Resonant and non-resonant femtosecond ionization mass spectrometry of organochlorine pesticides

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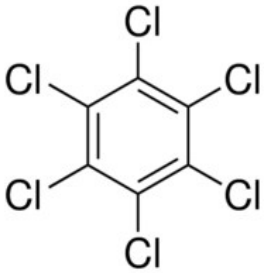
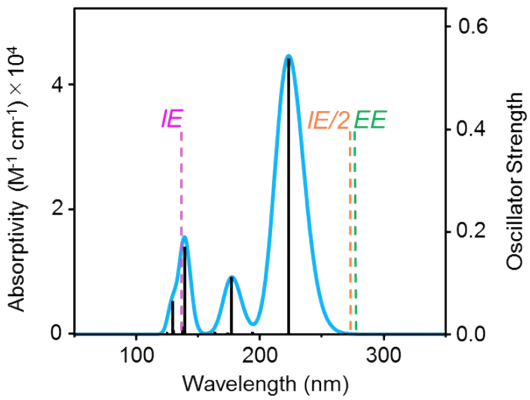
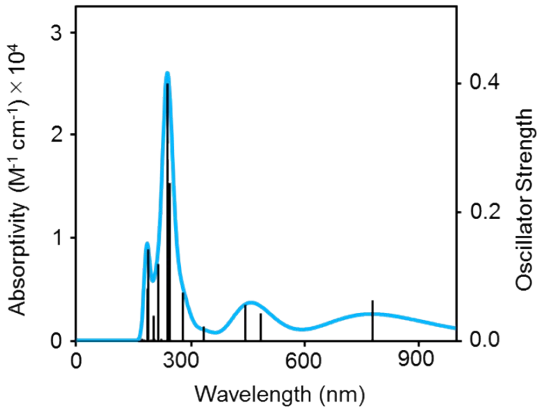
Electronic Supplementary Information provides information regarding the spectral properties for thirteen pesticides and the relationship between signal intensity and laser pulse width.

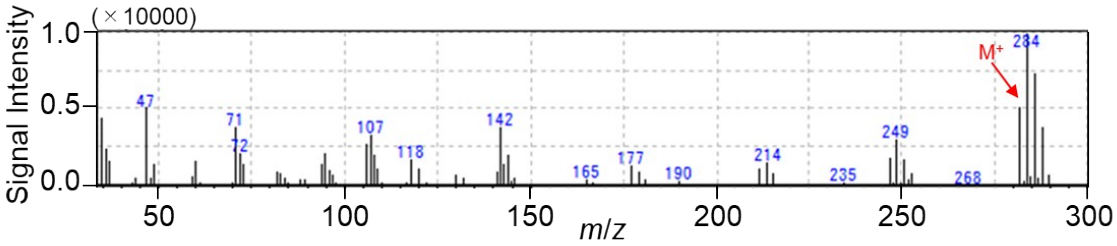
Figure S-1 provides the chemical structures of the pesticides, the calculated absorption spectra for neutral (left) and ionic (right) species, and the mass spectra obtained by EI and MPI ($\Delta t = 35$ fs) as shown in the series below. The wavelengths corresponding to the first excited energy (*EE*), the ionization energy (*IE*), and the half value of the ionization energy (*IE*/2) are indicated in the figure.

