Supporting Information

# Gas Phase Conformations of Selenocysteine and Related Ions: A Comprehensive Theoretical Study

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## Contents:

**Full citations for references 50:**

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**Table S1:** Hydrogen bond lengths ($d$), electron densities ($\rho_{CP}$) and potential energy ($V_{CP}$) at critical points, and bond energies ($E_{HB}$) for the Se–H···X and X–H···Se (X=O, N) in selected conformers of the selenocysteine and related ions

| Species | Type | $d$ (Å) | $\rho_{CP}$ | $V_{CP}$ (hartree) | $E_{HB}$ (kJ/mol) |
|---|---|---|---|---|---|
| **Neutral** | O–H···Se | 2.363 | 0.024 | -0.015 | -19.1 |
| | O–H···Se | 2.422 | 0.021 | -0.012 | -16.2 |
| | O–H···Se | 2.493 | 0.019 | -0.011 | -14.1 |
| | O–H···Se | 2.437 | 0.021 | -0.012 | -16.0 |
| | Se–H···O | 2.574 | 0.009 | -0.006 | -7.9 |
| | Se–H···O | 2.481 | 0.011 | -0.007 | -9.2 |
| | Se–H···O | 2.424 | 0.012 | -0.007 | -9.4 |
| | Se–H···O | 2.431 | 0.012 | -0.008 | -10.1 |
| **Deprotonated** | O–H···Se | 2.157 | 0.038 | -0.026 | -34.5 |
| | O–H···Se | 2.179 | 0.037 | -0.025 | -32.2 |
| | N–H···Se | 2.682 | 0.015 | -0.009 | -11.3 |
| | O–H···Se | 2.224 | 0.033 | -0.022 | -28.2 |
| | N–H···Se | 2.673 | 0.015 | -0.009 | -11.9 |
| | N–H···Se | 2.514 | 0.019 | -0.011 | -14.8 |
| | N–H···Se | 2.451 | 0.022 | -0.013 | -16.9 |
| | N–H···Se | 2.683 | 0.015 | -0.009 | -11.2 |
| | N–H···Se | 2.697 | 0.015 | -0.009 | -11.2 |
| | N–H···Se | 2.714 | 0.014 | -0.008 | -10.8 |
| | N–H···Se | 2.657 | 0.015 | -0.009 | -11.6 |
| | N–H···Se | 2.605 | 0.016 | -0.009 | -12.5 |
| | N–H···Se | 2.629 | 0.016 | -0.009 | -12.0 |
| | N–H···Se | 2.734 | 0.014 | -0.008 | -10.9 |
| | Se–H···N | 2.646 | 0.011 | -0.007 | -8.9 |
| | Se–H···O | 1.981 | 0.028 | -0.018 | -24.2 |
| | Se–H···N | 2.570 | 0.012 | -0.007 | -9.6 |
| **Protonated** | N–H···Se | 2.488 | 0.021 | -0.012 | -15.3 |
| | N–H···Se | 2.506 | 0.020 | -0.011 | -14.8 |
| | N–H···Se | 2.511 | 0.020 | -0.011 | -14.8 |
| | N–H···Se | 2.507 | 0.020 | -0.011 | -14.9 |
| | N–H···Se | 2.512 | 0.020 | -0.011 | -14.7 |
| | N–H···Se | 2.511 | 0.020 | -0.011 | -14.7 |
| | Se–H···O | 2.563 | 0.009 | -0.006 | -7.8 |
| | Se–H···O | 2.572 | 0.009 | -0.006 | -7.8 |
| | O–H···Se | 2.414 | 0.023 | -0.013 | -17.4 |
| | N–H···Se | 2.403 | 0.025 | -0.014 | -19.0 |
| | Se–H···O | 2.523 | 0.010 | -0.007 | -8.6 |
| | N–H···Se | 2.731 | 0.013 | -0.008 | -10.3 |
| | O–H···Se | 2.575 | 0.016 | -0.009 | -11.6 |

**Table S2:** First ionization energies (eV) of Se atom at different levels[a]

| State | BHandHLYP | B3LYP | MP2 | CCSD(T) | Experiment |
|---|---|---|---|---|---|
| $3d^{10}4s^24p^4$ | 0.00 | 0.00 | 0.00 | 0.00 | |
| $3d^{10}4s^24p^3$ | 9.67 | 9.85 | 9.23 | 9.38 | 9.75 |
| | | | (8.98) | (9.02) | |

[a] Electronic energies calculated at the 6–311++G(2df,2p) basis set. Data in parentheses obtained by the 6–311++G(d,p) basis set. Experimental data taken from http://www.webelements.com/selenium/atoms.html, and Kramida, A., Ralchenko, Yu., Reader, J., and NIST ASD Team (2013). NIST Atomic Spectra Database (ver. 5.1), National Institute of Standards and Technology, Gaithersburg, MD. Online available: http://physics.nist.gov/asd.

