

Theoretical Study of the Helio Hydrogen Cyanide Dication HeCNH^{2+}

Journal:	<i>Molecular Physics</i>
Manuscript ID:	TMPH-2009-0203
Manuscript Type:	Full Paper
Date Submitted by the Author:	06-Jul-2009
Complete List of Authors:	Wilson, Stephen; Oxford University, PTCL; Comenius University, Chemical Physics Hubac, Ivan; Comenius University, Chemical Physics Mach, Pavol; Comenius University, Chemical Physics Uhlár, Milan; Opava University, Institute of Physics
Keywords:	helio hydrogen cyanide, HeCNH ^{2} , inert gas molecules, interstellar molecules, MP2, CCSD, CCSD(T), CASSCF, CASPT2
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RESEARCH ARTICLE

Theoretical Study of the Helio Hydrogen Cyanide Dication
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(21 June 2009)

The structure and stability of the helio hydrogen cyanide molecular ion, HeCNH^{2+} , is investigated by standard quantum chemical methods. Single reference calculations are carried out using second order perturbation theory (MP2), the coupled cluster expansion in the CCSD approximation, and the hybrid approach using a perturbative estimate of the triple excitation energy component designated CCSD(T). Multireference calculations using a complete active space (CASSCF) and a second order perturbation theory estimate of correlation effects (CASPT2) are reported.

Keywords: helio hydrogen cyanide, HeCNH^{2+} , inert gas molecules, interstellar molecules, MP2, CCSD, CCSD(T), CASSCF, CASPT2

1. Introduction

Of the various techniques available for the study of matter on a molecular scale, computational quantum chemistry has particular strengths and weakness. In principle, *ab initio* quantum chemical methods can be applied to any grouping of atoms irrespective of whether they form a stable molecule or not. This has been found invaluable, for example, in the study of interstellar radicals and ions particularly in cases where the species under investigation are not stable in the terrestrial laboratory[12]¹.

Radicals, such as the cyanoethynyl and the butadiynyl radicals[7], and ions, such as the thioformyl ion[8], have been identified in interstellar environments[9–11] on the basis of *ab initio* quantum chemical calculations prior to their observation on Earth. The principle weakness of *ab initio* quantum chemical methods is the rapid increase in the complexity of the associated computations with the number of atoms and/or number of electrons in the system under study. The most abundant elements in the universe are those of the light atoms hydrogen, helium, carbon, nitrogen and oxygen. Contemporary non-relativistic quantum chemical methods can support accurate calculations on small molecular systems containing these light atoms. Helium is the second most abundant element in the universe and this led Wilson and Green[12] to suggest that, in spite of it being the most inert of the

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¹See, for example, [2–6] for recent reviews on the subject of molecules in space.

1 inert gases, helium-containing ions could have sufficient stability to be observed
2 in the interstellar medium. In particular, these authors suggested the HeCN^+ ion
3 as a candidate since the cyano-group ensures that the system has a large dipole
4 moment to enhance detection by radio-astronomy. Although the HeCN^+ ion has
5 not been found in space, it has nevertheless emerged from subsequent studies that
6 simple ions containing helium have a rich chemistry (see, for example, the recent
7 review by Grandinetti[13]).

8
9 The structure and stability of helium-containing polyatomic cations have been
10 investigated by a number of authors [12, 14–20]. In a paper published in 1999,
11 Olah et al[19] found the helionitronium trication, HeNO_2^{3+} , to be unusually stable.
12 These authors drew this conclusion from second order many-body perturbation
13 theory calculations. However, subsequent work by Eisfeld and Franciso[20] using
14 multireference configuration interaction demonstrated that the wave function for
15 this systems may have “extreme multireference character”.

