

Supporting Information

Intrinsic Structure of Pentapeptide Leu-enkephalin: Geometry Optimization and Validation by Comparison of VSCF-PT2 Calculations with Cold Ion Spectroscopy

Tapta Kanchan Roy,^a Vladimir Kopysov,^b Aleksandr Pereverzev,^b Jiří Šebek,^c R. Benny Gerber,^{*d} and Oleg V. Boyarkin^{*b}

^a *Department of Chemistry and Chemical Sciences, Central University of Jammu. Rahya-Suchani (Bagla), Jammu 181143, India.*

^b *Laboratoire de Chimie Physique Moléculaire, École Polytechnique, Fédérale de Lausanne, 1015 Lausanne (Switzerland). E-mail: oleg.boiarkin@epfl.ch*

^c *Department of Physical Chemistry, University of Chemistry and Technology, Prague, Czech Republic.*

^d *Institute of Chemistry, The Hebrew University Jerusalem 91904 (Israel) and Department of Chemistry, University of California Irvine, CA 92697, USA. E-mail: benny@fh.huji.ac.il*

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A) VSCF-PT2 approximation

When the non-separability effects are small, a suitable level of perturbation theory can be thus treated on top of the energy levels given by VSCF. If the vibrational levels are computed using second order perturbation theory (PT2) then the PT2 correction on VSCF is described by the following equation:

$$E_n^{PT2} = E_n^{VSCF} + \sum_{m \neq n} \frac{\left| \left\langle \prod_{j=1}^N \phi_j^{(n)}(Q_j) \middle| \Delta V \middle| \prod_{j=1}^N \phi_j^{(m)}(Q_j) \right\rangle \right|^2}{E_n^{(0)} - E_m^{(0)}} \quad (1)$$

Here, E_n^{PT2} is the correlation corrected energy of the target state n and ΔV represents the difference between the true potential and the separable potential that describes the system within the VSCF framework, and the corresponding equation for ΔV is given by

$$\Delta V(Q_1, \dots, Q_N) = V(Q_1, \dots, Q_N) - \sum_{i=1}^N \overline{V_i^{(n)}}(Q_i) \quad (2)$$

Following the standard expression the vibrational band intensities (in km mol^{-1}) are computed using anharmonic wave functions and the transition moment are calculated directly from the specified electronic structure method.

B) Computational Details

In this study, construction of the VSCF potential energy surface (PES) on a given equilibrium structure is an important and computationally most time demanding process. For the DFT based method, the VSCF PES has been generated around the minimum structure given by the electronic structure theory using the same level. For the hybrid method (HF/MP2) the VSCF PES has been generated using the HF theory around the minimum structure given by the MP2 electronic structure theory. Details are given in the section C below.

Choice of number of grid points per normal modes: It is found earlier that depending on the rigidity of the molecule 8 to 16 grid points per normal mode is required for good accuracy. Further, if the size of the molecule is too large like the studied system here, one has to restrict the VSCF PES to finish the calculation in a reasonable time scale. For example, following eq. 5 in the main text, numbers of single point energy computations considering 8 and 10 grid points per normal mode for ALE (237 vibrational modes) are 1791720 and 2798970, respectively. Increment of 8 to 10 grid points per normal modes requires as large as 1007250 more single point energy calculations. On the other hand, to achieve good accuracy, less than 8 grid points per normal modes is not recommended. Hence, 8 grid points per normal modes is chosen to balance between accuracy and computational time. The grid points are constructed along a normal mode with a maximum distance which is a function of its frequency. The calculated default values for each normal mode goes far enough past the classical turning points of the fundamentals so that it can address the appropriate part of the PES. Following eqns. 1-6 given in J. Chem. Phys. 129, 164107 (2008), the range of the PES points and total displacement from the equilibrium geometry are given below following the normal mode vector in both the directions.

