Supporting information

Mass-Spectrometry-Based Identification of Synthetic Drug Isomers Using Infrared Ion Spectroscopy

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Table S1. *m/z* values of selected $[M+H]^+$ precursor ions and observed fragment ions in the IRIS experiments.

compound	precursor	fragments
2-, 3- and 4-FA	154	137, 109
2-, 3- and 4-MMC	178	160, 147, 145
2,3- and 3,4-MDMA	194	163, 135, 133, 105, 79, 58
2,3- and 3,4-MDA	180	163, 135, 105, 95, 79

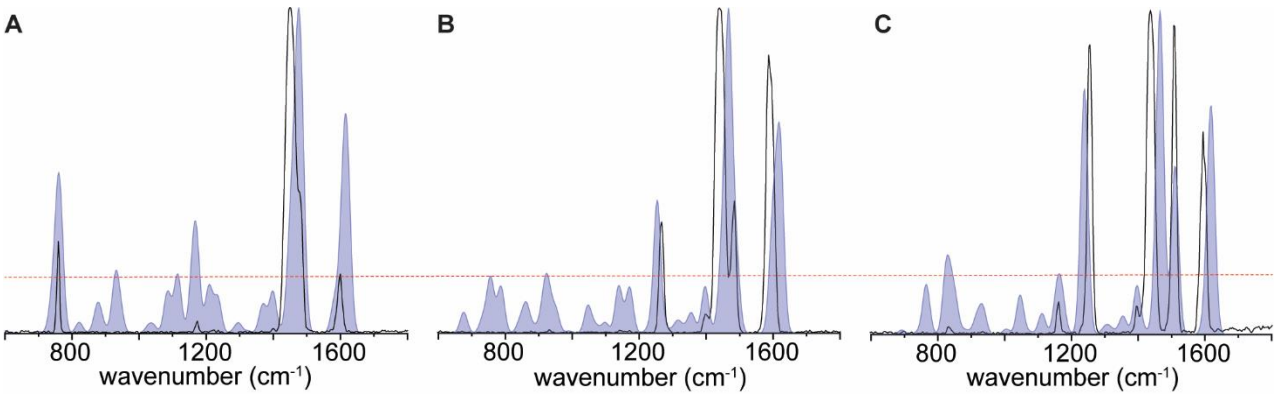

Figure S1. Overlays of obtained experimental (black lines) and theoretical IR spectra (blue lines/fill) for (A) 2-FA, (B) 3-FA, and (C) 4-FA. The horizontal dashed red line indicates an apparent (but approximate) cut-off; for these computed vibrational bands the dissociation energy was not reached with the laser power used (see main text for details).