**Cartesian coordinates of representative selenocysteine conformers**

Optimized at BHandHLYP/6–311++G(d, p) level of theory

***Neutral:***

c1

| | | | |
|---|---|---|---|
| H | 2.437162 | 0.728387 | -1.080413 |
| O | 2.543346 | -0.220610 | -0.932635 |
| C | 1.719052 | -0.548876 | 0.045344 |
| O | 1.579508 | -1.666733 | 0.429974 |
| C | 0.990969 | 0.640176 | 0.680438 |
| C | -0.392162 | 0.236381 | 1.173444 |
| Se | -1.686924 | -0.130606 | -0.256752 |
| N | 1.050117 | 1.787018 | -0.208705 |
| H | 1.589927 | 0.877715 | 1.559593 |
| H | -0.328346 | -0.641011 | 1.799418 |
| H | -0.833854 | 1.043860 | 1.744955 |
| H | 0.264735 | 1.793557 | -0.841116 |
| H | 1.067597 | 2.657436 | 0.290388 |
| H | -1.082604 | -1.395819 | -0.656397 |

c2

| | | | |
|---|---|---|---|
| H | 2.318441 | -2.108289 | 0.079617 |
| O | 1.790359 | -1.483326 | 0.576246 |
| C | 1.754127 | -0.333284 | -0.107565 |
| O | 2.298967 | -0.193410 | -1.156584 |
| C | 0.991248 | 0.753352 | 0.635667 |
| C | -0.353466 | 0.261337 | 1.157639 |
| Se | -1.670035 | -0.189364 | -0.230837 |
| N | 0.846239 | 1.972403 | -0.111803 |
| H | 1.597267 | 0.963356 | 1.518738 |
| H | -0.237709 | -0.598866 | 1.798910 |
| H | -0.817278 | 1.061617 | 1.718529 |
| H | 1.736406 | 2.291315 | -0.452231 |
| H | 0.261673 | 1.817147 | -0.917072 |
| H | -1.067333 | -1.469291 | -0.587144 |

c4

| | | | |
|---|---|---|---|
| H | 2.403983 | 1.317040 | -0.748450 |
| O | 2.928728 | 0.509315 | -0.672465 |
| C | 2.232265 | -0.333717 | 0.073057 |
| O | 2.626284 | -1.413783 | 0.375995 |
| C | 0.845866 | 0.175693 | 0.478353 |
| C | -0.164279 | -0.530470 | -0.420964 |
| Se | -2.039706 | -0.077348 | -0.063501 |

| | | | |
|---|---|---|---|
| N | 0.784532 | 1.618322 | 0.316427 |
| H | 0.689616 | -0.151388 | 1.503255 |
| H | -0.012594 | -0.248165 | -1.457363 |
| H | -0.044638 | -1.600305 | -0.338272 |
| H | 1.131501 | 2.096167 | 1.130562 |
| H | -0.164083 | 1.922907 | 0.172840 |
| H | -2.068721 | -0.667973 | 1.270572 |

c5

| | | | |
|---|---|---|---|
| H | 3.122144 | -0.983188 | -1.014942 |
| O | 2.681246 | -0.175523 | -0.751779 |
| C | 1.700193 | -0.498109 | 0.094059 |
| O | 1.476260 | -1.625601 | 0.413515 |
| C | 0.970719 | 0.726016 | 0.632470 |
| C | -0.410221 | 0.350977 | 1.143227 |
| Se | -1.696812 | -0.153436 | -0.255600 |
| N | 0.913044 | 1.867743 | -0.247270 |
| H | 1.556655 | 1.016058 | 1.507486 |
| H | -0.358746 | -0.464864 | 1.847690 |
| H | -0.849703 | 1.213699 | 1.624956 |
| H | 1.827850 | 2.134662 | -0.563294 |
| H | 0.350078 | 1.662841 | -1.056121 |
| H | -1.172179 | -1.500899 | -0.436919 |

