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Reprinted from

[redacted]

23–25 January 1992
Los Angeles, California

Volume 1638

P.O. Box 10, Bellingham, Washington 98227 USA. Telephone 206/676-3290

Vibrational spectroscopy and picosecond dynamics of gaseous trienes and tetraenes

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ABSTRACT

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1 INTRODUCTION

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2. EXPERIMENTAL

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All-trans-2,4,6,8-decatetraene (DT), *all-trans*-2,4,6,8-nonatetraene (NT), and octatriene were prepared respectively from the Wittig reaction between hexadienal (Aldrich) and crotyltriphenyl-

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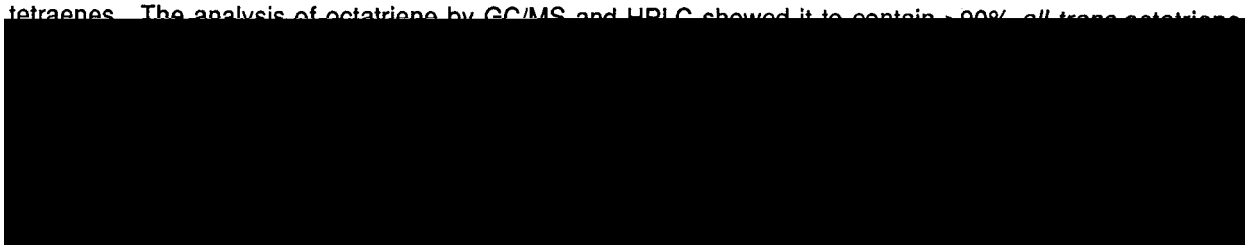
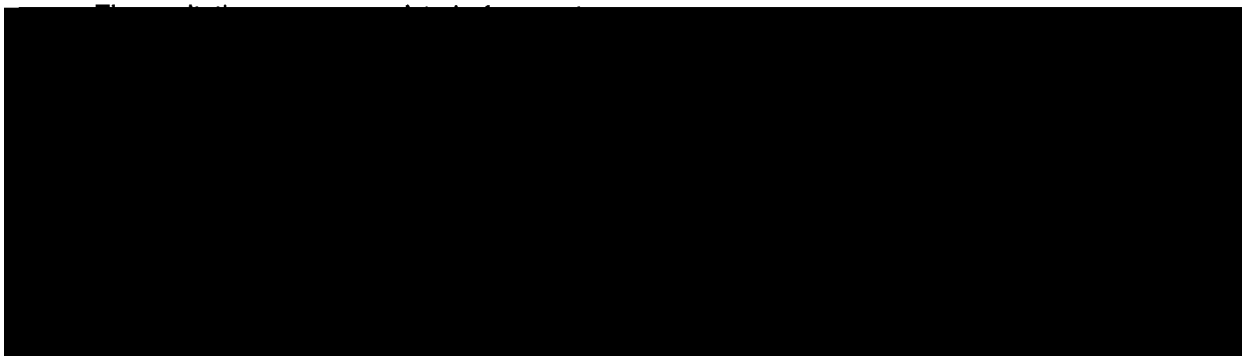
0-8194-0784-4/92/$4.00

