	
			Under-corrected	Over-corrected
3-Methylpentane	4	2.50	0.007	...
4-EtOH, 1-MeOH ^a	4.6	2.50	0.020	0.015
EPA ^b	4	2.52	0.011	...
PH ^c	4	2.47	0.025	...
4- (4-EtOH, 1-MeOH), 1-Ethyl Iodide ^d	4	1.23
4- (4-EtOH, 1-MeOH), 1-Propyl chloride	4.6	2.27	0.068	0.051
4- (4-EtOH, 1-MeOH), 1-Propyl Bromide	4.6	1.73	0.478	0.324
4- (4-EtOH, 1-MeOH), 1-Propyl Iodide	4.6	1.33	1.33	0.715
3-Methylpentane ^e	4	2.52
Glycerin ^f	4	Not observable

^a Four parts ethanol and 1 part methanol, by volume.

^b Five parts ethyl ether, 5 parts isopentane and 3 parts ethanol, by volume.

^c One part methylcyclohexane and 1 part methylcyclopentane, by volume.

^d I. J. Graham-Bryce and J. M. Corkhill, *Nature* **186**, 965 (1960).

^e Cracked glass.

^f Clear glass formed at dry ice and acetone temperature.

³ G. W. Robinson and R. P. Frosch, *J. Chem. Phys.* **37**, 1962 (1962) contains a good summary of the work of Robinson *et al.*

⁴ I. J. Graham-Bryce and J. M. Corkhill, *Nature* **186**, 965 (1960).

90° to each other renders the assumed path of 2 mm much too large. Overcorrection of a ratio ϕ_p/ϕ_f for selective absorption of fluorescence is then readily carried out and such grossly reduced ϕ_p/ϕ_f values are henceforth denoted "overcorrected." It is for the same reason (i.e., simplicity in making overcorrections) that the ratio ϕ_p/ϕ_f is quoted as the ratio of phosphorescence to fluorescence intensities at their most intense peaks (465 and 330 m μ , respectively). Nor is any correction made for the wavelength dependence of detector sensitivity at the moment, since this is not necessary to internal consistency of our data.

The spectral distribution of intensity in the xenon XBO-150 W lamp as well as the effects of excitation monochromatization are such as to render light of $\lambda \sim 280$ m μ maximally effective in inducing luminescence of naphthalene. In this work, excitation was carried out at 300 m μ . Inspection of Fig. 1 immediately makes important the competition between solvent and solute for excitation light; because of this the fluorescence yields (or phosphorescence yields) obtained in different media may not be compared, even though otherwise they are strictly proportional to absolute quantum yield values. It is for this reason that some reluctance is evident in quoting relative yields in different media of either phosphorescence or fluorescence values alone.

All solvents were purified as previously described.^{2c} The naphthalene was an Eastman Kodak product which had been extensively zone-refined and recrystallized.

RESULTS AND DISCUSSION

A sampling of the results obtained with naphthalene in various media is presented in Table I, and a graphic illustration of the effect is given in Fig. 2. It is perhaps well to reiterate that the "undercorrected" values contain no correction for spectral sensitivity of the detector or for selective absorption of fluorescence by the medium, while the "overcorrected" values overemphasize the latter correction and omit the former. It is

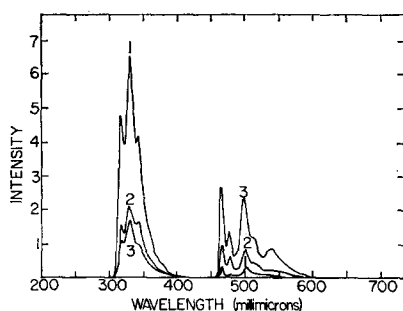


FIG. 2. Total emission spectra of naphthalene in propyl halide-alcoholic solvents at 77°K: 4-(4-ethanol, 1-methanol), 1-propyl halide. All spectra are uncorrected Aminco curves. Curve 3 should be reduced by factor of three (3): (1) propyl chloride alcoholic solvent, (2) propyl bromide alcoholic solvent, (3) propyl iodide alcoholic solvent. Excitation is at 300 m μ .

seen, in either case, that ϕ_p/ϕ_f increases by approximately two orders of magnitude in going from EPA glass to a medium which consists of $\frac{1}{3}$ 1-propyl iodide by volume.