c6

| | | | |
|---|---|---|---|
| H | -3.317914 | -1.669228 | -0.151900 |
| O | -2.437045 | -1.414507 | -0.426997 |
| C | -2.214228 | -0.163136 | -0.018555 |
| O | -3.025817 | 0.478137 | 0.573763 |
| C | -0.814038 | 0.313709 | -0.375519 |
| C | 0.180946 | -0.408254 | 0.533893 |
| Se | 2.045737 | -0.163075 | -0.004297 |
| N | -0.667267 | 1.743209 | -0.268290 |
| H | -0.618869 | 0.010340 | -1.398776 |
| H | 0.067535 | -0.070309 | 1.557130 |
| H | 0.018010 | -1.477999 | 0.505552 |
| H | -1.097028 | 2.214131 | -1.044346 |
| H | -1.115759 | 2.080890 | 0.567378 |
| H | 1.966654 | 1.291311 | -0.023963 |

z1

| | | | |
|---|---|---|---|
| H | 0.225369 | -1.478667 | -0.152154 |
| O | 1.204405 | -1.589639 | -0.118446 |
| C | 1.807331 | -0.444755 | 0.049479 |

| | | | |
|---|---|---|---|
| O | 2.970206 | -0.274158 | -0.162181 |
| C | 0.975279 | 0.758064 | 0.534347 |
| H | 1.642630 | 1.329100 | 1.168854 |
| N | 0.693629 | 1.584629 | -0.683266 |
| H | 0.472279 | 2.541495 | -0.441489 |
| H | -0.198577 | 1.118750 | -1.068949 |
| H | 1.462429 | 1.575296 | -1.341651 |
| C | -0.357539 | 0.453540 | 1.198270 |
| H | -0.202073 | -0.286387 | 1.973094 |
| H | -0.742047 | 1.349871 | 1.673721 |
| Se | -1.631257 | -0.203900 | -0.161062 |

***Deprotonated***

ds1

| | | | |
|---|---|---|---|
| H | 0.172149 | -1.267895 | -0.456058 |
| O | 1.144154 | -1.461567 | -0.415296 |
| C | 1.810143 | -0.440566 | 0.082390 |
| O | 2.994811 | -0.515099 | 0.283089 |
| C | 1.051024 | 0.866489 | 0.332081 |
| C | -0.300598 | 0.697787 | 1.020954 |
| Se | -1.693314 | -0.212131 | -0.063515 |
| N | 0.891016 | 1.635162 | -0.896039 |
| H | 1.706977 | 1.426836 | 0.994379 |
| H | -0.162492 | 0.146148 | 1.945085 |
| H | -0.661600 | 1.688747 | 1.271891 |
| H | 1.709557 | 1.572672 | -1.476207 |
| H | 0.095849 | 1.270866 | -1.402189 |

ds2

| | | | |
|---|---|---|---|
| H | 0.173696 | -1.431699 | -0.064179 |
| O | -0.769198 | -1.740460 | 0.015431 |
| C | -1.606357 | -0.730645 | -0.012880 |
| O | -2.785744 | -0.897043 | 0.165165 |
| C | -1.033288 | 0.652171 | -0.346325 |
| C | 0.231918 | 1.011118 | 0.431284 |
| Se | 1.831487 | -0.052322 | -0.037803 |
| N | -2.040892 | 1.694314 | -0.183233 |
| H | -0.759205 | 0.601487 | -1.399320 |
| H | 0.443204 | 2.053291 | 0.224976 |
| H | 0.039097 | 0.915857 | 1.498068 |
| H | -2.948944 | 1.289955 | -0.347199 |
| H | -2.046244 | 1.994030 | 0.778336 |

ds3

| | | | |
|---|---|---|---|
| H | 0.224278 | -1.224760 | -0.587486 |
| O | 1.193308 | -1.407689 | -0.537828 |
| C | 1.834010 | -0.414496 | 0.049585 |
| O | 2.985957 | -0.523697 | 0.368087 |
| C | 1.047949 | 0.872448 | 0.287934 |
| C | -0.272034 | 0.649181 | 1.037344 |
| Se | -1.687753 | -0.229412 | -0.038695 |
| N | 0.902119 | 1.567141 | -0.989355 |
| H | 1.709698 | 1.469063 | 0.909317 |
| H | -0.087941 | 0.060682 | 1.931721 |
| H | -0.641344 | 1.620312 | 1.354728 |
| H | 0.089222 | 1.180994 | -1.452964 |
| H | 0.681206 | 2.532031 | -0.805458 |

db1

| | | | |
|---|---|---|---|
| O | 2.451358 | -1.503014 | 0.307437 |
| C | 2.293651 | -0.305008 | 0.046302 |
| O | 3.086278 | 0.509238 | -0.449401 |
| C | 0.867367 | 0.256431 | 0.385254 |
| C | -0.145025 | -0.534659 | -0.424757 |
| Se | -2.025345 | -0.115262 | 0.001485 |
| H | -1.848596 | 1.322406 | -0.166522 |
| N | 0.755659 | 1.687573 | 0.122773 |
| H | 0.691630 | 0.047844 | 1.437127 |
| H | -0.015107 | -0.350641 | -1.483721 |
| H | -0.030337 | -1.592097 | -0.230266 |
| H | 0.765500 | 2.197524 | 0.988026 |
| H | 1.611998 | 1.930475 | -0.359633 |