Molecule: LL_0, B3LYP-D2/6-31+g method: 14 selected modes: 8 grid points per normal mode**

MODE # 1	QRANGE=	29.370023	DEL-Q=	8.391435
MODE # 2	QRANGE=	30.386467	DEL-Q=	8.681848
MODE # 3	QRANGE=	30.493839	DEL-Q=	8.712525
MODE # 4	QRANGE=	30.542347	DEL-Q=	8.726385
MODE # 5	QRANGE=	30.729153	DEL-Q=	8.779758
MODE # 6	QRANGE=	30.838601	DEL-Q=	8.811029
MODE # 7	QRANGE=	32.129698	DEL-Q=	9.179914
MODE # 8	QRANGE=	32.330269	DEL-Q=	9.237220
MODE # 9	QRANGE=	32.356993	DEL-Q=	9.244855
MODE #10	QRANGE=	43.271668	DEL-Q=	12.363334
MODE #11	QRANGE=	44.233838	DEL-Q=	12.638239
MODE #12	QRANGE=	45.629746	DEL-Q=	13.037070
MODE #13	QRANGE=	47.638550	DEL-Q=	13.611014
MODE #14	QRANGE=	52.585196	DEL-Q=	15.024342

Truncated PES scheme: From the perspective of electronic structure calculations, even to carry out the optimization, harmonic frequency calculations and single point energy calculations to construct VSCF potential at MP2 level of a large system with 81 atoms, 304 electrons and 237 vibrational modes is a daunting task. While B3LYP and HF are faster than MP2, the computation of VSCF potential including the full pair-wise coupling terms is a nearly impossible task using the present state-of-the-art computers as it requires as large as 1791720 numbers of single point energy computation considering 8 grid points per normal mode. Hence calculation of full pair-wise coupling VSCF PES is unfeasible. For this molecule, a 16 processor *Intel Xeon(R) CPU (E5520 @ 2.27GHz)* machine takes ~76 min to perform a single point calculation at B3LYP-D2/6-31+G(d,p) level of theory, and for 1791720 points it requires ~250 years which is certainly impractical. To reduce such huge number of calculations further approximation is adapted. If two modes are far apart the magnitude of coupling between the modes must be small, which is common for large systems, and can be ignored. Following this fact, the number of full pair-wise potential terms is truncated to a small set of normal modes. First, we chose the regions whose vibrations are experimentally observed, such as NH and OH stretches. Then we consider the modes those are in close proximity, interacting and strongly coupled with NH and OH stretches, such as NH bending and CO stretches. No threshold values for distance and magnitude of coupling between modes are considered for this purpose. In this study, B3LYP potential with dispersion correction (at GD2 level) was used with 6-31+G(d,p) basis set for the calculation of VSCF-PT2 using 14 selected vibrational modes for the pair-wise coupling potential functions following to the experimentally observed data. For the hybrid HF/MP2 potential 6-31G(d,p) basis set was used considering as large as 80 vibrational modes. As the single point calculations at HF/6-31G(d,p) level of theory is much faster than the B3LYP-D2/6-31+G(d,p) level of theory we have the flexibility to choose the large number of vibrational modes for the pair-wise coupling calculations using the former method.

C) Hybrid Potential

The contribution of the harmonic part of the potential to each frequency is much larger than the anharmonic part and hence harmonic part requires maximum accuracy. Consequently, the magnitude of the differences for harmonic part calculated at two different (high/low) levels of theory such as MP2 and HF is more significant than that of the anharmonic one. Following this fact, a hybrid potential scheme is employed by "upgrading" the PESs of a lower level calculation to more accurate anharmonic frequencies.¹ This upgraded potential can be written for N -mode systems as

$$V^{ULM}(Q_1, \dots, Q_N) = V^{LM}(\lambda_1 Q_1, \dots, \lambda_N Q_N), \text{ where } \lambda_i = \frac{w_i^{HM}}{w_i^{LM}}, \quad (3)$$

where V^{LM} and V^{ULM} are the potentials at the low-level method (LM) and upgraded low-level method (ULM), respectively, and the ratio of the harmonic frequencies of the LM (w_i^{LM}) to the high-level method (w_i^{HM}) is the scaling coefficients λ_i . These coefficients are designed such that the upgraded potential reproduces the harmonic frequencies of the high level potential. This protocol was applied successfully for small to medium sized systems. In this study the hybrid potentials are built using computationally faster HF method while the harmonic potential at this level are upgraded by more accurate MP2 method in conjunction with 6-31G(d,p) basis set for both the cases.