It is possible to be more explicit. If we admit of a kinetic scheme which includes the first-order rate constants: k_f , the fluorescence rate constant; k_{qf} , the rate constant for internal quenching of fluorescence; k_p , the phosphorescence rate constant; k_{qp} , the rate constant for internal quenching of phosphorescence; and k_{IS} , the rate constant for intersystem crossing ($S' \rightarrow T$); we may write⁵:

$$\tau_p = 1/(k_p + k_{qp}), \quad (1)$$

$$\phi_p/\phi_f \tau_p = k_p k_{IS}/k_f, \quad (2)$$

and

$$\phi_f = k_f/(k_{qf} + k_{IS} + k_f). \quad (3)$$

If we now set $k_f = 1.06 \times 10^6$ sec⁻¹ as found by Kasha and Nauman,⁶ and if we presume, as seems reasonable, that k_f changes but little from one environment to another, we note that Eqs. (1) and (2) contain two observables and three unknowns. We further note that τ_p for the ethanol-methanol glass is much the same as for EPA, and that we may accordingly adopt the values $k_p \approx 0.05$ and $k_{qp} \approx 0.35$ sec⁻¹ as found by Robinson⁷ for EPA, for both glasses. We may now adopt two extreme attitudes: we may assume that $k_{qp} = 0.35$ sec⁻¹ in all media, and thus maximize the variation in k_p and minimize the variation in k_{IS} [cf. Eq. (2)], or we may suppose that $k_p = 0.05$ sec⁻¹, and thus maximize the increase of both k_{qp} and k_{IS} ; we call these two extremes Case a and Case b, respectively, and it seems that by this expedient we may at least obtain some idea of the relative effects of heavy-atoms on the rate constants k_{qp} , k_p , and k_{IS} which connect states of differing multiplicities. The necessary abstractions are carried out in Table II, where it can be observed from the bracketed numbers that the maximum increase of k_p on going from the ethanol:methanol glass (EM) to the ethanol:methanol:propyl iodide glass (PI) is by a factor of 8, of k_{qp} by a factor of 2, and of k_{IS} by a factor of 89; the minimal increases of k_p and k_{qp} are by factors of unity (no change) and of k_{IS} by a factor of 11. *It is necessary to conclude therefore that the process most sensitively affected by external heavy-atom perturbation is the intersystem crossing process.* It is further of note that the values of ϕ_p/ϕ_f used in construction of Table II are designated as "overcorrected" in Table I, and that as a consequence Table II understates the evidence in favor of the high sensitivity of intersystem crossing.

The values of k_{IS} quoted in Table II are not corrected for varying spectral sensitivity of the 1P21 photomultiplier detector. It is best to correct empirically:

⁵ M. Kleinerman, L. Azzarraga, and S. P. McGlynn, J. Chem. Phys. **37**, 1825 (1962).

⁶ M. Kasha and R. V. Nauman, J. Chem. Phys. **17**, 516 (1949).

TABLE II. The limits of variation of the intersystem crossing rate constant.

Glass	$\phi_p/\phi_f\tau_p^a$	k_p+k_{qp}	Case (a) ^a		Case (b) ^b	
			k_p	$k_{IS}\times 10^{-6}, ^c$	k_{qp}	$k_{IS}\times 10^{-6}, ^c$
EM	0.006	0.40	0.05(≡1) ^d	0.006(≡1) ^d	0.35(≡1) ^d	0.006(≡1) ^d
PCI	0.022	0.44	0.09(1.8)	0.012(2)	0.39(1.1)	0.022(3.7)
PBr	0.182	0.58	0.23(4.6)	0.04(6.7)	0.52(1.5)	0.182(33)
PI	0.536	0.75	0.40(8)	0.067(11.2)	0.70(2)	0.536(89)

^a $k_{qp}\equiv 0.35\text{ cm}^{-1}$ in all four media.^b $k_p\equiv 0.05\text{ sec}^{-1}$ in all four media.^c In order to convert these values to absolute values they must be multiplied by a factor of approximately 50.^d Relative values are quoted in brackets.