16
17 In this paper, an *ab initio* quantum chemical study of the structure and stability
18 of the ground state of the HeCNH^{2+} ion is presented. The previous work summa-
19 rized above points to the need for a thorough description of electron correlation
20 effects including the use a multireference formalism. It is well known that when
21 truncated, as it must be in practical applications, multireference configuration in-
22 teraction suffers from non-linear scaling with particle number (*i.e.* lack of extensiv-
23 ity). Although an *a posteriori* correction of the type suggested by Davidson[21–25]
24 for the single reference case can be applied, this is only approximate. On the other
25 hand, multireference many-body methods (*i.e.* perturbation theory and cluster ex-
26 pansions) are plagued by the ‘intruder state problem’ which can impair or even
27 destroy convergence. Furthermore, it should be emphasised that, for novel species
28 such as the ion under investigation here, the algebraic approximation must be im-
29 plemented in a sequence of basis sets in order to explore the basis sets dependence
30 of the electron correlation calculations and to estimate the complete basis set limit.

31
32 Most contemporary applications of quantum mechanics to the molecular elec-
33 tronic structure problem use what is termed the ‘theoretical model chemistry’ ap-
34 proach championed by Pople and his coworkers[26]. A composite theoretical model
35 chemistry involves a series of compromises[28, 29], based on the methods and basis
36 sets employed and dictated by the computing resources available. Systematic com-
37 parison of the results supported by a given model with corresponding data derived
38 from experiment may give that model a predictive capability in situations where
39 experiment is difficult or impossible, or simply too expensive. However, when quan-
40 tum chemical methods are used to study novel systems such as that investigated
41 here the highest level of theory and basis which is feasible for a system of this size
42 should be employed.

43
44 HeCNH^{2+} is a 14-electron system which is isoelectronic with the well charac-
45 terised HCN molecule. The carbon and nitrogen atoms each have a $1s^2$ core leaving
46 a total of 10 ‘valence’ electrons. Of all the elements helium has the highest ionization
47 potential (24.587 eV) and the lowest polarizability (0.205 \AA^{-3}) [30] and forms very
48 few neutral molecular species. Although helium will form clusters He_n , $n \geq 2$, [31]
49 only a few neutral partners, such as Hg[32, 33] or endohedral C_{60} complexes[34, 35]
50 are able to fix helium. A few compounds such as OBeHe[36] and RNBHe[37] have
51 been predicted to be stable in theoretical studies. Grandinetti[13] observes that for
52 cationic binding partners “*the capability of fixing helium dramatically increases,*
53 *and numerous singly- and multiply-charged cations containing one or more helium*
54 *atoms have been experimentally or theoretically investigated”.*

2. Methodology

Calculations were performed for the ground state of the HeCNH^{2+} cation using ‘standard’ *ab initio* quantum chemical methods. Specifically, we employed (i) single reference second order many-body perturbation theory in its Møller-Plesset form, MP2; (ii) the coupled cluster expansion including single and double excitations from a single reference function, CCSD; (iii) CCSD with a perturbative estimate of the triple excitation energy component, CCSD(T); (iv) multiconfiguration self-consistent field theory in the complete active space self-consistent field form, CASSCF; (v) second order perturbation theory based on a CASSCF reference function, CASPT2.

The algebraic approximation[38, 39] was realized using the correlation consistent basis sets developed by Dunning and his coworkers[46]. Specifically, we employed a polarized valence basis set of ‘quadruple zeta’ quality designated *cc-pVQZ*. The molecular basis set contains a total of 201 primitive Gaussian-type functions which are contracted to give a set of 170 contracted Gaussian-type functions. The basis sets were taken from the MOLCAS library and the GAUSSIAN and can be found on the EMSL Basis Set Library at <https://bse.pnl.gov/bse/portal>.

The MP2, CCSD, CCSD(T), CASSCF and CASPT2 calculations were carried out using the MOLCAS 7.2 program package[41]. Geometry optimizations for the CCSD(T) model were performed with the GAUSSIAN03 program package[43]. The MOLMOL 4.6 package[42] was used to visualize the results.