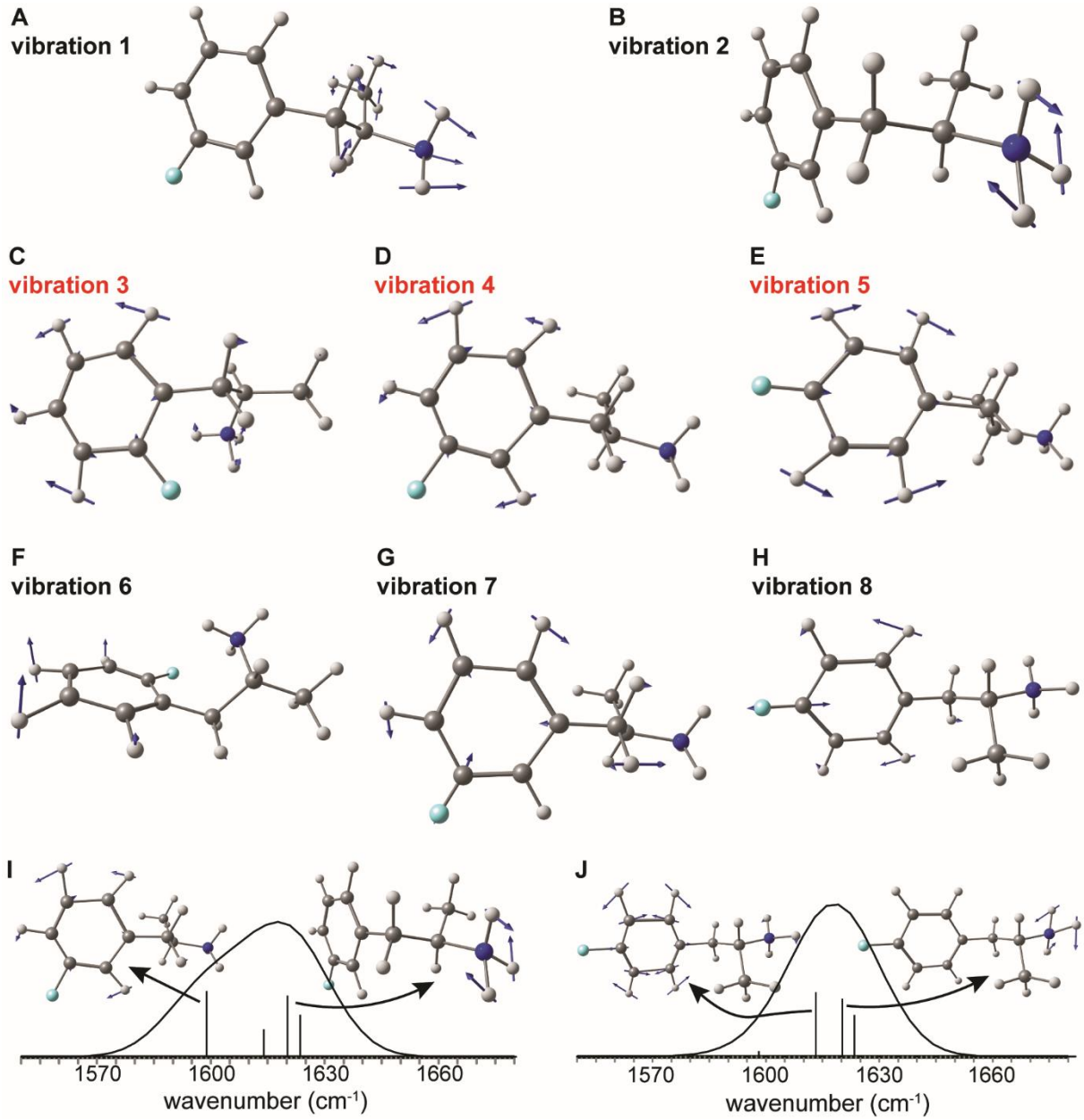

Figure S2. Visualized computed vibrations corresponding with the fluoroamphetamine IRIS spectra shown in Figure 2.

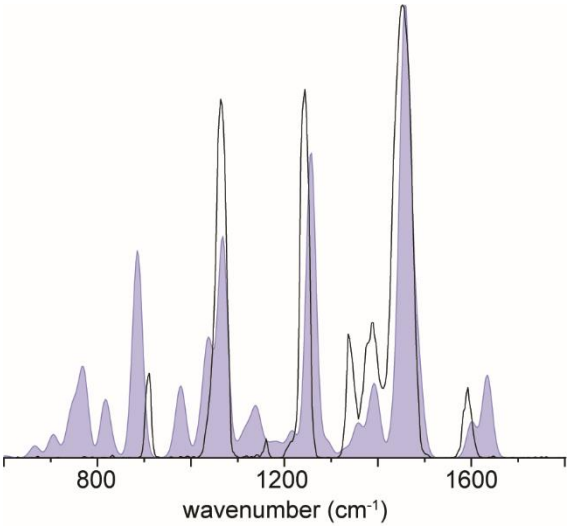

Figure S3. Overlay of obtained experimental (black line) and theoretical IR spectra (blue line/fill) for 2,3-MDMA.