the ratio $\phi_p(502\text{ m}\mu)/\phi_p(315\text{ m}\mu)$ quoted by Gilmore, Gibson, and McClure⁷ in EPA is 0.16; our uncorrected ratio in EPA at the same wavelengths is 0.003, yielding a multiplicative correction of 50 to the values of k_{IS} quoted in Table II. Thus k_{IS} of naphthalene in EPA is $0.3\times 10^6\text{ sec}^{-1}$. The values of k_{IS} in the other media may readily be obtained by multiplication by the bracketed numbers of Table II. The value of k_{IS} quoted by Robinson⁸ is $0.56\times 10^6\text{ sec}^{-1}$ if we assume the value of Kasha and Nauman⁶ for k_f ($\sim 10^6\text{ sec}^{-1}$) to be correct. This agreement is certainly within the limits of error of our experimental work and is gratifying.

Since ϕ_f for naphthalene in EPA is 0.52, and since k_{IS}/k_f in the same medium⁷ is 0.62, we conclude from Eq. (3) that $k_f:k_{qp}:k_{IS}=1:0.33:0.62$. It seems reasonable to presume that k_f and k_{qp} which connect states of the same multiplicity are not altered much by heavy-atom perturbation. Accordingly, using Eq. (3) and the data of Table II it is predicted that in the propyl iodide glass ϕ_f will have decreased to $\sim \frac{1}{8}$ in Case (a) and $\sim \frac{1}{51}$ in Case (b), thus enabling one to conclude that the heavy-atom quenching of fluorescence so much speculated about^{9,10} is to a large extent, or perhaps entirely, due to an increase of k_{IS} , the intersystem crossing rate constant.

One may now utilize Eq. (3) and the data of Table II to predict that:

$$\phi_f(\text{PCI}):\phi_f(\text{PBr}):\phi_f(\text{PI})=1:49:32\text{ in Case (a),}$$

and

$$\phi_f(\text{PCI}):\phi_f(\text{PBr}):\phi_f(\text{PI})=1:18:07\text{ in Case (b),}$$

while it is found experimentally that the ratio is 1:0.33:0.09. Despite the fact that much uncertainty attaches to these last experimental values the authors

feel that the actual situation approaches more closely that of Case (b) than of Case (a).

Phosphorescence Spectra

The phosphorescence spectra of naphthalene in various media are given in Fig. 3. It seems evident that there is no significant self-absorption of the phosphorescence. The triplet state experiences a red shift relative to the ground state as the spin-orbital coupling nature of the matrix is increased, which is entirely to be expected if the perturbing singlet which mixes with the triplet of the aromatic lies higher in energy than the triplet state. These results are in agreement with Tsubomura and Mulliken¹¹ who presume that this singlet is the charge-transfer singlet state of a donor-acceptor complex; as far as the present results are concerned, however, it could be any higher energy singlet. The 0,0 frequencies of the phosphorescence in different media are abstracted in Table III.

It is noted that the 1L_a transition of naphthalene¹² experiences a red shift of 101 cm^{-1} upon variation of solvent from 1-bromobutane to 1-iodobutane, and that this shift is of the same order of magnitude and in the same direction as that observed for naphthalene between the two cracked glasses containing propylbromide and propyliodide, respectively. It would appear then that the major portion of the red shifts observed

TABLE III. Effect of medium on the frequency (0,0) of phosphorescence.

Solvent	$\theta_{0,0}(\text{cm}^{-1})$	Red shift(cm^{-1})
Ether-isopentane glass	21 335	...
Propyl chloride cracked glass	21 280	55
Propyl bromide cracked glass	21 180	155
Propyl iodide cracked glass	21 010	325

⁷ E. H. Gilmore, G. E. Gibson, and D. S. McClure, J. Chem. Phys. **20**, 829 (1952); **23**, 399 (1955).

⁸ G. W. Robinson, J. Mol. Spectry. **6**, 58 (1961).

⁹ P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1949).