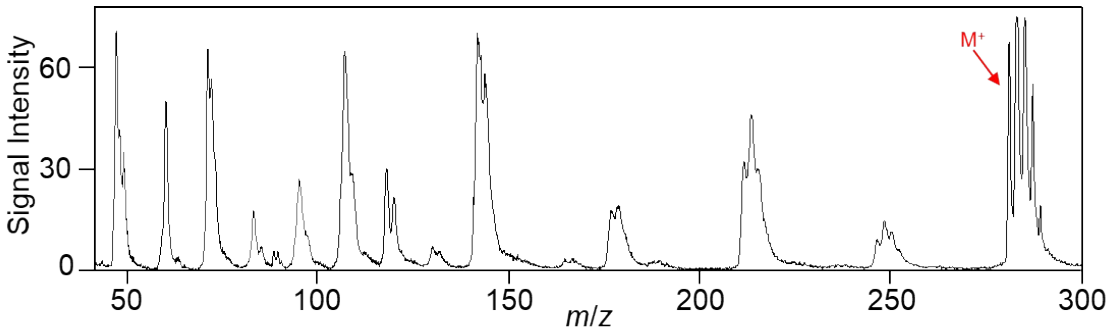
1. HCB



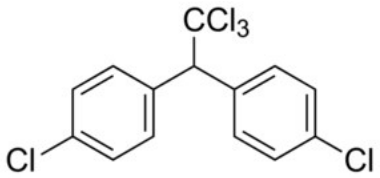


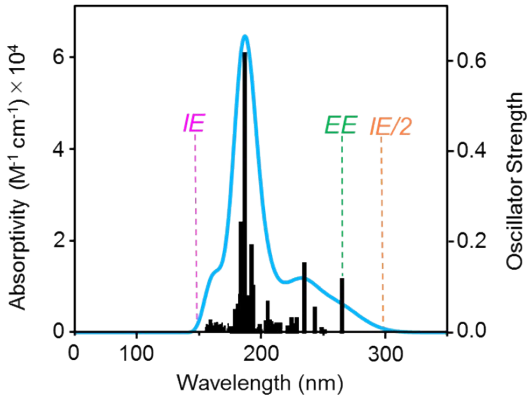


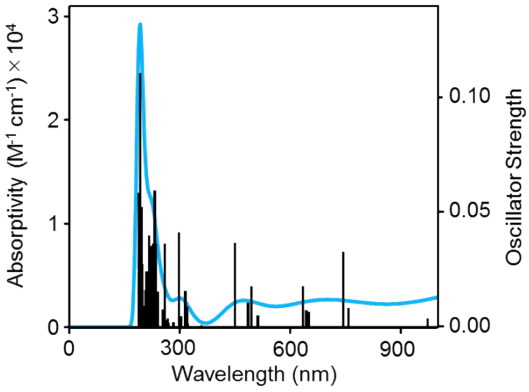


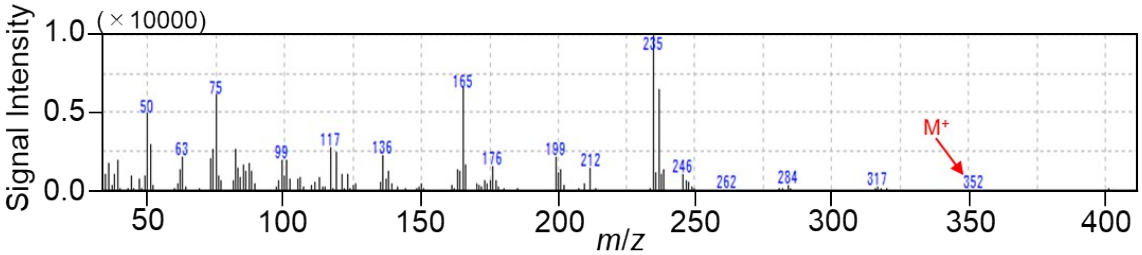


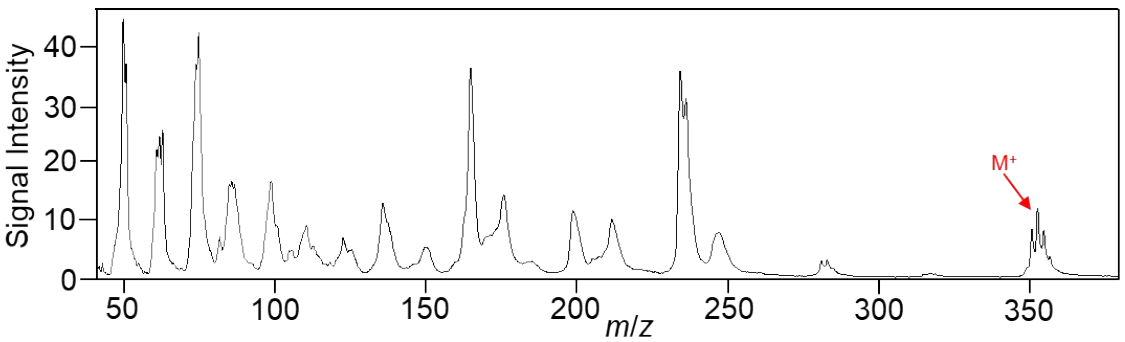
2. DDT


CCl3
Cl
Cl

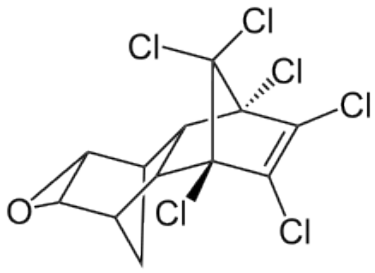

Absorptivity (M-1 cm-1) × 10^4
Oscillator Strength
Wavelength (nm)
IE
EE
IE/2

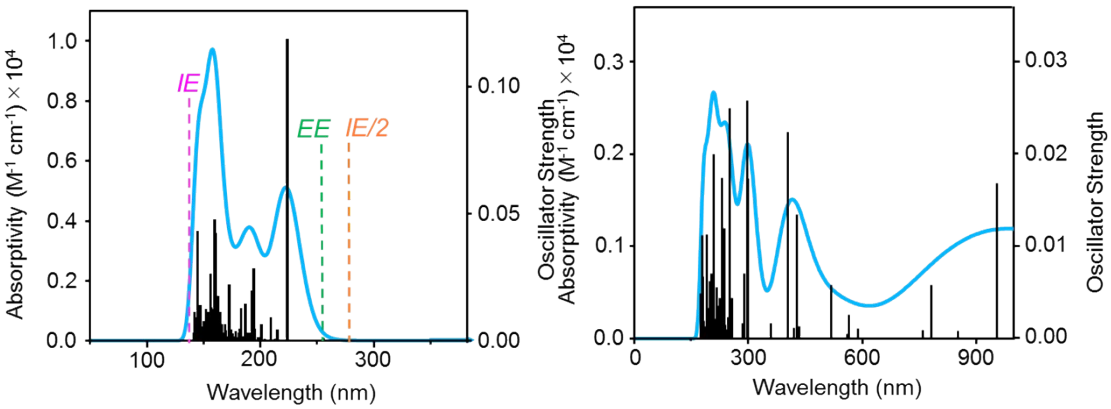

Absorptivity (M-1 cm-1) × 10^4
Oscillator Strength
Wavelength (nm)

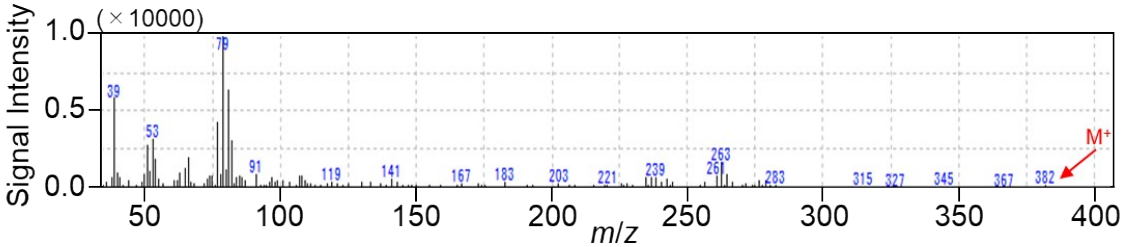

Signal Intensity
(× 10000)
m/z
M+

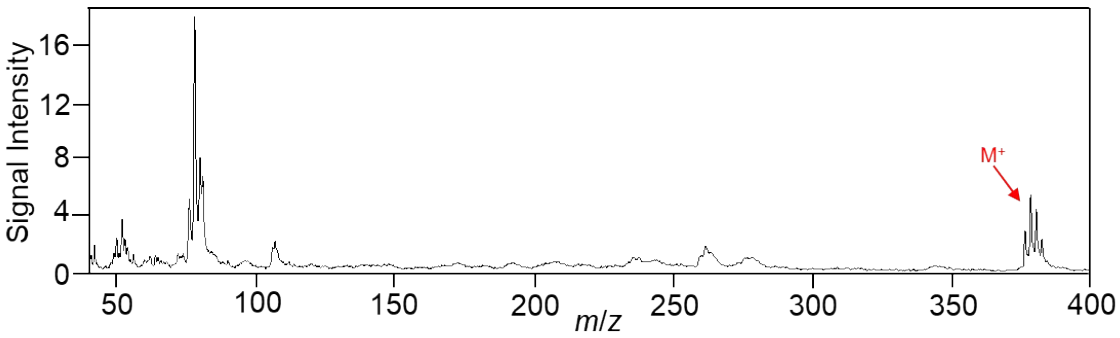

Signal Intensity
m/z
M+

3. dieldrin

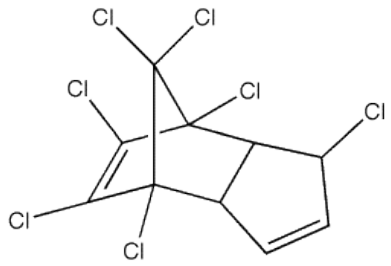

Cl
Cl
Cl
Cl
Cl
Cl
O

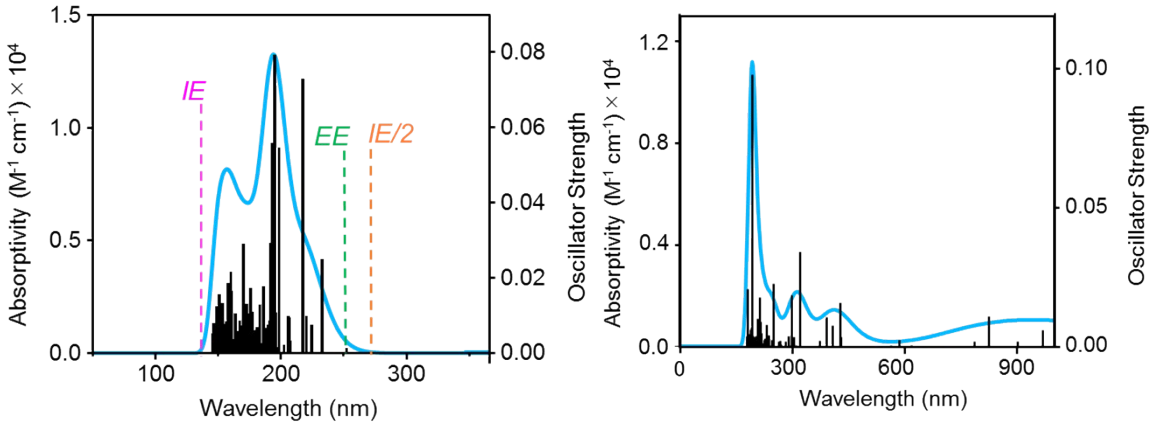

Absorptivity (M-1 cm-1) × 10⁴
IE
EE
IE/2
Wavelength (nm)
Oscillator Strength
Absorptivity (M-1 cm-1) × 10⁴
Oscillator Strength
Wavelength (nm)