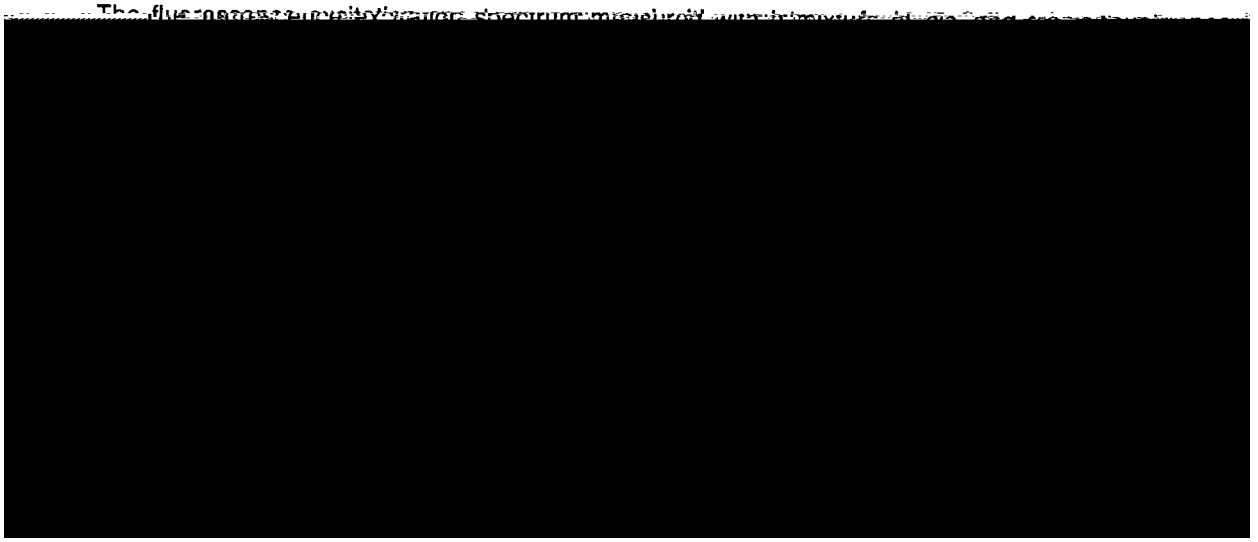
tetraenes. The analysis of octatriene by GC/MS and HPLC showed it to contain > 99% *all-trans* octatriene