References:

¹B. Brauer, G. M. Chaban and R. B. Gerber, *Phys. Chem. Chem. Phys.*, 6, 2543-2556, **2004**.

D) Conformational Analysis

ALE is a highly flexible molecule (Fig. S1), which, potentially, may adopt a huge number of low energy conformers. It may happen that a single protocol may fail to spot the truly lowest structure(s). A systematic conformational search, which can accurately generate a set of low energy conformers, is therefore essential. Here we adopt three different protocols for the systematic conformational analysis.

First, a conformational search for the low-energy structures of ALE was performed within the TINKER molecular modelling package¹ using the OPLS-AA/L force field. The search starts from the local minimization of an initial structure, which becomes the first local minimum in the search list. The normal mode activation step is performed for each structure from the search list and, whenever a previously unknown minimum is located, it is added to the search list, if its energy falls within a 7.5 kcal/mol window with respect to the lowest-energy structure. The convergence criterion for the local geometry minimization was set to 10^{-4} kcal/mol/Å. Next, the quantum chemical calculations for better accuracy were performed in three steps. First, all the conformers of ALE within a 7.5 kcal/mol energy window (to sample structures from all conformational families) were optimized at the B3LYP/3-21G level²⁻⁴ with a convergence criterion 10^{-3} a.u. for the largest component of the nuclear gradient. Thus, after the first step one obtained roughly reliable geometries of 123 conformers of ALE and their relative energies, which are, however, still not accurate enough. At the next step a fraction of these structures within a 7.5 kcal/mol energy window was re-optimized at the B3LYP-D/6-31G* level with a convergence criterion of 10^{-4} a.u., which resulted in 70 final structures. This level of theory should be sufficient to adequately describe peptide geometries and predict the relative energies of conformers with an error not exceeding 1 kcal/mol. Therefore, only the conformers within a 1 kcal/mol energy window were finally optimized at the dispersion corrected B3LYP/6-31+G** level of theory with a convergence criterion of 10^{-5} a.u. All quantum chemical calculations were performed using the Firefly software package.⁵ For the B3LYP hybrid functional and Grimme's DFT-D version 3 with Becke-Johnson damping dispersion correction were used.⁶ In case of the 6-31+G** basis set, the diffuse functions were added only on nitrogen and oxygen atoms. Later, all the structures obtained from this method are further reoptimized at B3LYP-D2/6-31+G(d,p) method for equal footing with other structures.

In the second protocol, a diffusion equation evolutionary programming simulated annealing method (DEEPSAM)⁷ was used which follows global optimization evolutionary algorithm based on hybrid PES. This locally developed algorithm is implemented in TINKER

with a PYTHON wrapping. This method has been proved suitable for the conformational search of biomolecules. For better precision, DEEPSAM was used with three different force fields AmberFF99, CharmmFF27 and Oplsaa, to find cluster of a pool of low energy structures. The cluster of minimum structures was optimized for a string of low energy conformers for each force-field. A set of lowest energy conformers, out of over 30000 were calculated, with the cutoff of 10% energy difference from the lowest were further optimized by B3LYP method with 6-31G(d) basis set using *QChem* program package.⁸ The initial DEEPSAM calculation was performed for neutral molecule and the following optimization are performed by protonating it by adding a hydrogen in the distance of 1.0 Å from the oxygen of COO terminus.

In the third protocol, the conformer library search method was used based on MMFF94 force-field using Spartan14 program package. Initially one of the lower energy structures achieved by the DEEPSAM search was considered. This structure was then modified by protonating the carboxyl terminal followed by a conformer search using Spartan14. A set of 25 lowest energy structures, out of over 30000, with cut off at ~10% energy difference from the lowest one are considered. Those are further optimized by B3LYP method with 6-31G(d) basis set using *QChem* program package.