Single reference self-consistent field calculations gave the following ground state configurations

$$\begin{aligned} \text{linear: } & 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 \\ \text{non-linear: } & 1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 6a'^2 1a''^2 \\ C_s \text{ symmetry: } & 1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 6a'^2 1a''^2 \end{aligned}$$

Geometry optimization was carried out for the MP2 model and the optimized geometries thus obtained were employed in CCSD and CCSD(T) calculations the results of which were labelled CCSD/MP2 and CCSD(T)/MP2, respectively. Geometry optimization was also carried out for the CCSD(T) model.

The multireference calculations employed a complete active space of 12 orbitals to describe the 10 valence electrons, designated CASSCF(10e/12o). For the linear geometry, the active space was constructed from three bonding orbitals of σ symmetry and two bonding orbitals of π symmetry together with two non-bonding orbitals of π symmetry and five non-bonding orbitals of σ symmetry. Geometry optimization was carried out both for the CASSCF model and for the CASPT2 model.

For both the single reference and multireference cases, the potential energy surfaces were explored and stationary points identified and characterized as a global minimum, local minima and transition states.

The dissociation of the structures determined in this way into fragments of the type $\text{AB}^+ + \text{CD}^+$ was studied by performing calculations for the supersystem $\text{AB}^+ \dots \text{CD}^+$ with the distance between the two fragments set to a large value (9000 Å). Other coordinates were optimized using 15 active orbitals to describe the 10 valence electrons in the CASSCF model. Then a second order perturbation theory calculations using the geometry so determined was carried out using the CASPT2 method.

3. Results

A summary of the results of the quantum chemical calculations employing single reference models is collected in Table 1. Total electronic energies, correlation energies and structural parameters, *i.e.* bond lengths, bond angles and dihedral angles, are presented for the MP2, CCSD and CCSD(T) models. The MP2 model was used to explore the potential energy surface and a total of seven stationary points were identified. In addition to a global minimum, three local minima were found as well as three transition states. The geometries corresponding to these stationary points are shown in Figure 1. The global minimum corresponds to the linear structure HeCNH^{2+} shown in Figure 1(a) and labelled *L*. One of the local minima in the potential energy surface is associated with the non-linear structure HeNCH^{2+} in Figure 1(b) and labelled *N* and the other two local minima correspond to trigonal pyramidal configurations, labelled *T1* and *T2*, and shown in Figure 1(c) and (d) with the formulae $\text{NC}(\text{He})\text{H}^{2+}$ and $\text{CN}(\text{He})\text{H}^{2+}$, respectively. The three transition states corresponding to the formulae $\text{NC}(\text{He})\text{H}^{2+}$, $\text{NC}(\text{He})\text{H}^{2+}$ and $\text{NC}(\text{He})\text{H}^{2+}$, respectively, are displayed in Figure 1(e), (f) and (g). The energies for the CCSD and CCSD(T) models presented in Table 1 were calculated at the geometries determined by using the MP2 model and are labelled $E_{\text{CCSD}/\text{MP2}}$ and $E_{\text{CCSD(T)}/\text{MP2}}$. Energies obtained by optimizing the geometries for the CCSD(T) model are labelled $E_{\text{CCSD(T)}}$. The *t1* diagnostic suggested by Lee *et al*[44, 45] was used in the CCSD(T) calculations to determine whether a single reference wave function is adequate for each of the geometries examined. For the CCSD(T) calculations in which the geometry was optimized within that model, the *t1* diagnostic took the values 0.0138 and 0.0352 for the *L* and *N* structures, respectively. For the *T1* and *T2* geometries, the *t1* diagnostic was 0.0261 and 0.0267, respectively, whilst for the transition states *TS1*, *TS2*, *TS3*, the values recorded were 0.0226, 0.0835 and 0.0322. It can be seen that of the different structures studied, the *L* is best described by the CCSD(T). Reasonably low values of the *t1* diagnostic (≤ 0.03) were measured for both of the trigonal pyramidal structures and the transition state *TS1*. However, for the non-linear geometry and the *TS2* and *TS3* transition states substantial multireference character is indicated. For these geometries, the single reference coupled cluster theory CCSD(T) is not as reliable as it is for the other structures.