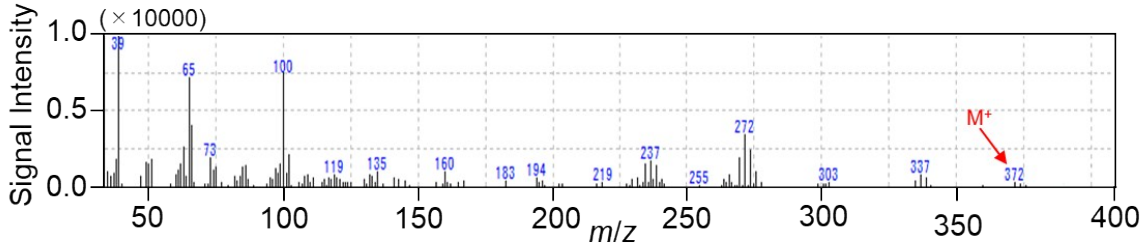

(× 10000)
Signal Intensity
M+
m/z

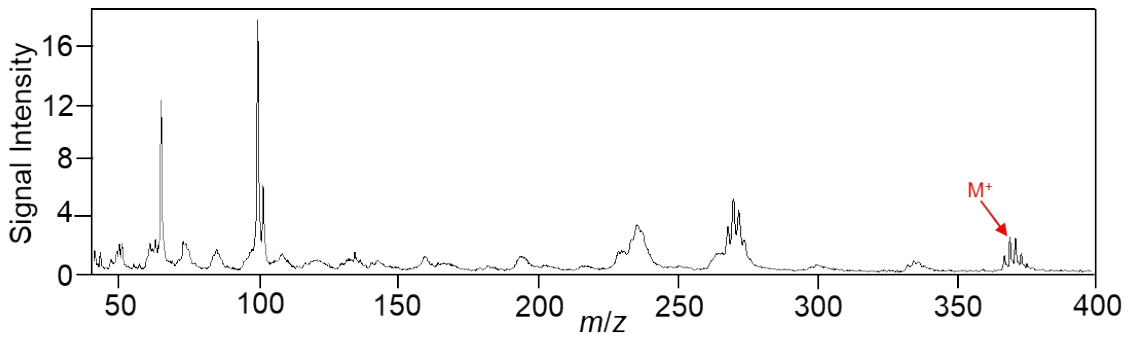

Signal Intensity
M+
m/z

4.heptachlor

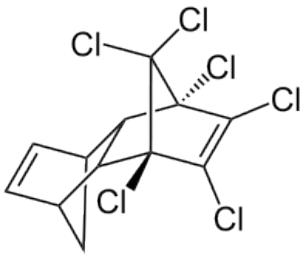


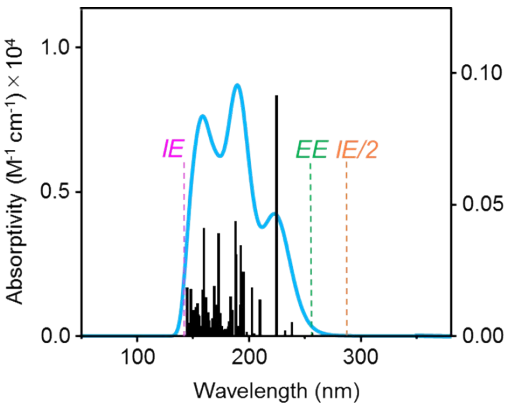


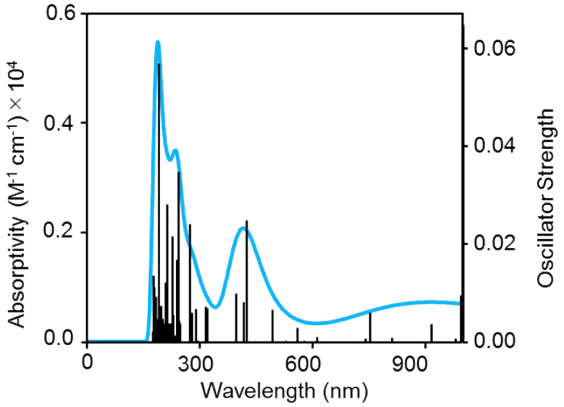


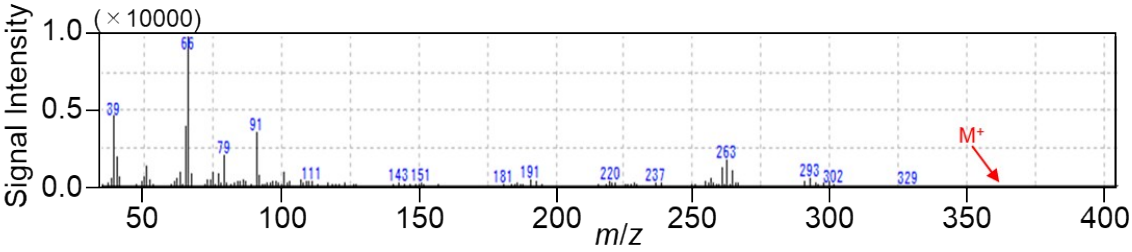


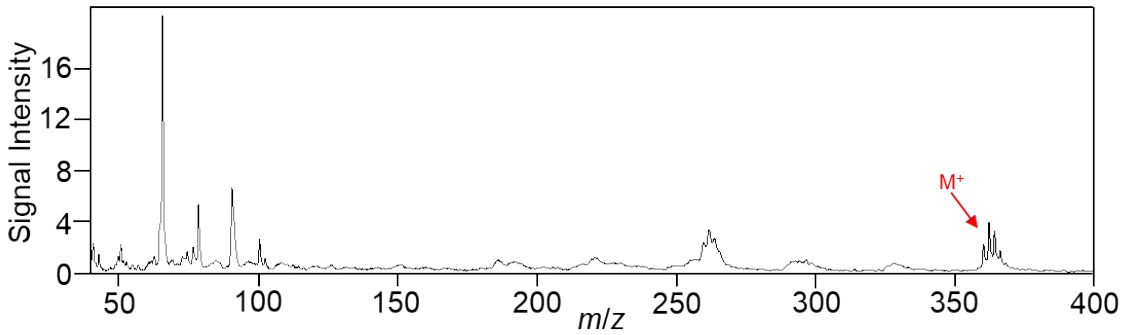
5. aldrin


Cl
Cl
Cl
Cl
Cl
Cl

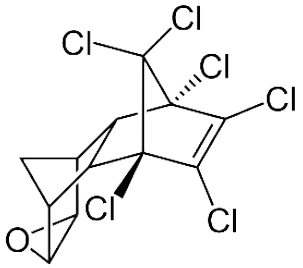

Absorptivity (M-1 cm-1) × 10^4
Oscillator Strength
Wavelength (nm)
IE
EE
IE/2
1.0
0.5
0.0
0.10
0.05
0.00
100
200
300

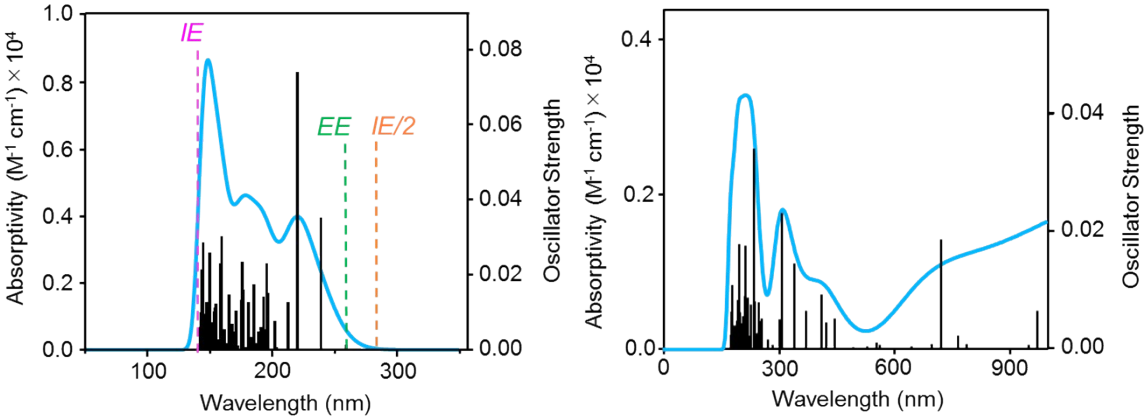

Absorptivity (M-1 cm-1) × 10^4
Oscillator Strength
Wavelength (nm)
0.6
0.4
0.2
0.0
0.06
0.04
0.02
0.00
0
300
600
900