¹⁰ S. Lipsky, W. P. Helman, and J. F. Merklin, *Luminescence of Organic and Inorganic Materials*, edited by H. Kallmann and G. Spruch (John Wiley & Sons, Inc., New York, 1962), p. 83.

¹¹ H. Tsubomura and R. S. Mulliken, J. Am. Chem. Soc. **82**, 5996 (1960).

¹² O. E. Weigang and D. D. Wild, J. Chem. Phys. **37**, 1180 (1962).

in the various glassy media is due to simple electrostatic interaction with the solvent, and is attributable to the polarizability of the triplet states. In other words, the red shifts are due at least in part to triplet-triplet mixing, and it seems unlikely that any other than a small part of the observed shifts is due to solvent-chromophore interaction via spin-orbital coupling, i.e., through solvent induced singlet-triplet mixing.

CONCLUSION

In view of the limitations imposed by solvent absorptivity (see Fig. 1), naphthalene is hardly an ideal case for investigation. It is concluded that a solute species capable of significant excitation in the 4000-Å

region with fluorescence above this wavelength should be utilized, since thereby re-absorption of fluorescence by the solvent and competition by the solvent for the excitation light is minimized. Such work is presently underway on a number of solutes. It is suggested that use of heavy-atom solvents may facilitate the following:

(1) A decrease in the lower concentration limit of phosphorimetric detection, in certain cases, by a factor of 10 or greater would not be unexpected.

(2) Stimulated emission from triplet states of suitable organics might be more feasible. The increasing rate of population of the triplet state, and the increasing emissive rate constant for phosphorescence which are associated with heavy-atom perturbations are both conducive to the onset of laser oscillations. However, the difficulties associated with linewidth (cf. Fig. 3) and the nonemissive phosphorescence rate constant (cf. Table II) would, if anything, increase; quality factor difficulties and the wasteful loss of pumping energy and inversion capacity in $T \rightarrow T'$ absorption processes would still persist.

(3) This last observation might however prove utilitarian for the study of $T \rightarrow T'$ absorption processes of molecules which normally possess low triplet populations.

(4) It is also suggested that study of triplet-triplet energy transfer between like species in noncrystalline matrices or solutions would be more readily studied.

(5) The bimolecular recombination of two excited triplets to yield an excited singlet¹³ might be facilitated by heavy-atom techniques.

The present work is semiquantitative in nature, but is sufficiently accurate to bear the deductive burdens imposed on it. More quantitative studies are in progress.

ACKNOWLEDGMENTS

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¹³ T. Azumi and S. P. McGlynn, J. Chem. Phys. (to be published).

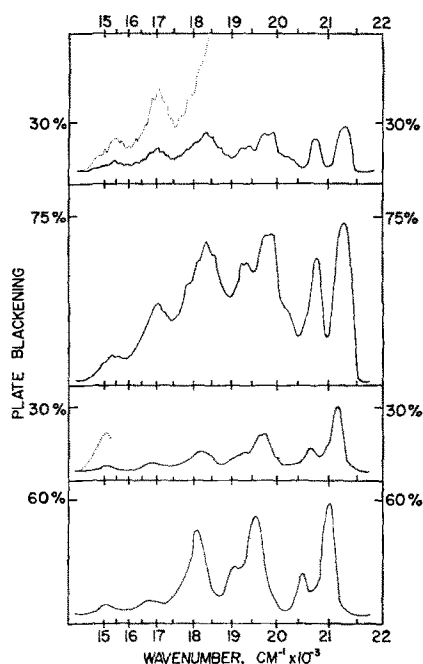


FIG. 3. The phosphorescence spectra of naphthalene, in descending order, in EP (diethyl ether and isopentane in a 1:1 v/v mixture), propyl chloride cracked glass, propyl bromide cracked glass, and propyl iodide cracked glass. Exposure times were in all cases about 20 min. Conclusions regarding quantum yields should not be deduced from this graph since a phosphoroscope was interposed between spectrograph and sample, and the decay times of the samples were not identical. The dashed lines belong to traces of longer exposures, and are shown merely to validate some weak emission bands. All "cracked" glasses consisted of a 2:5 mole ratio solution of naphthalene and propyl halide. Kodak spectroscopic plates 103a-F(3) were used throughout.