The pool of low energy structures obtained by three protocols were further optimized at three higher level of theories B3LYP/6-31+G(d,p), B3LYP-D2/6-31+G(d,p) and M06-2X/6-31+G(d,p),⁹ using Gaussian program package.¹⁰⁻¹¹ Finally, a few candidates near the global minima were considered following the structural constraints given by experiment.

Note that, three different protocols generated several different structures. It is found that, near the global minima, some structures obtained from different protocols are same or very much similar (with a small difference in the dihedral/torsional angles e.g. in -CH₃ group). However, all the protocols did not find the global minima structure, say LL_0, but only the TINKER/OPLS-AA/L force field. That shows the limitations of a conformational search method and why we need multiple conformational search protocols. It is also found that the structures obtained from different force-fields are changing noticeably while optimized in a quantum mechanical method which is expected and occasionally converge to a unique structure. We also note that, the structures have undergone further changes while dispersion correction is added with the B3LYP functional which shows dispersion correction is important.

In table 1, some structural properties and zero-point corrected (at HO level) relative energies of such ten conformers near the global minima are given which are obtained by using three different conformational search protocols, followed by two different high level DFT calculations. We note that, the most stabilising factor for a structure is the intra-molecular

hydrogen bonding and the main destabilizing factor is torsional strain. More hydrogen bonding interactions such as NH...OC and OH...OC lead to stabilization. Moreover, hydrogen bonding interaction between π -electrons of Phe to NH is also an important factor, specially while the cation (NH_3^+) is interacting with the Phe ring. The similar observation is found in our other studies ((1) *ChemPhysChem*, 16, 1374-1378, **2015**; (2) *J. Phys. Chem. A*, 121, 9401-9408, **2017**).

The comparisons of scaled-harmonic IR spectra of all ten structures with the experimental values show the best match for the lowest energy structure (**LL_0**) showed in fig. S2. That finally drives to select this conformer for the VSCF calculations.

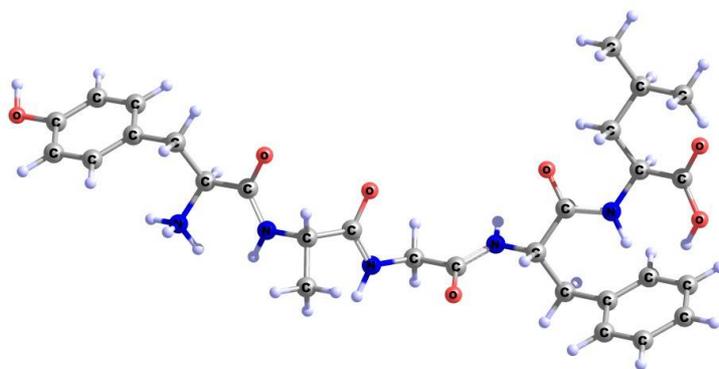


Fig. S1. Schematic view of [L-Ala², L-Leu⁵]-Enkephalin, $m/z = 556.3$ Da

Table S1. Conformational analysis of LL (relative energies are in kcal/mol)

Conformer	Distance between two Phe rings (Å)	H-bonding in C-terminus OH	H-bonding in all NH	Relative energy ¹	Relative energy ²
LL_0	~10-12	Yes	Yes	0.00	0.00
LL_1	~9-11	Yes	Yes	2.88	2.57
LL_2	~10-12	Yes	Yes	2.99	2.12
LL_3	~4-5	No	No	4.05	2.91
LL_4	~9-11	Yes	Yes	4.25	2.45
LL_5	~4-5	No	No	5.36	4.41
LL_6	~4-5	No	No	5.53	4.39
LL_7	~8-10	No	No	7.94	5.49
LL_8	~ 6-8	No	No	8.17	8.17
LL_9	~8-10	No	No	10.54	10.57
LL_10	~8-10	No	No	11.60	10.46