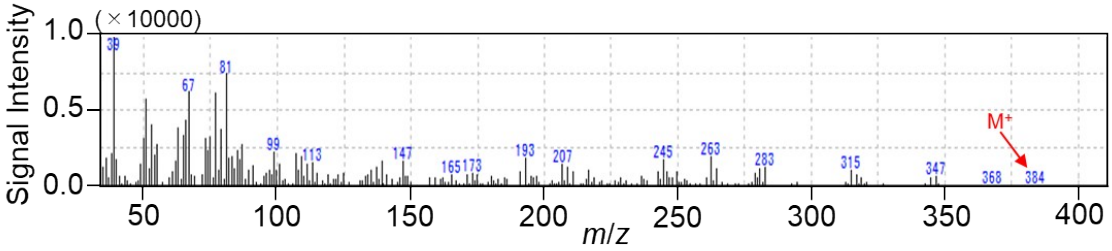

Signal Intensity
(× 10000)
1.0
0.5
0.0
39
65
79
91
111
143 151
181
191
220
237
263
293
302
329
M+
50
100
150
200
250
300
350
400
m/z

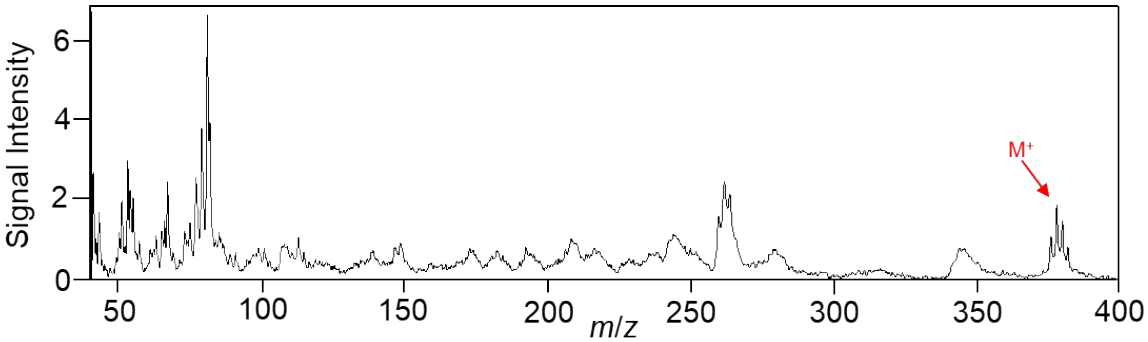

Signal Intensity
16
12
8
4
0
M+
50
100
150
200
250
300
350
400
m/z

6. endrin

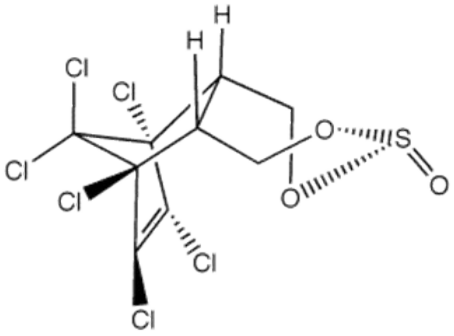

Cl
Cl
Cl
Cl
Cl
Cl
O

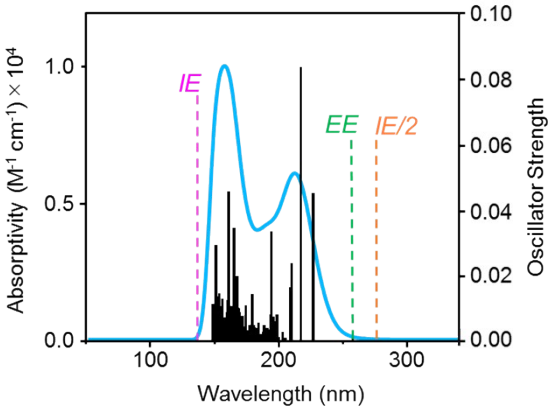

IE
EE
IE/2
Absorptivity (M-1 cm-1) × 10^4
Oscillator Strength
Wavelength (nm)
Absorptivity (M-1 cm-1) × 10^4
Oscillator Strength
Wavelength (nm)