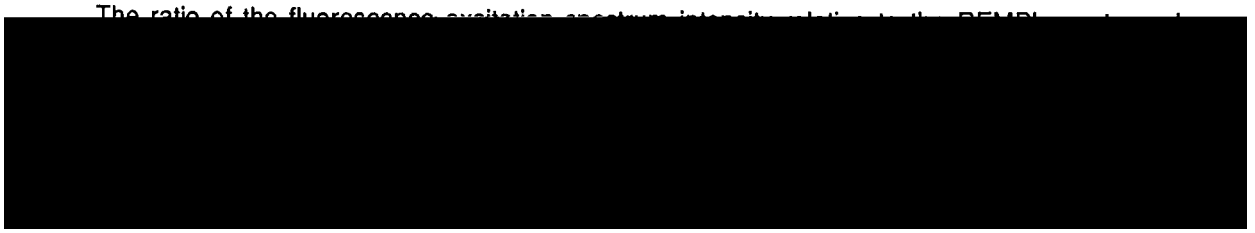


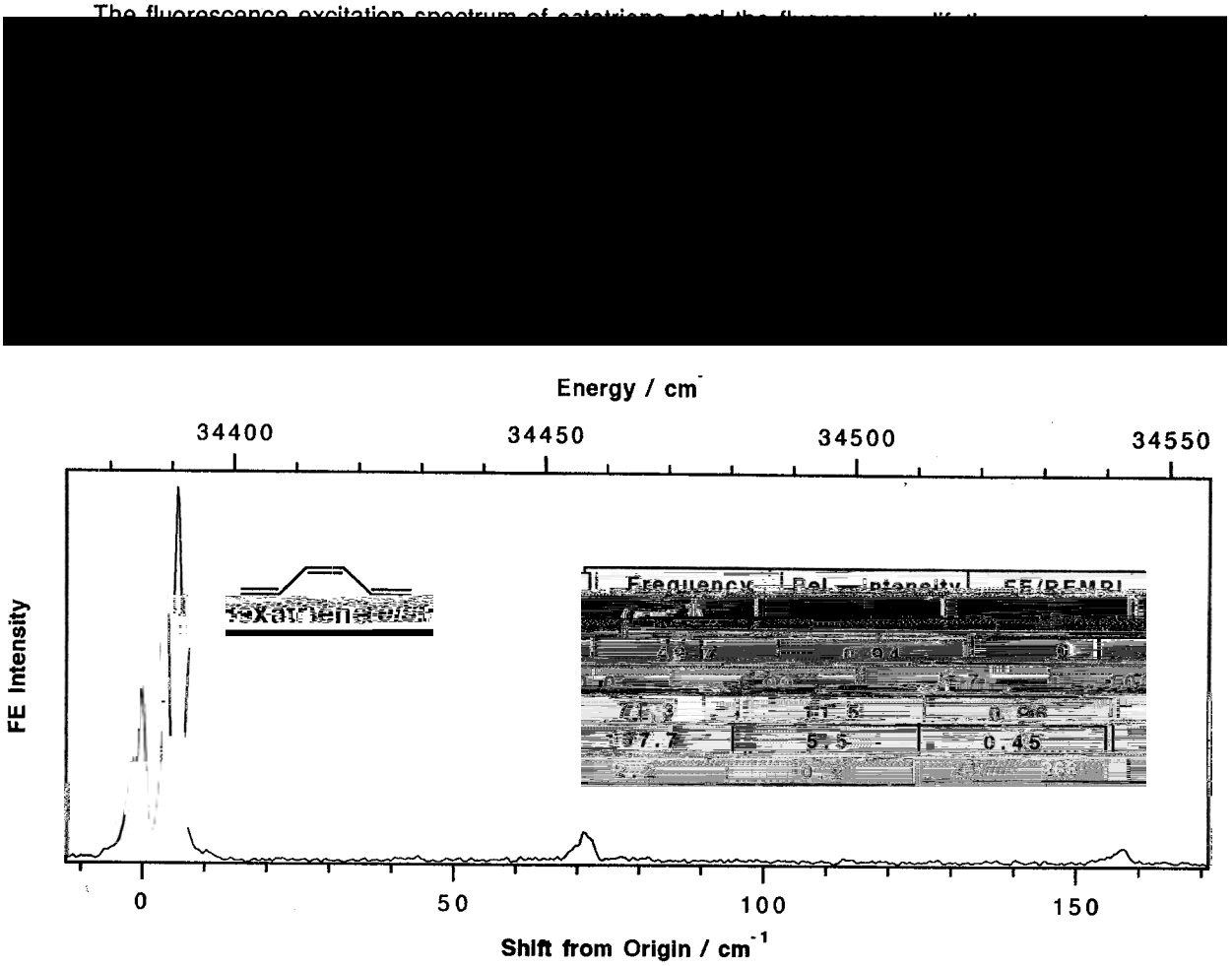
3. S_1 STATE SPECTRA OF TRIENES

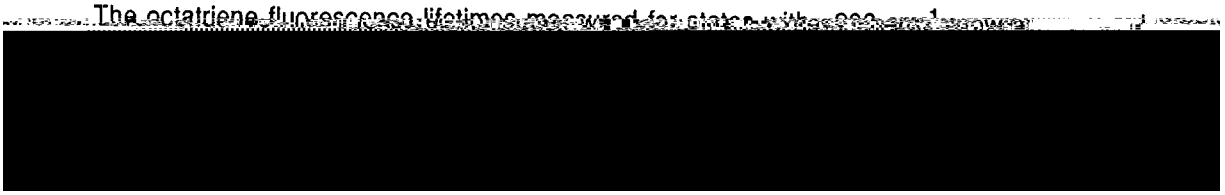
The fluorescence excitation spectrum measured with