¹B3LYP-D2/6-31+G(d,p), ²M06-2X/6-31+G(d,p)

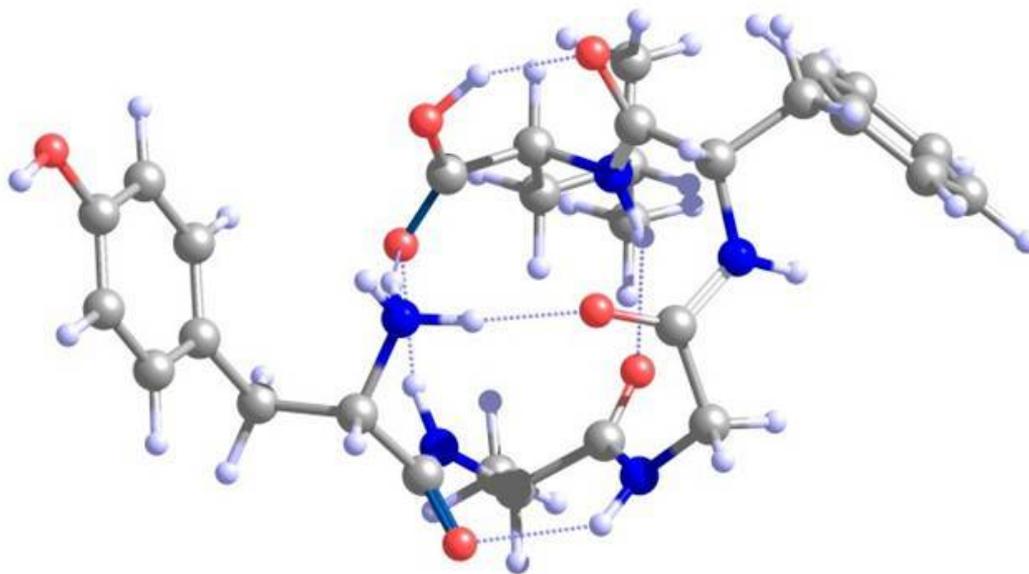


Fig. S2. Optimized structure of the global minima of ALE (LL_0)

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11. Frisch et al., M.J. (Gaussian 016, Revision A.03, Gaussian, Inc., Wallingford CT, 2016).

E) Optimized coordinates (at B3LYP-D2/6-31+G(d,p) level of theory)