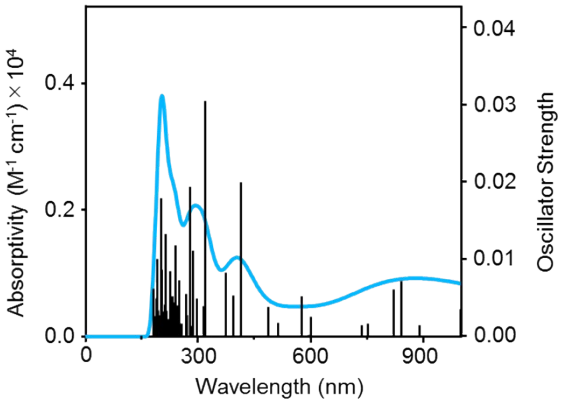

(×10000)
Signal Intensity
m/z
M+

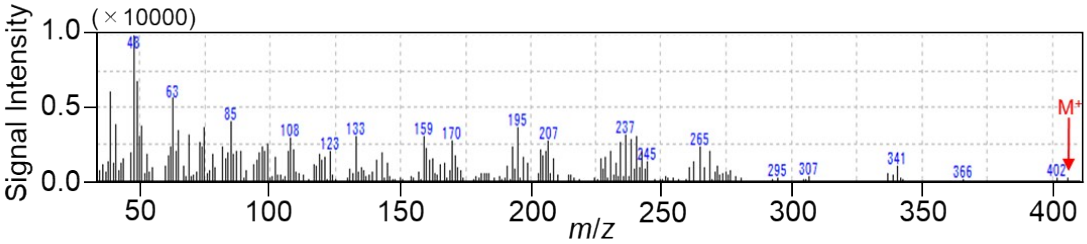

Signal Intensity
m/z
M+

7. *α*-endosulfan

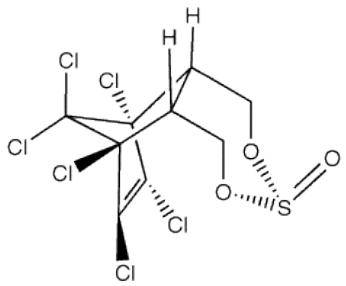


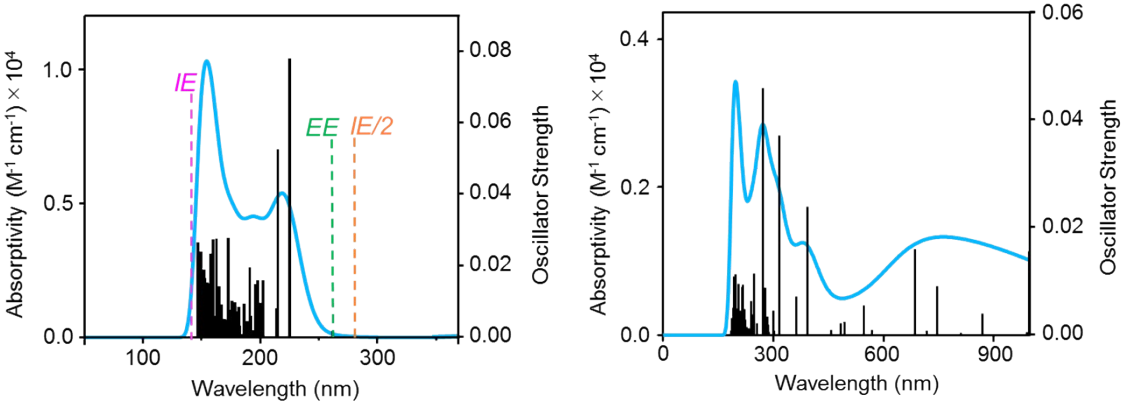


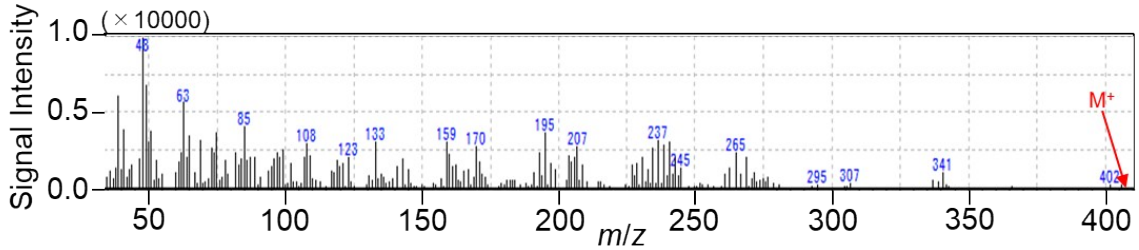


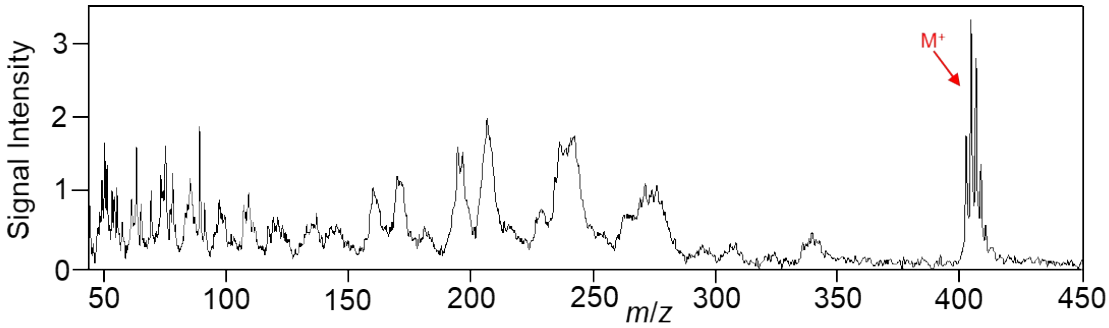


8. *β*-endosulfan

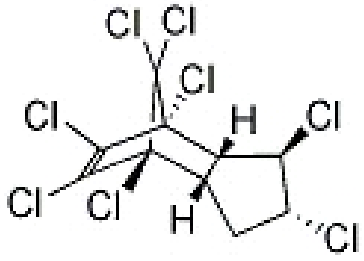


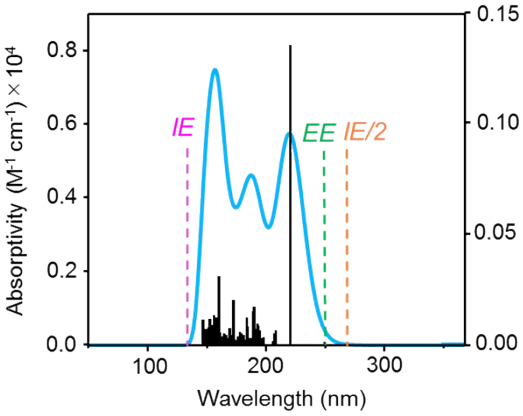


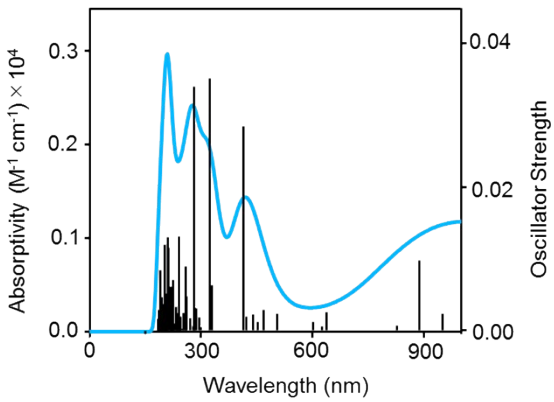


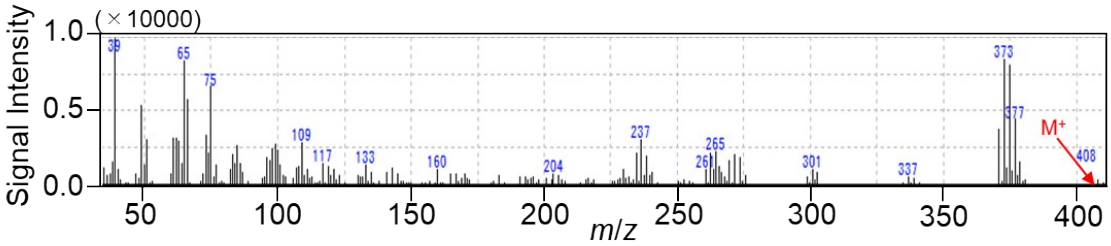


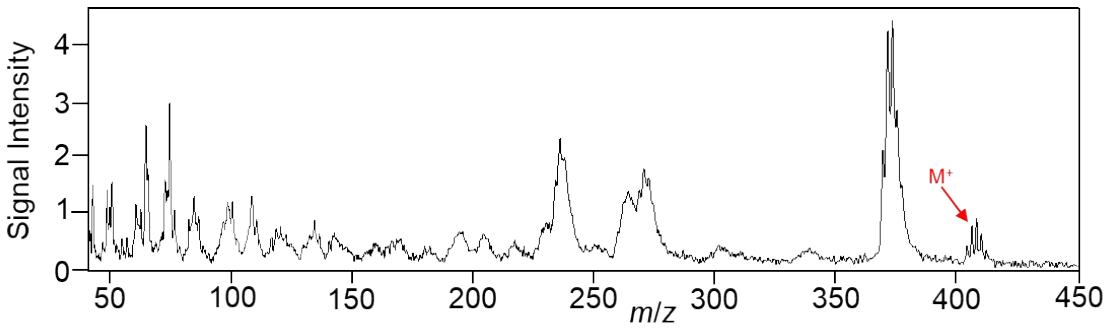
9. *trans*-chlordane



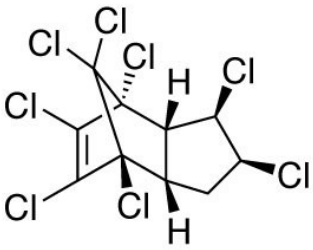