The results of the quantum chemical calculations employing multi-reference models are summarized in Table 2.

In Table 3, the calculated total energies, in kJ mol^{-1} , associated with the structures displayed in Figure 1 are shown relative to the most stable structure, the linear configuration *L*. In this Table it can be seen that the linear structure *L* HeCNH^{2+} is the most stable with other structures having energies lying $\sim 200 \text{ kJ mol}^{-1}$ or more above. Of the five different models employed in the present study, the largest differences in the calculated total energies occur for the MP2 model. For some of the structures studied the difference between the energies supported by the CCSD and CASPT2 models is quite large. For these structures some of cluster amplitudes were found to be larger than ~ 0.1 .

Three transition states were identified on the potential energy surface which correspond to the migration of the H or He atom from CN to NC. These transition states lie between the local minima and the global minimum.

Dissociation energies corresponding to the following decay schemes were calcu-

Table 1. Total electronic energies^a, correlation energies^a and geometries^b obtained from calculations using a single reference function. Geometries were optimized for the MP2 model giving the energy E_{MP2} . $E_{CCSD(T)/MP2}$ and $E_{CCSD(T)}$ were evaluated at the geometry corresponding to E_{MP2} . Geometries were also optimized for the CCSD(T) model and the energies labelled $E_{CCSD(T)}$.

Structure	E_{MP2}	$E_{CCSD(T)/MP2}$	$E_{CCSD(T)}$	r_{MP2}	$r_{CCSD(T)}$	θ_{MP2}	$\theta_{CCSD(T)}$
Linear L	-94.929 100 4	-94.933 178 9	-94.951 581 2	HN	1.0683	1.0688	180.0
HeCNH ²⁺	-0.374 909 6	-0.378 988 2	-0.395 718 4	CN	1.1406	1.1329	180.0
Non-linear N	-94.833 730 0	-94.852 993 6	-94.873 311 5	HeC	1.0826	1.0893	
HeNCH ²⁺	-0.341 368 0	-0.360 611 3	-0.379 129 1	HC	1.1308	1.1372	132.9
				CN	1.1890	1.2171	163.9
				HeN	1.0149	1.0584	
Trigonal pyramidal $T1$	-94.806 296 8	-94.843 175 5	-94.858 074 5	CH	1.1374	1.1414	109.5
NC(HeH) ²⁺	-0.310 066 6	-0.346 970 7	-0.361 742 8	CN	1.2961	1.3030	134.1
				CHe	1.1758	1.1910	135.3
Trigonal pyramidal $T2$	-94.781 591 0	-94.819 817 8	-94.833 987 6	HN	1.0791	1.0797	110.5
CN(HeH) ²⁺	-0.306 753 7	-0.344 980 8	-0.359 150 6	CN	1.3773	1.3872	140.9
				HeN	1.1011	1.1449	141.3
Transition state $TS1$	-94.791 823 2	-94.828 459 4	-94.843 144 7	NC	1.3091	1.3159	68.8
NC(He)H ²⁺	-0.306 670 5	-0.342 673 8	-0.357 359 0	CHe	1.5633	1.6119	173.9
				CH	1.1468	1.1498	174.5
Transition state $TS2$	-94.753 289 7	-94.769 455 2	-94.803 642 1	CN	1.2290	1.2178	147.0
CN(H)He ²⁺	-0.398 312 4	-0.414 930 1	-0.449 116 9	NHe	1.3700	2.6062	80.0
				NH	1.5766	1.3316	
Transition state $TS3$	-94.800 658 8	-94.830 741 9	-94.845 563 3	CN	1.2324	1.2172	137.2
CN(H)He ²⁺	-0.328 456 2	-0.359 869 4	-0.377 430 7	CH	1.2096	1.1384	97.0
				CHe	1.1195	1.2874	79.1

^aTotal electronic energies are in hartree.

