Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

IR Spectroscopy of Protonated Leu-Enkephalin and its 18-crown-6 Complex Embedded in Helium Droplets

- Supporting Information -

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1. Computational Methods

1.1. Conformational search of [Leu-Enk+CE+H]$^+$

1.1.1. Relative energies

The zero point corrected relative B3LYP-D3 energies of the 24 structures obtained for [Leu-Enk+CE+H]$^+$ are summarized in Table S1. The structures were obtained by straight minimization of the MD structures at the B3LYP-D3 level and might not be the global minimum structure. Therefore, the relative energies should be regarded as a guide.

Table S 1: Zero point energy corrected energies of the 24 calculated structures. The hydrogen bond acceptors are labeled O1 - O5. The hydrogen bond donors are labeled NH1 - NH4 for the four amide groups, and OHT for the Tyr-OH group.

	O1	O2	O3	O4	O5
OHT	–	0	4.88	8.14	24.71
NH1	–	45.99	24.85	10.88	17.31
NH2	14.74	–	14.74	24.49	17.31
NH3	66.09	2.04	–	47.11	75.69
NH4	47.02	14.73	17.28	–	7.00
OHA	44.62	30.97	24.28	14.74	–

2. Results

2.1. IR Spectroscopy of [Leu-Enk+H]$^+$

Figure **S1** shows three different IR wavelength scans, each of which probes [Leu-Enk+H]$^+$ in helium droplets at somewhat different laser conditions. Each spectrum is linearly corrected for power variations. At least five bands can be counted between 1600 cm^{-1} and 1800 cm^{-1}, one at 1523 cm^{-1} and three low intensity bands between 1200 cm^{-1} and 1500 cm^{-1}. The three spectra are clearly highly reproducible in terms of peak positions and shapes, not only for high intensity peaks but also for weak bands. For example, in all three spectra the asymmetry of the peak at 1523 cm^{-1}, as well as the little shoulder on the red is reproduced.

Additionally, the three low intensity bands between 1200 cm^{-1} and 1500 cm^{-1} are present in the two spectra obtained over that range. Considering the inherent spectral width of the FEL of about 0.5 %, the transition peaks can be remarkably narrow. For example, the width of the transition peak in the top trace at 1623 cm^{-1} is only 8 cm^{-1}. It is also observed, however, that the measured peak widths depend on the laser power. When measuring the spectrum in the top trace, the laser power varied from 26 mJ at 1500 cm^{-1} to 8 mJ at 1700 cm^{-1}. For the lower two spectra, the laser power varied from 30 mJ at 1500 cm^{-1} to 15 mJ at 1700 cm^{-1}. Concomitant with that, a slight increase in width of the peaks is observed, especially between 1600 cm^{-1} and 1800 cm^{-1}.

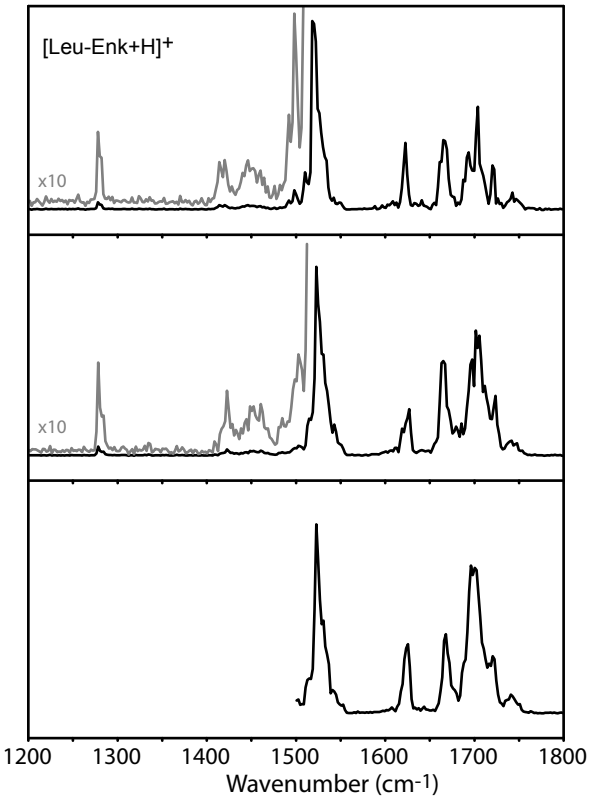

Figure S 1: Three different IR excitation spectra of $[Leu\text{-}Enk+H]^+$ in helium droplets measured at slightly different laser powers.

Figure S2 shows the IR spectra of $[Leu\text{-}Enk+H]^+$ obtained using helium droplets (upper panel) and a cold ion trap (lower panel, see Ref. 10).