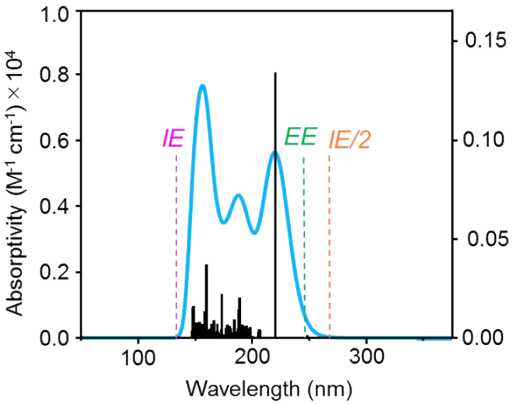


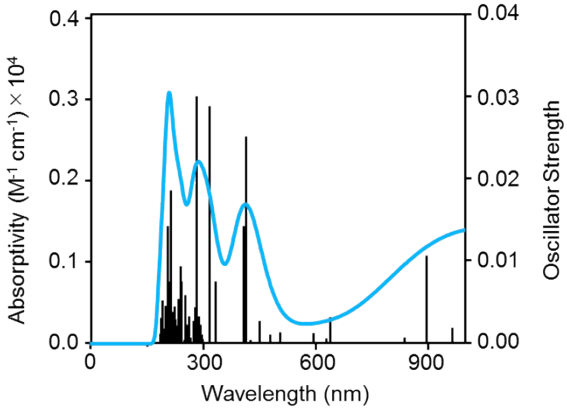


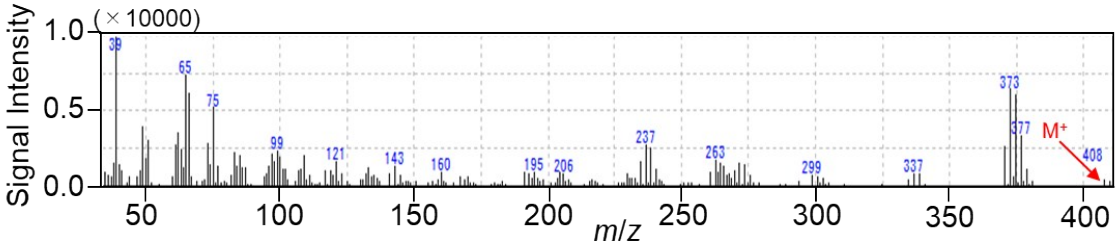


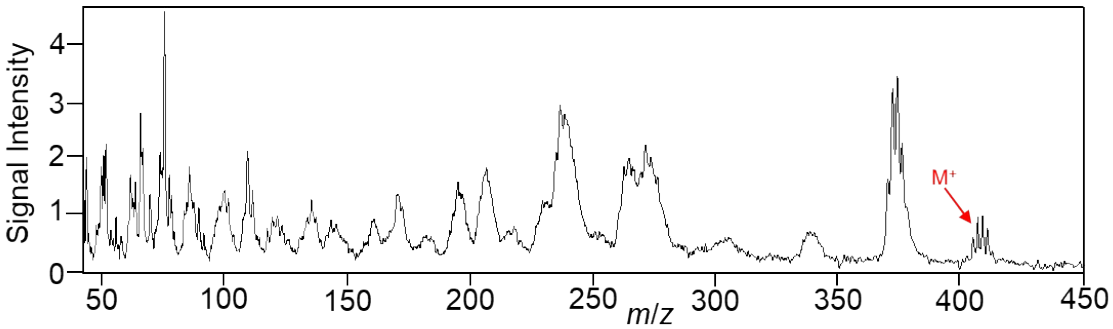
10. *cis*-chlordane



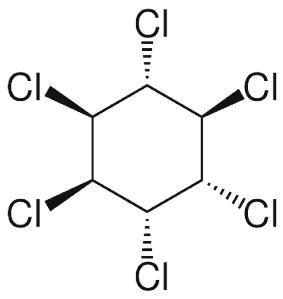


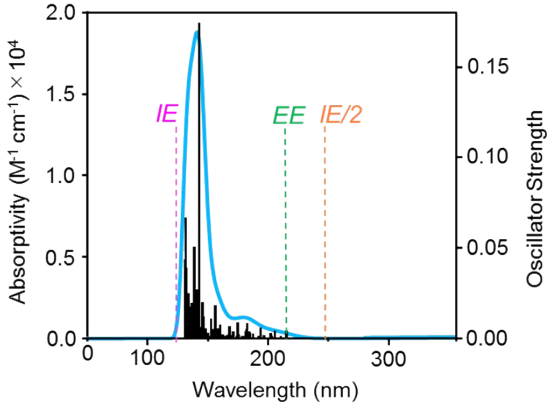


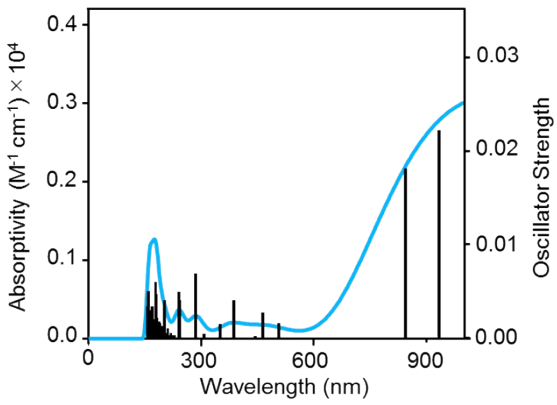


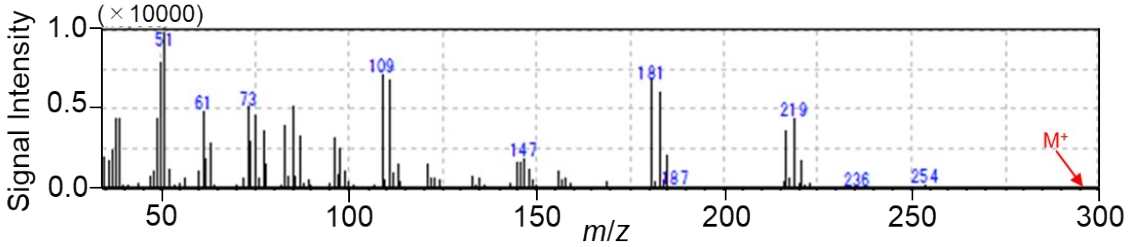


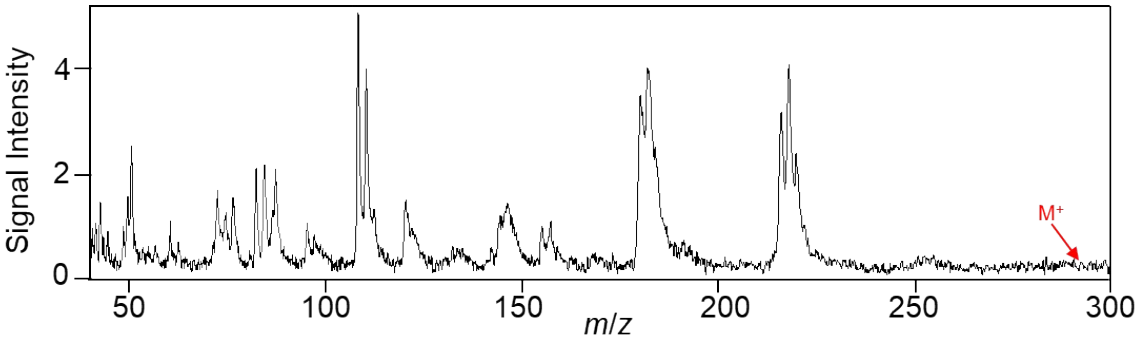
11. *α*-HCH


Cl
Cl
Cl
Cl
Cl
Cl

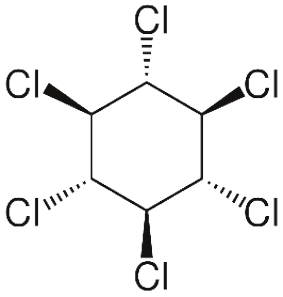

Absorptivity (M-1 cm-1) × 10^4
Oscillator Strength
Wavelength (nm)
IE
EE
IE/2

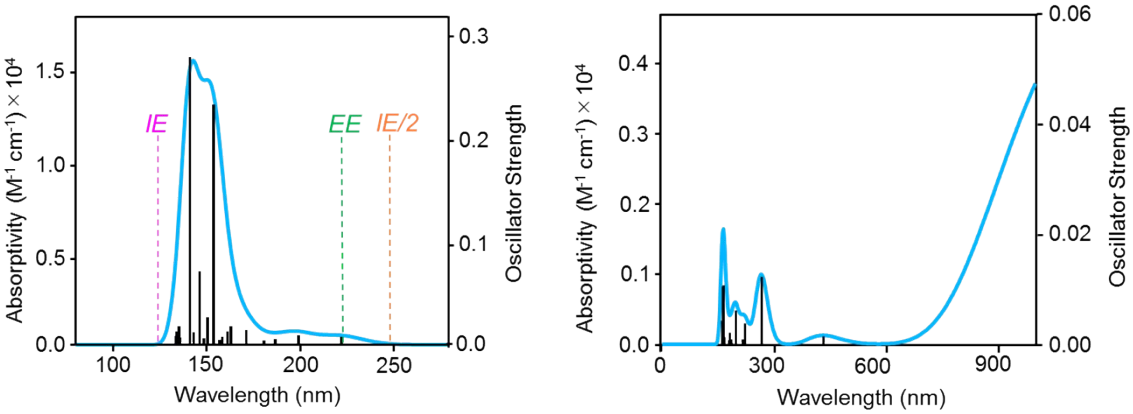

Absorptivity (M-1 cm-1) × 10^4
Oscillator Strength
Wavelength (nm)