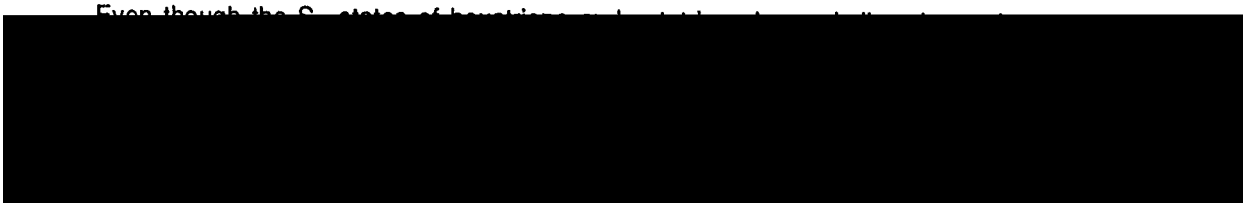


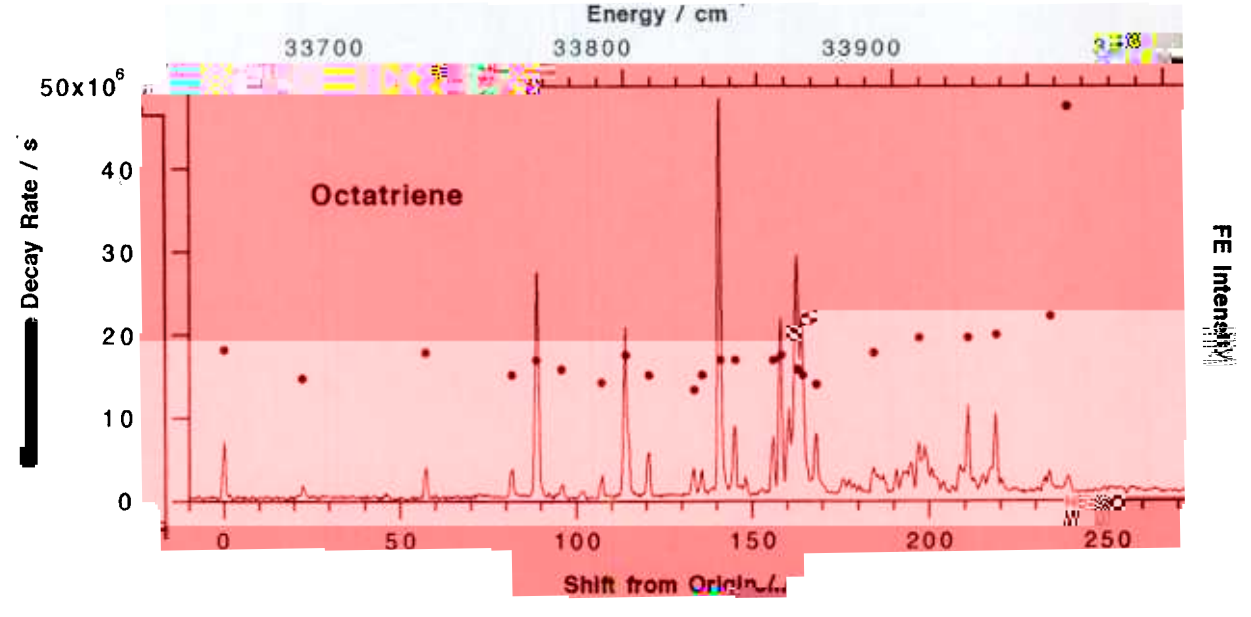
The ratio of the fluorescence excitation spectrum intensity relative to the DEMP




Energy / cm
34400
34450
34500
34550
FE Intensity
Frequency
Rel. Intensity
FE/REMPI
0
50
100
150
Shift from Origin / cm-1



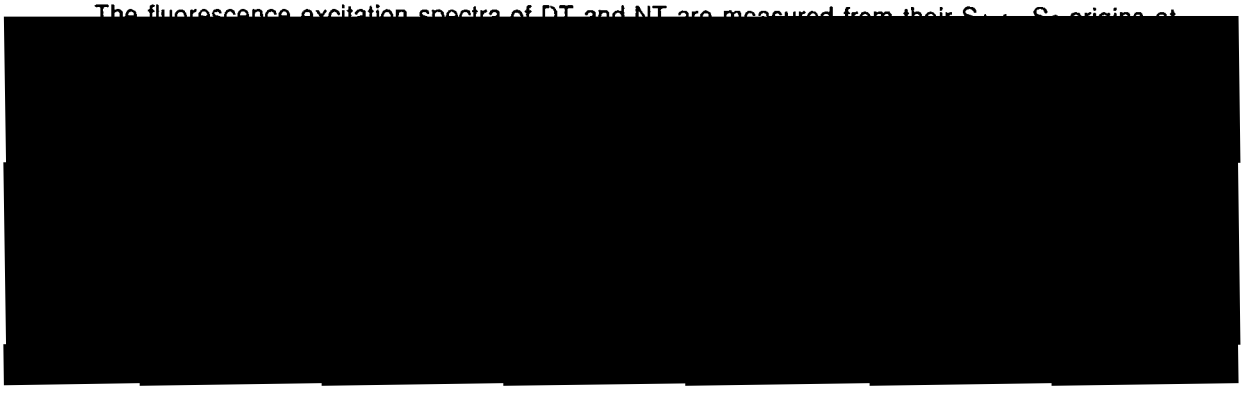



Energy / cm
33700
33800
33900
50x10^6
40
30
20
10
0
Decay Rate / s
Octatriene
0
50
100
150
200
250
Shift from Origin /
FE Intensity