2d1

| | | | |
|---|---|---|---|
| O | -2.866979 | 0.527130 | 0.809091 |
| C | -2.310696 | -0.235080 | -0.008252 |
| O | -2.755873 | -1.303407 | -0.466176 |
| C | -0.885645 | 0.177003 | -0.480279 |
| C | 0.151605 | -0.504209 | 0.423356 |
| Se | 2.073764 | -0.108619 | 0.026897 |
| N | -0.770604 | 1.633556 | -0.501269 |
| H | -0.753644 | -0.206066 | -1.488418 |
| H | -0.031153 | -0.204779 | 1.451238 |
| H | 0.017775 | -1.577253 | 0.354576 |
| H | -1.298272 | 1.962626 | 0.293266 |
| H | 0.202767 | 1.867570 | -0.368549 |

***Protonated***

p1

| | | | |
|---|---|---|---|
| H | 2.538552 | -2.044578 | -0.186219 |
| O | 1.941830 | -1.521897 | 0.356314 |
| C | 1.825592 | -0.309154 | -0.119677 |
| O | 2.341235 | 0.121021 | -1.102997 |
| C | 0.950527 | 0.567125 | 0.767509 |
| H | 1.537627 | 0.814848 | 1.647630 |
| N | 0.740361 | 1.825382 | -0.010732 |
| H | 0.648476 | 2.646312 | 0.575623 |
| H | -0.117746 | 1.709282 | -0.567012 |
| H | 1.518664 | 1.941844 | -0.663461 |
| C | -0.375245 | -0.057185 | 1.191998 |
| H | -0.188218 | -1.035590 | 1.609108 |
| H | -0.845146 | 0.547014 | 1.958933 |
| Se | -1.704131 | -0.180447 | -0.246155 |
| H | -1.004051 | -1.219323 | -0.995721 |

p2

| | | | |
|---|---|---|---|
| H | 3.535301 | -1.504808 | 0.000538 |
| O | 2.649888 | -1.332048 | 0.332034 |
| C | 2.251207 | -0.133494 | -0.006872 |
| O | 2.861718 | 0.674645 | -0.632870 |
| C | 0.831800 | 0.135692 | 0.467519 |
| H | 0.736959 | -0.091822 | 1.521869 |
| N | 0.608256 | 1.602413 | 0.291368 |
| H | -0.401248 | 1.771522 | 0.216216 |
| H | 1.096403 | 1.917721 | -0.547886 |
| H | 0.977768 | 2.143141 | 1.065798 |
| C | -0.186247 | -0.665982 | -0.345254 |
| H | -0.009347 | -0.549118 | -1.409316 |
| H | -0.080164 | -1.713572 | -0.103566 |
| Se | -2.043152 | -0.099430 | -0.070000 |
| H | -2.119725 | -0.567408 | 1.311094 |

p3

| | | | |
|---|---|---|---|
| H | 2.467827 | -2.079601 | -0.187106 |
| O | 1.886817 | -1.539646 | 0.355709 |
| C | 1.812828 | -0.321837 | -0.113836 |
| O | 2.354732 | 0.101278 | -1.085910 |
| C | 0.951048 | 0.576910 | 0.767118 |
| H | 1.547310 | 0.826870 | 1.640316 |
| N | 0.758237 | 1.826585 | -0.027683 |
| H | 0.658932 | 2.654667 | 0.547076 |
| H | -0.089817 | 1.704209 | -0.597147 |

| | | | |
|---|---|---|---|
| H | 1.547879 | 1.931653 | -0.668897 |
| C | -0.379726 | -0.021980 | 1.209566 |
| H | -0.191129 | -0.993400 | 1.642532 |
| H | -0.844297 | 0.598840 | 1.963203 |
| Se | -1.647187 | -0.235542 | -0.286335 |
| H | -2.637292 | 0.687493 | 0.253709 |