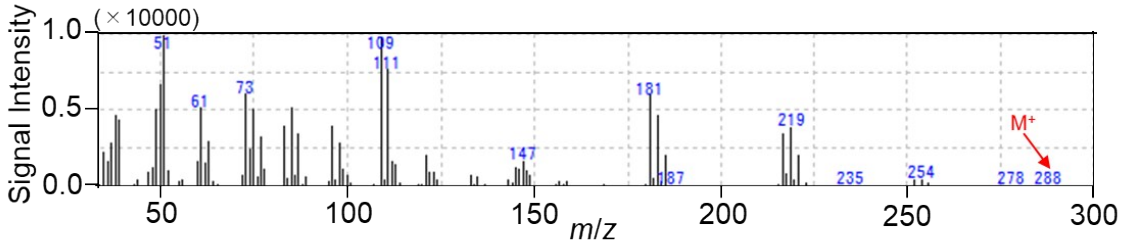

(× 10000)
Signal Intensity
m/z
51
61
73
109
147
181
187
219
236
254
M+

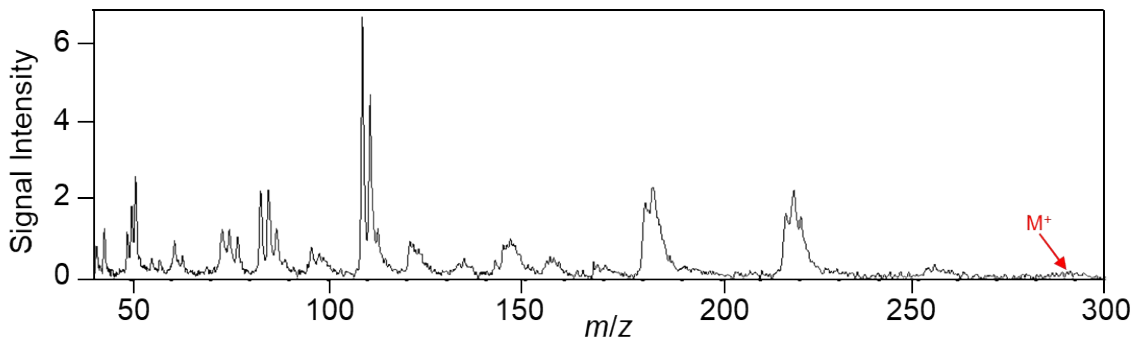

Signal Intensity
m/z
M+

12. *β*-HCH

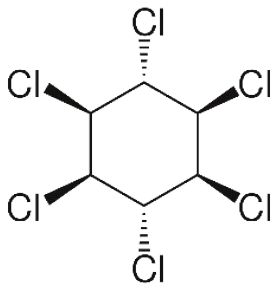

Cl
Cl
Cl
Cl
Cl
Cl

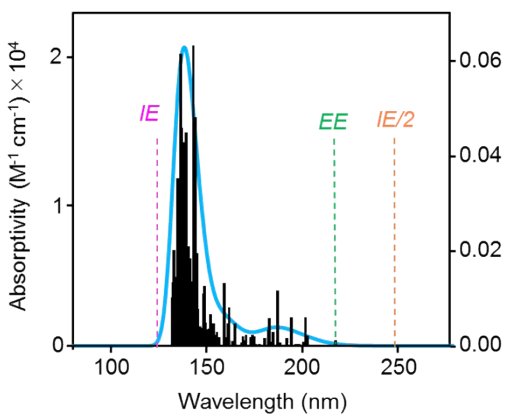

Absorptivity (M-1 cm-1) × 10^4
Oscillator Strength
Wavelength (nm)
IE
EE
IE/2
0.0
0.5
1.0
1.5
0.0
0.1
0.2
0.3
100
150
200
250
0.0
0.1
0.2
0.3
0.4
0.00
0.02
0.04
0.06
0
300
600
900

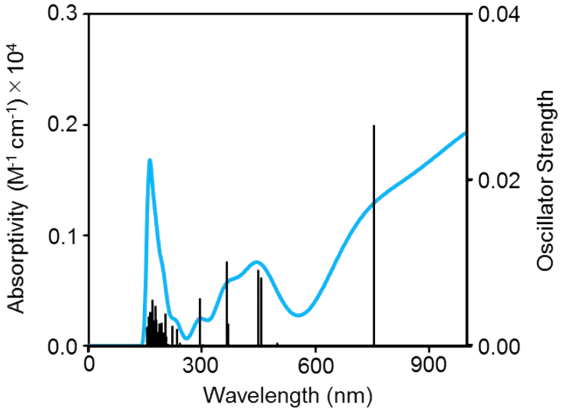

Signal Intensity
(× 10000)
1.0
0.5
0.0
51
61
73
109
111
147
181
187
219
235
254
278
288
M+
50
100
150
200
250
300
m/z

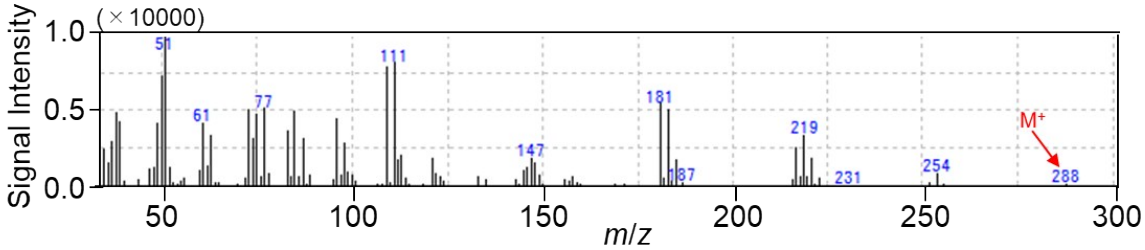

Signal Intensity
0
2
4
6
M+
50
100
150
200
250
300
m/z

13. γ-HCH


Cl
Cl
Cl
Cl
Cl
Cl


Absorptivity (M-1 cm-1) × 10^4
Oscillator Strength
IE
EE
IE/2
Wavelength (nm)


Absorptivity (M-1 cm-1) × 10^4
Oscillator Strength
Wavelength (nm)