Although the octatriene lifetimes are significantly longer than those of hexatriene, their shortness

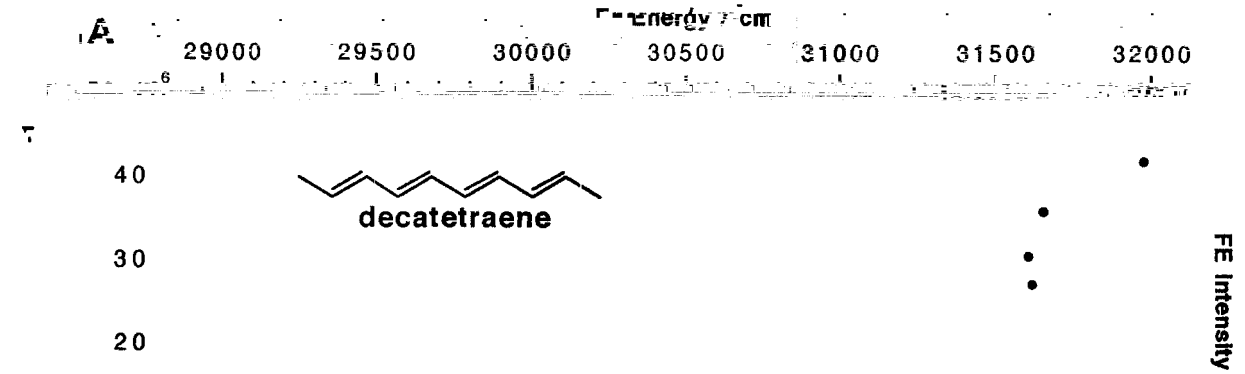
4. FLUORESCENCE EXCITATION SPECTRA OF DT AND NT

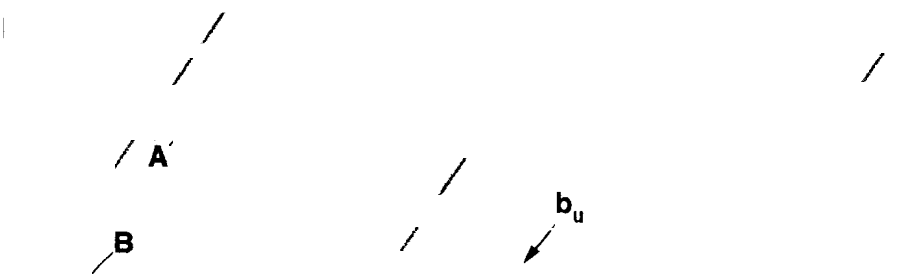
The fluorescence excitation spectra of DT and NT are measured from their $S_1 \leftarrow S_0$ origins at



4.1 $S_1 \leftarrow S_0$ Fluorescence Excitation Spectra

Decatetraene. The measured fluorescence excitation spectra of the $S_1 \leftarrow S_0$ transition are plotted


A
Energy / cm
29000
29500
30000
30500
31000
31500
32000
40
30
20
decatetraene
FE Intensity


A
B
b_u

The origin of the NT spectrum cannot be trivially assigned to the lowest energy feature. In the

[redacted]