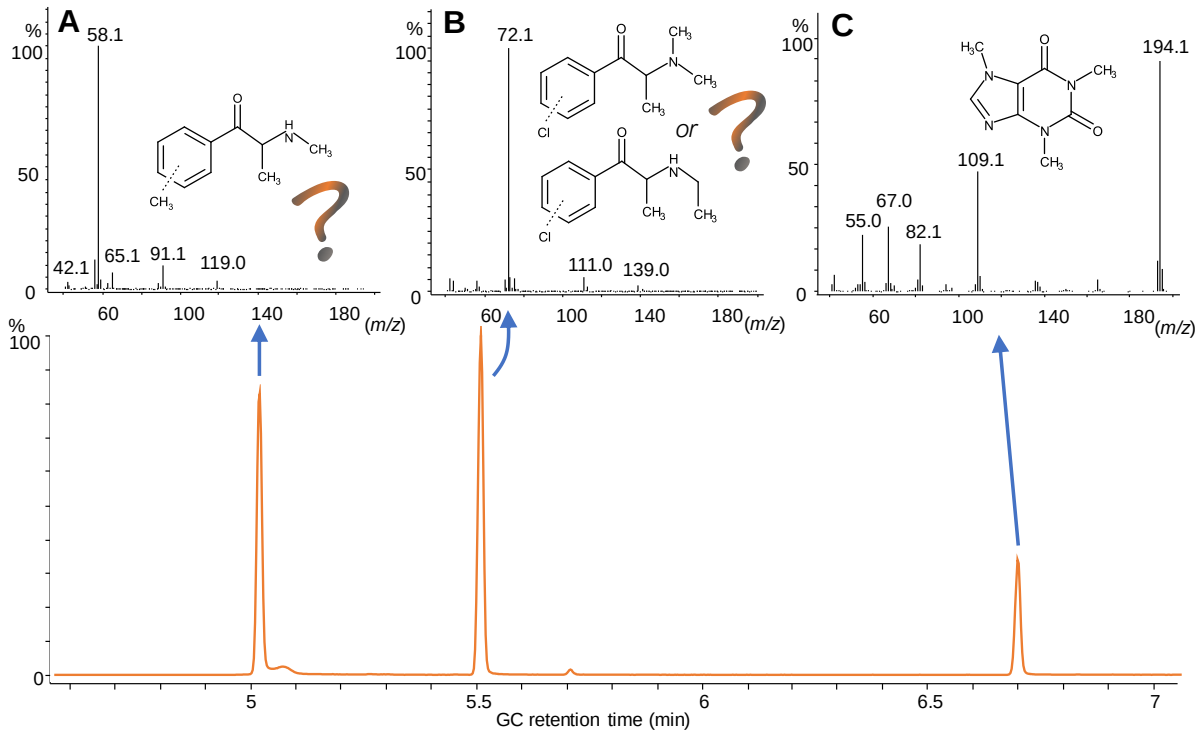

Figure S4. Inconclusive GC-MS results from the case sample, showing a mixture of at least caffeine and two NPS. (A) presents the mass spectrum of the 5.02 min. chromatographic peak giving library scores ~900 for all isomeric forms of MMC, (B) shows the mass spectrum of the 5.51 min. peak yielding library match scores around 900 for both chloroethcathinone (CEC) and chlorodimethcathinone (CdMC) isomers, and (C) the mass spectrum for caffeine. The MS library scores for the two unknown peaks are given in Table S2.

Table S2. MS library match scores for the two unknown peaks in the case sample. sw = SWGDRUG 3.3 spectral library, M = NIST14 main library, R = NIST14 replicate library, ca = Cayman Spectral Library version 12212018, match = forward search match score, r.match = reversed search match score.