Signal Intensity
(× 10000)
51
61
77
111
147
181
187
219
231
254
M+
288
m/z

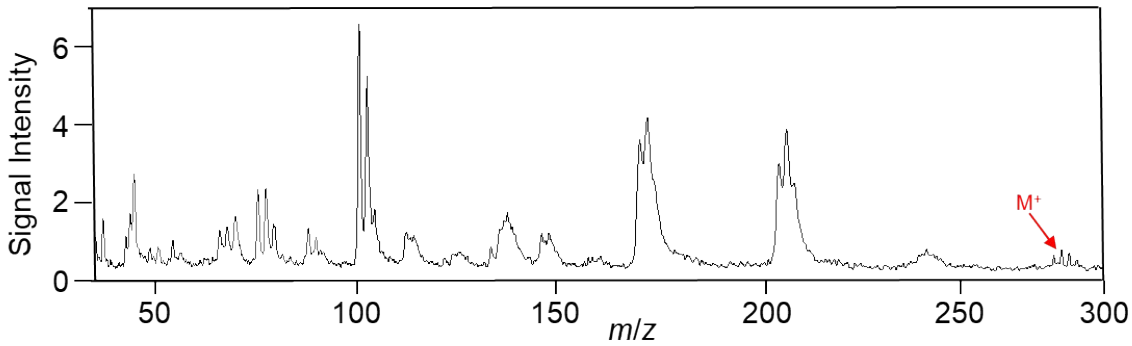
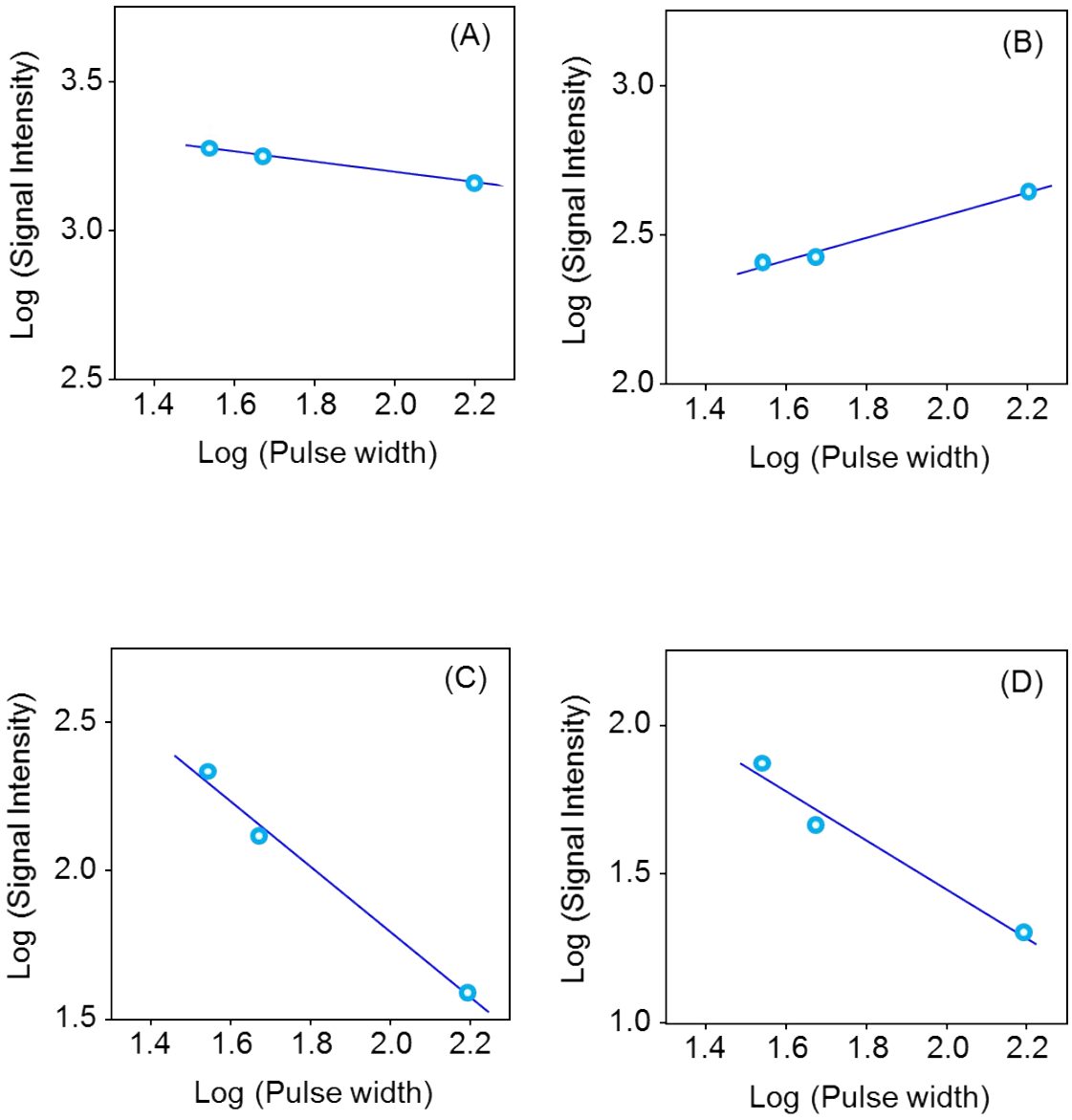
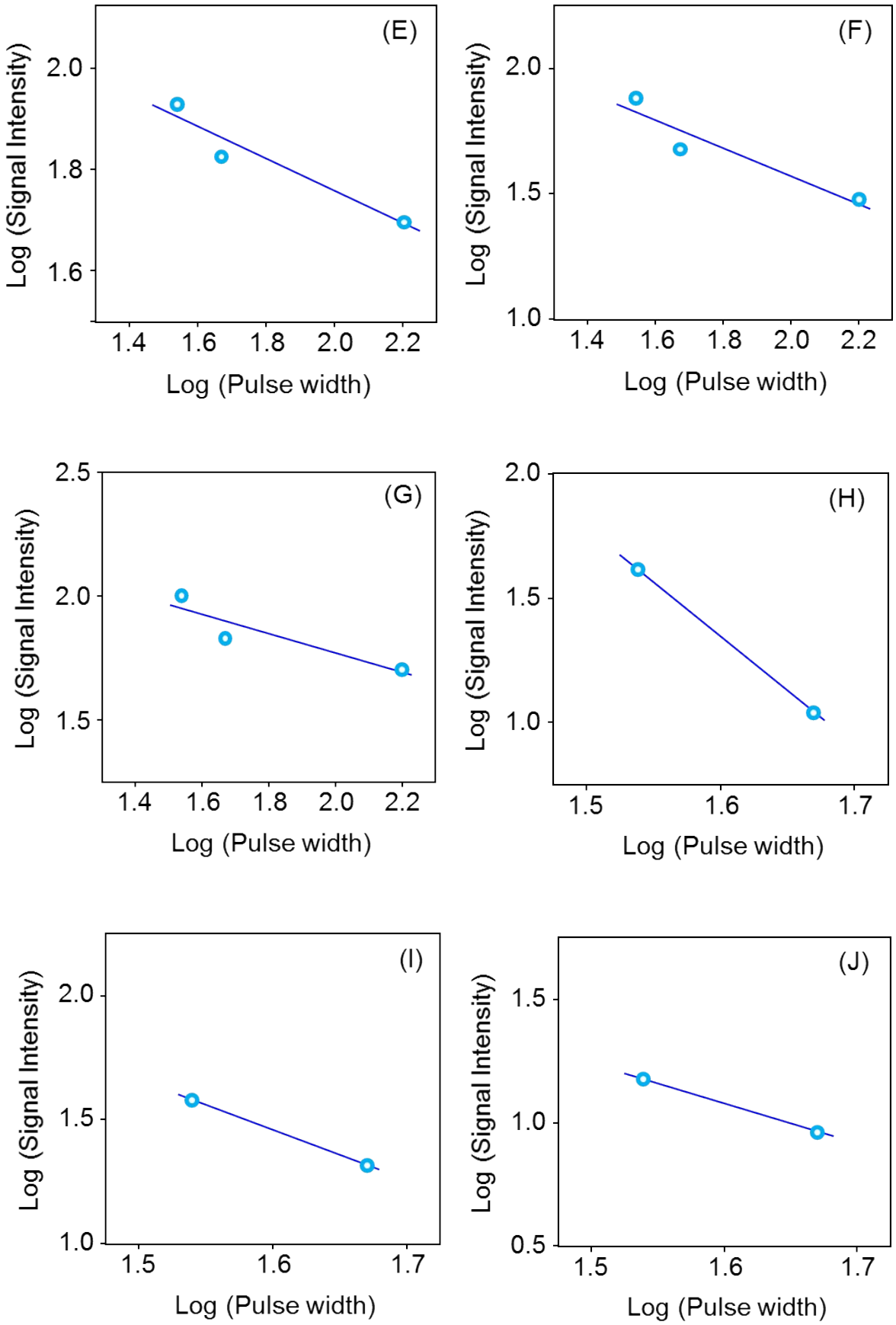

Signal Intensity
M+
m/z

Figure S-2 provides information on dependence of laser pulse width on the signal intensity of the molecular ion for the pesticides examined in this study. (A) HCB (B) DDT (C) dieldrin (D) heptachlor (E) aldrin (F) endrin (G) *β*-endosulfan (H) *trans*-chlordane (I) *cis*-chlordane (J) *γ*-HCH.




(E)
Log (Signal Intensity)
2.0
1.8
1.6
1.4
1.6
1.8
2.0
2.2
Log (Pulse width)
(F)
Log (Signal Intensity)
2.0
1.5
1.0
1.4
1.6
1.8
2.0
2.2
Log (Pulse width)
(G)
Log (Signal Intensity)
2.5
2.0
1.5
1.4
1.6
1.8
2.0
2.2
Log (Pulse width)
(H)
Log (Signal Intensity)
2.0
1.5
1.0
1.5
1.6
1.7
Log (Pulse width)
(I)
Log (Signal Intensity)
2.0
1.5
1.0
1.5
1.6
1.7
Log (Pulse width)
(J)
Log (Signal Intensity)
1.5
1.0
0.5
1.5
1.6
1.7
Log (Pulse width)