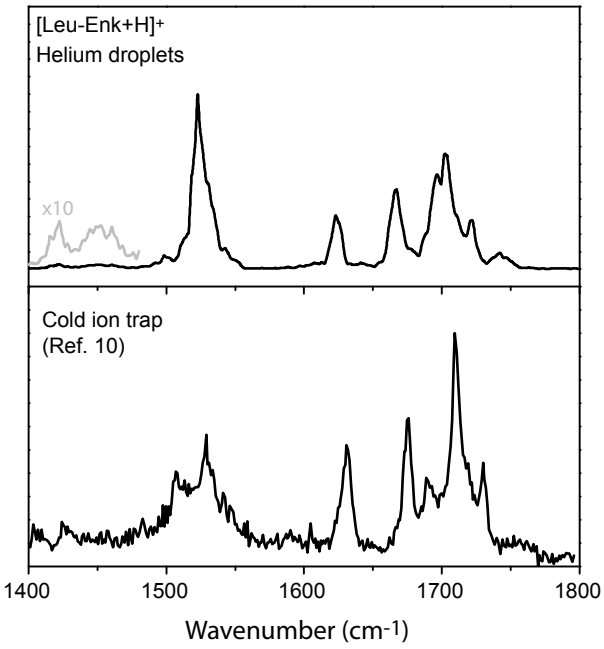

Figure S 2: IR spectra of $[\text{Leu-Enk+H}]^+$ measured using helium droplets (upper panel) and a cold ion trap (lower panel, obtained from Ref. 10).

3. Computational

3.1. Assignment of vibrational bands

For comparison with the experiment, vibrational frequencies of the theoretical model structures were calculated (shown in Figure 3 on the manuscript). The most important transitions of the calculated structure of $[\text{Leu-Enk}_D\text{+D}]^+$ are summarized in Tables S2 and S3 for a moleculewith 8 H/D exchanges and for a fully H/D exchange respectively.

The most important vibrational transitions of the calculated structure of $[\text{Leu-Enk+CE+H}]^+$ which shows the best agreement with the experimental results and its deuterated counterpart are summarized in Tables S4 and S5 (shown in Figure 5 on the manuscript).

Table S 2: Assignment of calculated IR bands for the deuterated molecule [Leu-Enk$_D$+D]$^+$ for 8 H/D exchanges.

Expt. (cm^{-1})	Calc. (cm^{-1})	Intensity (km mol^{-1})	Assignment
1274	1286	129.81	Tyr ring deform. and C-H bend
1460	1444	243.69	N-H bend
1518	1504	120.88	Tyr ring deform.
	1619	109.14	Tyr ring deform.
1619	1632	182.32	Phe C=O stretch
1658	1675	384.61	Gly_2 C=O stretch
1677	1688	74.72	Gly_1 C=O stretch
1694	1698	981.03	Leu C=O stretch
	1715	213.35	Tyr C=O stretch
1740			

Table S 3: Assignment of calculated IR bands for the deuterated molecule [Leu-Enk$_D$+D]$^+$ for fully exchanged molecule (9 H/D exchanges).

Expt. (cm^{-1})	Calc. (cm^{-1})	Intensity (km mol^{-1})	Assignment
1279	1281	81.439	Tyr ring deform. and C-H bend
1460	1444	162.12	N-H bend
1518	1502	140.66	Tyr ring deform.
	1618	120.262	Tyr ring deform.
1619	1632	182.50	Phe C=O stretch
1658	1675	384.87	Gly_2 C=O stretch
1677	1688	74.16	Gly_1 C=O stretch
1694	1699	981.02	Leu C=O stretch
	1715	213.35	Tyr C=O stretch
1740			

Table S 4: Assignment of IR transitions of [Leu-Enk+CE+H]$^+$ for the 0 kJ/mol structure shown in figure 4A

Exp. (cm^{-1})	calc. (cm^{-1})	Intensity (km mol^{-1})	Assignment
1253	1276	122.17	Tyr ring deform., C-H and O-H bend
1402	1430	156.27	O-H and C-H bend
	1495	215.44	N-H bend and Tyr ring deform.
1505	1508	165.97	N-H bend
1526	1516	207.52	N-H bend
	1530	232.00	N-H bend
	1590	31.39	Antisym. NH_3^+ umbrella
	1603	31.97	Antisym. NH_3^+ umbrella
	1620	72.11	Tyr ring deform.
1678	1646	200.52	Phe C=O stretch
1691	1681	286.72	Gly_1 C=O stretch
1705	1718	349.59	Gly_2 C=O stretch
1725	1722	308.87	Tyr C=O stretch
1748	1757	512.87	Leu C=O stretch

Table S 5: Assignment of IR transitions of [Leu-Enk$_D$+CE+D]$^+$ for the 14.8 kJ/mol structure shown in figure 4B

Exp. (cm^{-1})	Calc. (cm^{-1})	Intensity (km mol^{-1})	Assignment
	1330	44	C-H bend
	1337	53	C-H bend
1356	1351	42	C-H bend
	1438	89	N-H bend and C-H bend
1454	1446	105	N-H bend and C-H bend
1518	1507	138	Tyr ring deform.
	1622	72	Tyr ring deform.
1643	1655	152	Phe C=O stretch
1674	1671	84	Gly_1 C=O stretch
1686	1683	490	Tyr C=O stretch
1722	1711	562	Gly_2 C=O stretch
	1735	400	Leu C=O stretch