The C = C stretching fundamental, which is expected to be the

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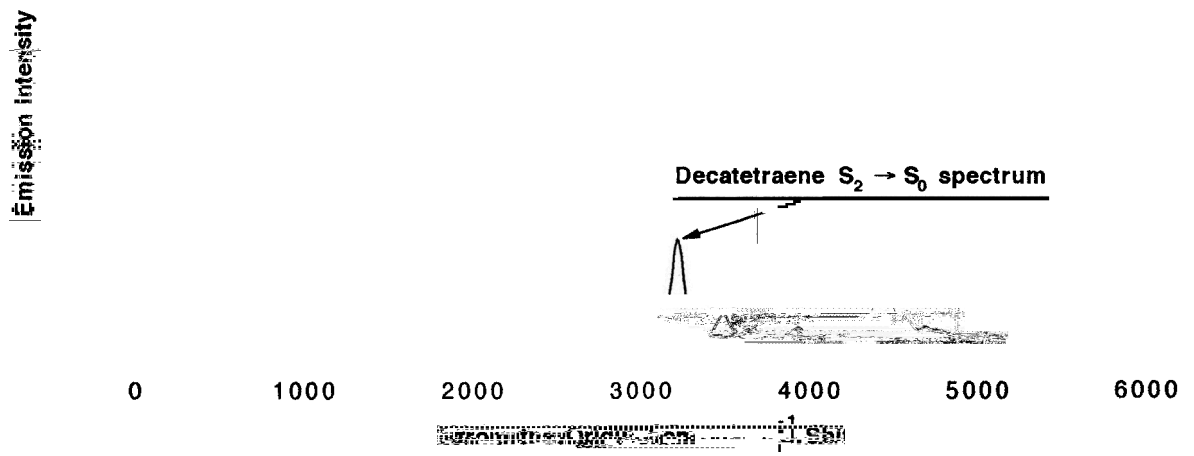

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Further information on the nature of origins A and B can be gained from the rotational bandshapes

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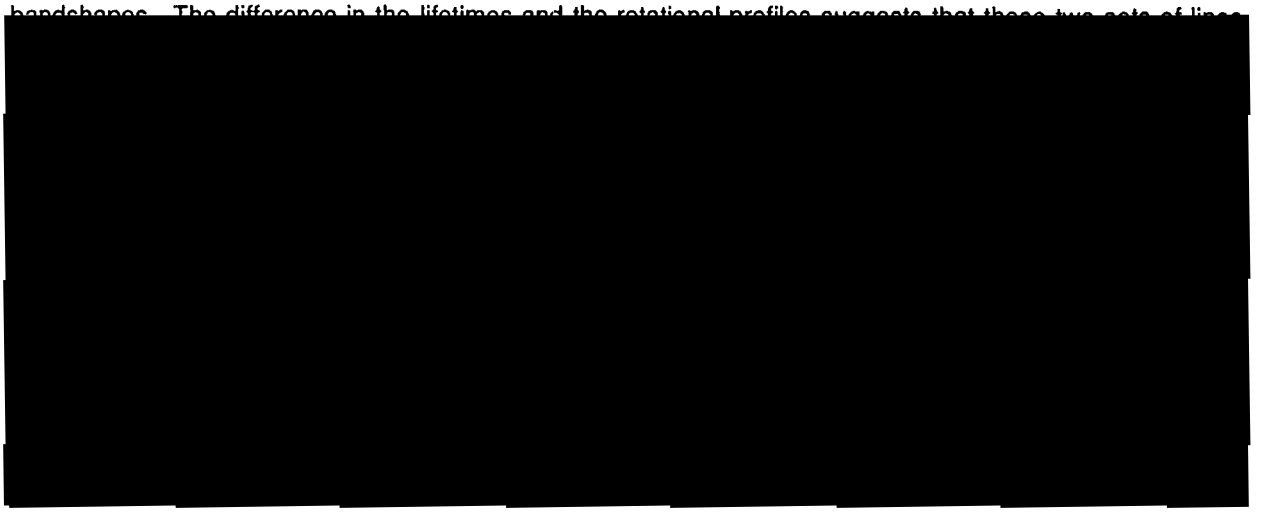
bandshapes. The difference in the lifetimes and the rotational profiles suggests that these two sets of lines