^bBond lengths are in Ångstrom. Bond angles are in degrees.

Table 2. Total electronic energies^a and geometries^b obtained from calculations using a multi-reference function. Geometries were optimized for the CASSCF model giving the energy E_{CASSCF} . Geometries were also optimized for the E_{CASPT2} model giving the energy E_{CASPT2} .

Structure	E_{CASSCF}	E_{CASPT2}	r_{CASSCF}	r_{CASPT2}	θ_{CASSCF}	θ_{CASPT2}
Linear L HeCNH ²⁺	-94.772 333 1	-94.936 320 2	NH	1.0701	1.0665	CNH 180.0 180.0
			CN	1.1360	1.1337	HeCN 180.0 180.0
			HeC	1.0989	1.0889	
Non-linear N HeNCH ²⁺	-94.692 917 2	-94.855 380 7	HC	1.1422	1.1366	HeNC 121.0 121.1
			CN	1.2209	1.2189	HCN 160.1 160.4
			HeN	1.0772	1.0606	
Trigonal pyramidal $T1$ NC(HeH) ²⁺	-94.685 050 9	-94.839 481 6	CH	1.1438	1.1422	NCHe 108.1 110.7
			CN	1.3113	1.3014	NCH 137.8 133.7
			CHe	1.2219	1.1843	
Trigonal pyramidal $T2$ CN(HeH) ²⁺	-94.652 972 6	-94.814 495 5	HN	1.0870	1.0811	CNHe 110.0 113.9
			CN	1.3891	1.3855	NCH 143.4 139.4
			HeN	1.1957	1.1714	
$TS1$ NC(He)H ²⁺	-94.672 397 6	-94.824 445 9	NC	1.3261	1.3163	NCHe 67.9 70.0
			CHe	1.6943	1.6044	NCH 174.9 174.2
			CH	1.1551	1.1503	
$TS2$ CN(H)He ²⁺	-94.672 397 6	-94.791 784 9	CN	1.2251	1.2202	CNHe 137.5 141.4
			NHe	1.5910	1.5247	NCH 84.8 78.7
			NH	1.7186	1.6234	
$TS3$ CN(H)He ²⁺	-94.666 157 6	-94.829 405 0	CN	1.2198	1.2202	NCHe 153.2 150.8
			CH	1.3123	1.2821	NCH 75.3 80.2
			CHe	1.1551	1.1392	

^aTotal electronic energies are in hartree.

^bBond lengths are in Ångstrom. Bond angles are in degrees.

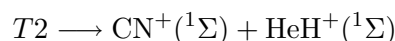
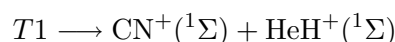
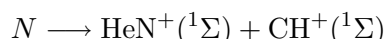
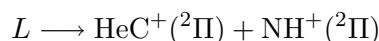
Table 3. Calculated total energies, in kJ mol^{-1} , associated with the structures shown in Figure 1 relative to the most stable structure, the linear configuration L .

Energy	MP2	CCSD/MP2	CCSD(T)/MP2	CCSD(T)	CASSCF	CASPT2
$E(L)$	0.0	0.0	0.0	0.0	0.0	0.0
$E(N)$	250.4	210.5	210.2	205.9	208.5	212.5
$E(T1)$	322.4	236.3	245.8	246.0	229.2	254.2
$E(T2)$	387.2	297.6	308.7	307.5	313.4	319.9
$E(TS1)$	360.4	274.9	284.7	284.8	262.4	293.7
$E(TS2)$	461.6	429.9	388.4	378.9	363.0	379.5
$E(TS3)$	337.2	268.9	271.2	278.8	278.8	280.7

Table 4. Reaction paths between the non-linear structure N and the trigonal pyramidal structures $T1$ and $T2$. There are three transition states, $TS1$, $TS2$ and $TS3$, which correspond to the migration of the H or He atom from CN to NC. Energies are given in kJ mol^{-1} .