library	match	r.match	name (peak 5.02 min.)
sw	927	933	3-methylmethcathinone
sw	921	921	4-methylmethcathinone
M	921	921	4-methylmethcathinone
M	916	922	3-methylmethcathinone
R	912	918	4-methylmethcathinone
M	897	909	2-methylmethcathinone
sw	879	888	2-methylmethcathinone
R	876	879	4-methylmethcathinone

library	match	r.match	name (peak 5.51 min.)
ca	934	934	4-chloro-N,N-dimethylcathinone
ca	900	900	2-chloroethcathinone
ca	899	899	4-chloroethcathinone
sw	893	898	2-chloroethcathinone
sw	891	894	4-chloroethcathinone
ca	890	890	3-chloroethcathinone
sw	885	891	3-chloroethcathinone

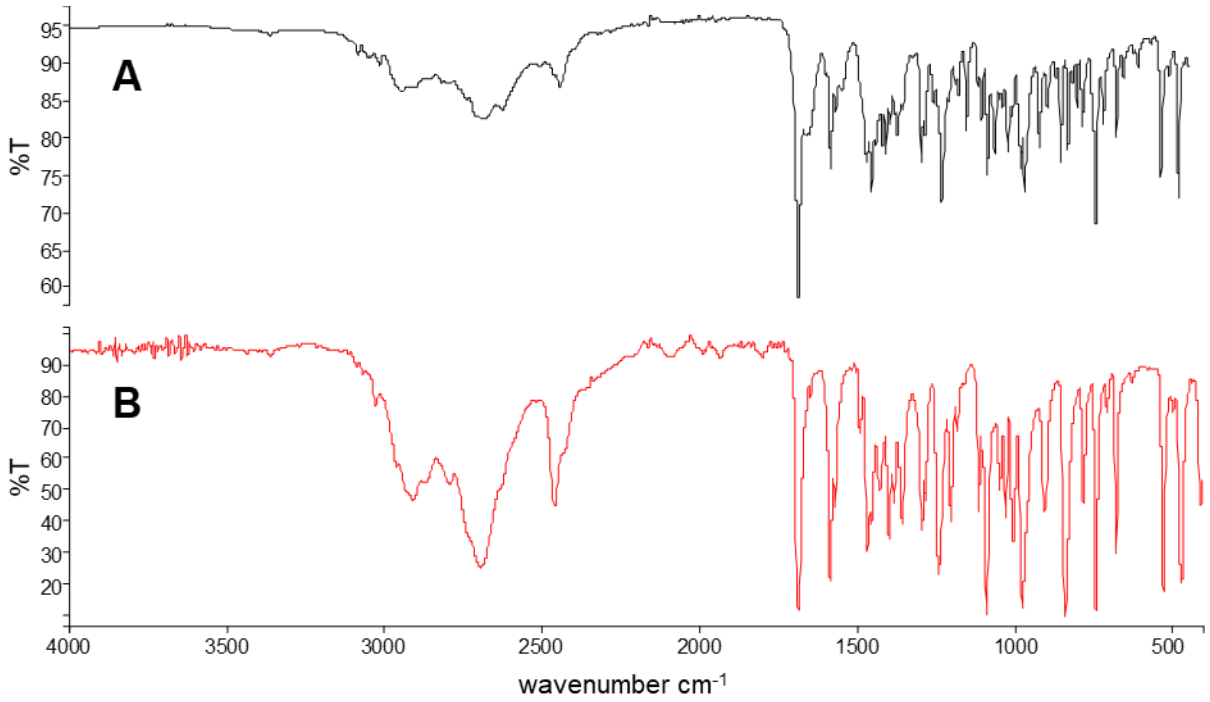

Figure S5. FTIR spectra from the case sample (A) and from a 4-chloromethcathinone reference standard (B), which gives the highest match. The library scores for the best 5 spectral matches are given in Table S3.