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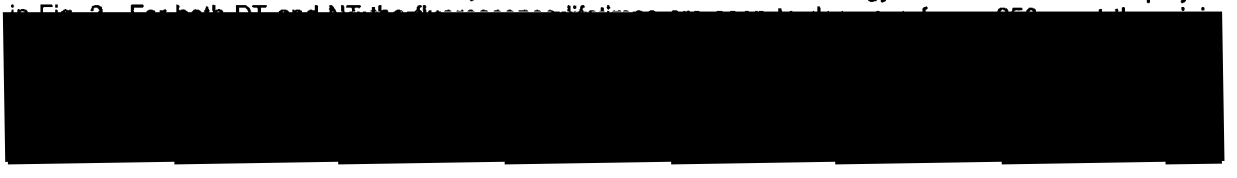
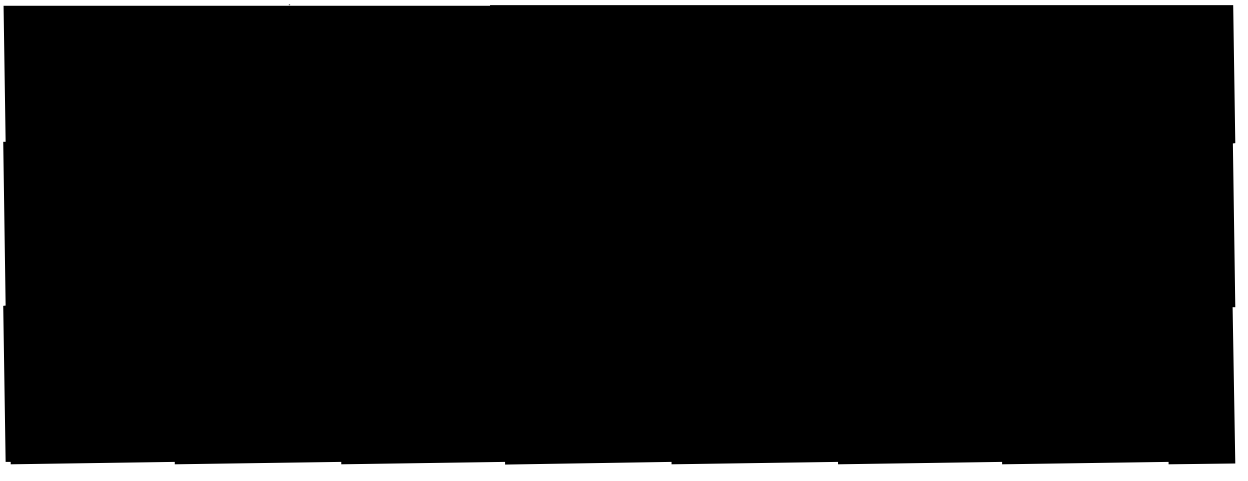
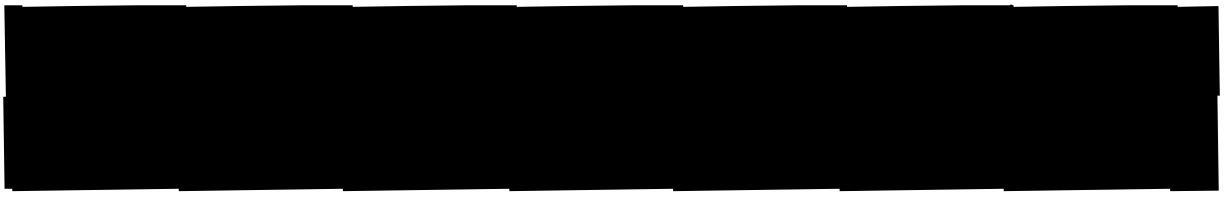
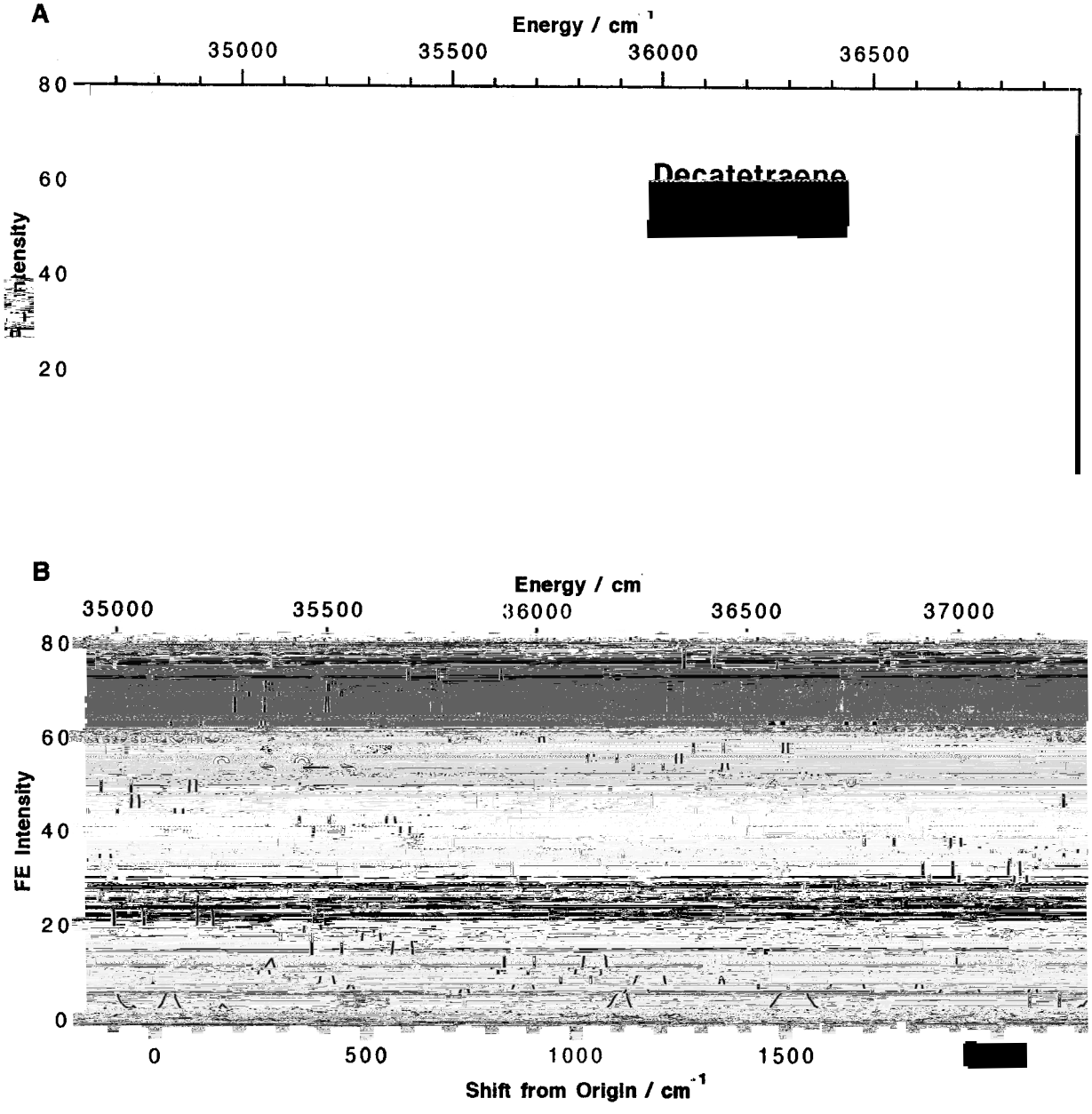
The measured fluorescence decay rates as a function of excess energy for DT and NT are displayed





5. S_2 STATE SPECTRA OF TETRAENES




A
Energy / cm⁻¹
35000
35500
36000
36500
80
60
40
20
FE Intensity
Decatetraene
B
Energy / cm
35000
35500
36000
36500
37000
80
60
40
20
0
FE Intensity
0
500
1000
1500
Shift from Origin / cm⁻¹

[redacted]

tetraenes in the S_2 state or in the isoenergetic highly vibrationally levels of the S_1 state is very small for isolated molecules. Apparently the dissociation of

[redacted]

[redacted]

The increase in linewidths with excess energy in the

[redacted]

6. EMISSION SPECTRA FROM THE S_1 AND S_2 STATES OF TETRAENES

The observed

[redacted]

7. CONCLUSIONS

Linear polyenes show several interesting trends in structure and reactivity as a function of

[redacted]

Both tetraenes show evidence for an coordinate. This may be a common feature in longer polyenes which is tentatively assigned to a twist-activated nonradiative channel with a ~2000 cm^{-1} barrier.

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8. ACKNOWLEDGEMENTS

We are grateful to Royal Society/Japan Society for the Promotion of Science for support of A.IP.

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9. REFERENCES

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