Optimized coordinates of LL_0

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=====
7      -2.546617000    -0.238581000     0.758135000
6      -3.320806000    -1.509457000     0.487955000
6      -2.316762000    -2.643577000     0.251550000
8      -2.270194000    -3.593040000     1.034763000
1      -3.179152000     0.477421000     1.128533000
1      -2.176310000     0.129523000    -0.140246000
1      -1.737359000    -0.383562000     1.398607000
1      -3.856189000    -1.755489000     1.405773000
6      -4.305496000    -1.255155000    -0.668540000
6      -5.209488000    -0.081828000    -0.367412000
6      -6.362652000    -0.242027000     0.412628000
6      -4.870105000     1.209196000    -0.806834000
6      -7.162125000     0.852771000     0.744060000
6      -5.656424000     2.312700000    -0.479651000
6      -6.808753000     2.134808000     0.298156000
8      -7.541086000     3.245485000     0.583295000
1      -3.737377000    -1.071938000    -1.587520000
1      -4.880325000    -2.176186000    -0.811387000
1      -6.650243000    -1.233283000     0.755025000
1      -3.986298000     1.350854000    -1.424882000
1      -8.061502000     0.713358000     1.338910000
1      -5.402332000     3.308632000    -0.826749000
1      -8.331415000     3.017872000     1.091815000
7      -1.495028000    -2.507473000    -0.818165000
6      -0.318027000    -3.375809000    -0.988438000
6      0.744697000     -2.797530000    -0.036018000
8      1.600657000     -1.983127000    -0.401099000
1      -1.493819000    -1.644216000    -1.355484000
1      -0.605973000    -4.374641000    -0.650093000
6      0.127634000     -3.403546000    -2.442902000
1      1.030279000     -4.012466000    -2.544746000
1      0.356369000     -2.395904000    -2.799285000
1      -0.664275000    -3.833997000    -3.062496000
7      0.592670000     -3.161811000     1.259783000
6      1.317912000     -2.457724000     2.299293000
6      1.039311000     -0.950345000     2.239074000
8      -0.110610000    -0.498755000     2.121489000
1      -0.240591000    -3.686963000     1.508885000
1      2.391729000     -2.651258000     2.205773000
1      0.978577000     -2.833700000     3.268376000
7      2.123859000     -0.155846000     2.318188000
6      2.042911000     1.296310000     2.231088000
6      1.512071000     1.787220000     0.882881000
8      1.042275000     2.938798000     0.810164000
1      3.043535000     -0.578769000     2.251314000
1      1.309546000     1.649123000     2.961342000
6      3.417195000     1.939057000     2.549356000
6      4.529160000     1.389413000     1.686234000
6      5.358680000     0.364540000     2.167291000
6      4.712054000     1.847969000     0.373541000
6      6.346554000     -0.198932000     1.351510000
6      5.698590000     1.290042000    -0.441569000
6      6.515022000     0.262008000     0.043023000
1      3.301107000     3.018032000     2.410317000
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1	3.631370000	1.756972000	3.607609000
1	5.248841000	0.028213000	3.196685000
1	4.084866000	2.649433000	-0.006995000
1	6.988651000	-0.983121000	1.741354000
1	5.830784000	1.659930000	-1.452943000
1	7.285018000	-0.166815000	-0.590990000
7	1.562242000	0.964199000	-0.179288000
6	0.997922000	1.362225000	-1.477006000
6	-0.522140000	1.286650000	-1.288090000
8	-1.224594000	0.350998000	-1.668970000
1	1.832799000	-0.013429000	-0.080373000
1	1.268905000	2.408494000	-1.648707000
6	1.518908000	0.469894000	-2.596677000
6	3.044461000	0.540469000	-2.776845000
6	3.468341000	-0.462544000	-3.856405000
6	3.513952000	1.957231000	-3.131691000
1	1.227245000	-0.560252000	-2.380757000
1	1.023961000	0.771286000	-3.528126000
1	3.517283000	0.246571000	-1.831513000
1	4.557166000	-0.465839000	-3.977935000
1	3.021734000	-0.198698000	-4.824012000
1	3.148691000	-1.478050000	-3.594919000
1	3.337551000	2.667976000	-2.315759000
1	4.587313000	1.963200000	-3.349267000
1	2.991727000	2.323413000	-4.025169000
8	-1.072422000	2.252558000	-0.562323000
1	-0.359572000	2.807348000	-0.126486000

Optimized coordinates of LL_1

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7	2.030820000	-0.603588000	-0.828927000
6	3.056192000	-1.602494000	-0.361445000
6	2.338577000	-2.811083000	0.266709000
8	2.353949000	-3.906685000	-0.288201000
6	4.060686000	-0.897624000	0.570322000
6	4.676701000	0.310728000	-0.095595000
6	4.144864000	1.592258000	0.123314000
6	5.740363000	0.174709000	-0.997664000
6	4.655866000	2.710124000	-0.534021000
6	6.265109000	1.284576000	-1.661416000
6	5.721674000	2.556612000	-1.430651000
8	6.184086000	3.681420000	-2.042386000
1	1.569245000	-0.128779000	-0.031097000
1	2.468250000	0.134419000	-1.388408000
1	1.268848000	-1.049288000	-1.381501000
1	3.556373000	-1.975118000	-1.256533000
1	3.548230000	-0.598210000	1.491465000
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6	-0.530254000	-3.347545000	1.350276000
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1	1.207953000	-4.552392000	1.811896000
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1	0.370875000	-2.353595000	3.799450000
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6	-1.252820000	-2.262252000	-1.450038000
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Optimized coordinates of LL_2

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