Table S3. FTIR library match scores for the case sample on the SWGDRUG 2.0 spectral library. Match scores below 0.980 are considered inconclusive.

match	name
0.682	4-chloromethcathinone HCl
0.678	4-Bromomethcathinone HCl (LOT 1)
0.649	4-Bromomethcathinone HCl (LOT 2)
0.627	4-Chloroethcathinone HCl
0.615	4-Chloro-alpha-PPP HCl

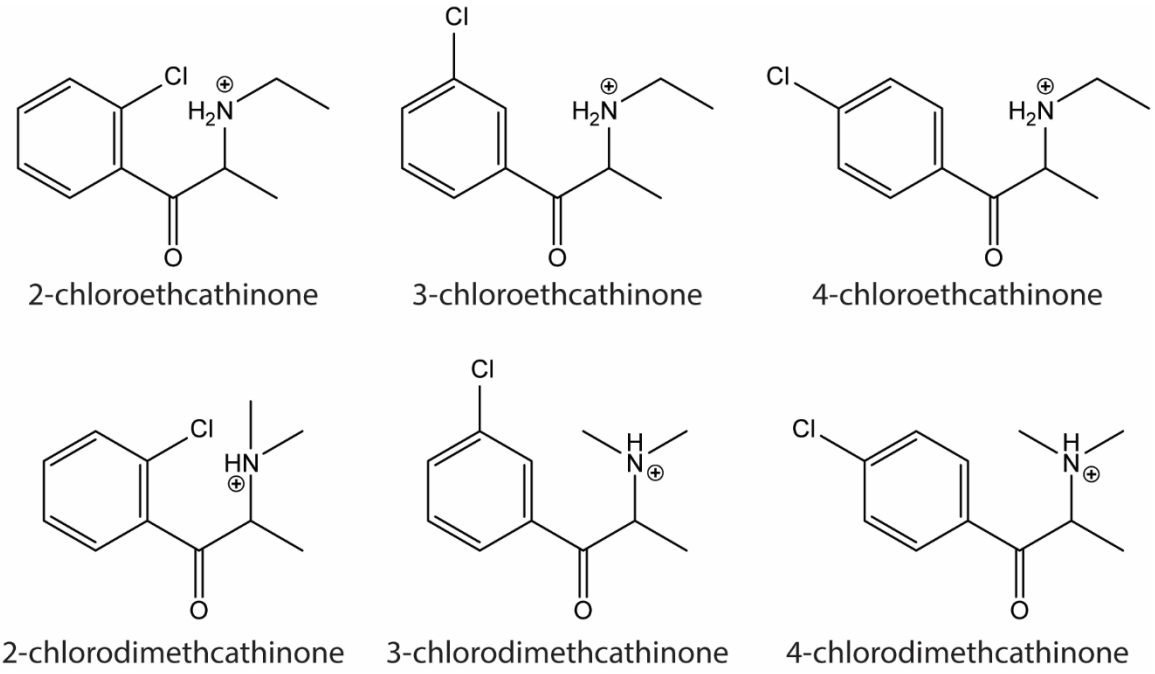

Figure S6. Molecular structures of the cloroethcathinone and chlorodimethcathinone compounds used for computations.

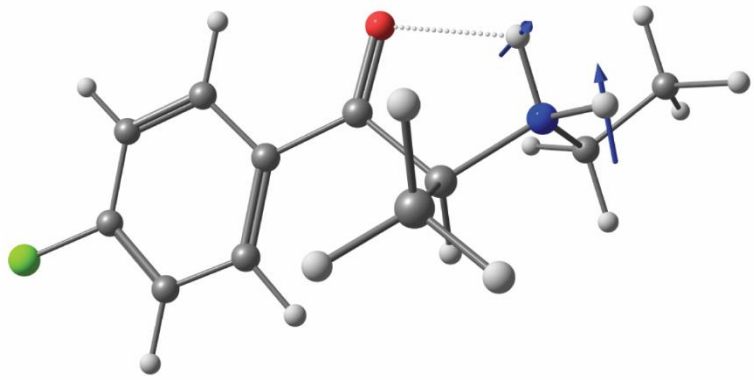

Figure S7. Computed vibration band (1567 cm^{-1}) for 4-chloroethcathinone (4-CEC) that is highlighted in green in Figure 5C. This band is originating from a scissoring vibration of two hydrogen atoms attached to the amine moiety and this vibration is indicated by the two blue arrows.