Path	MP2	CCSD/MP2	CCSD(T)/MP2	CCSD(T)	CASSCF	CASPT2
$N \rightarrow TS1$	110.0	64.4	74.5	78.8	53.9	81.2
$N \rightarrow TS2$	211.2	219.4	178.2	173.0	154.5	167.0
$L \rightarrow TS3$	337.2	268.9	271.2	278.8	278.8	280.7
$TS1 \rightarrow T1$	-38.0	-38.6	-38.9	-38.8	-33.2	-39.5
$TS2 \rightarrow T2$	-74.4	-132.3	-79.7	-71.5	-49.6	-60.0
$TS3 \rightarrow T1$	-14.8	-32.6	-25.4	-32.8	-49.5	-26.5

lated:



For these calculations the CASSCF and CASPT2 models were employed. Three additional orbitals were included in the active space. The results of these calculations

Table 5. Dissociation energies given by the CASSCF(10e/15o) and CASPT2(10e/15o) models. Energies are given in kJ mol^{-1} .

Path	CASSCF	CASPT2
<i>L</i>	-15.3	36.4
<i>N</i>	192.8	162.9
<i>T1</i>	-544.5	-544.7
<i>T2</i>	-628.7	-610.3

are given in Table 5. It can be seen that the decay channels in which the *T1* or *T2* structure decays into two diatomic cations, CN^+ and HeH^+ are strongly exothermic.

4. Conclusions

We have investigated the structure and stability of the helio hydrogen cyanide dication using standard *ab initio* quantum chemical methods. Both single reference and double reference models were employed together with a correlation consistent basis set of ‘quadruple zeta’ quality. The global minimum in the potential energy surface corresponds to the linear structure HeCNH^{2+} . Three local minima were identified as well as three transition states

Acknowledgement(s)

The support of the Grant Agency of the Czech Republic under project number MSM 4781305903 is acknowledged. MU acknowledges the help of Professor Ivan Cernusak (Comenius University) with his initial CAS calculations.

References

- [12] S. Wilson, Chem. Rev. **80**, 263 (1980)
- [2] E.F. van Dishoeck, Molecules in Astrophysics: Probes and Processes, Kluwer Academic Publishers (1997)
- [3] T.W. Hartquist and D.A. Williams, eds., The Molecular Astrophysics of Stars and Galaxies, Clarendon Press, Oxford (1998)
- [4] J. Tennyson, in Handbook of Molecular Physics and Quantum Chemistry, volume 3, Molecules in Different Environments, ed: S. Wilson, P.F. Bernath and R. McWeeny, chapter ??, John Wiley, Chichester (2003)
- [5] J. Tennyson, Astronomical Spectroscopy: An Introduction to the Atomic and Molecular Physics of Astronomical Spectra Imperial College Press (2005)
- [6] T.W. Hartquist and D.A. Williams, The Chemically Controlled Cosmos: Astronomical Molecules from the Big Bang to Exploding Stars Cambridge University Press (2008)
- [7] S. Wilson and S. Green, Astrophys. J. **212**, L87, (1977)
- [8] S. Wilson, Astrophys. J. **220**, 739 (1978)
- [9] M. Guélin, and P. Thaddeus, Astrophys. J. **212**, L81 (1977)
- [10] M. Guélin, S. Green, and P. Thaddeus, Astrophys. J. **224**, L27 (1978)
- [11] P. Thaddeus, M. Guélin and R.A. Linke, Astrophys. J. **246**, L41 (1981)
- [12] S. Wilson and S. Green, J. Chem. Phys. **73**, 419 (1980)
- [13] F. Grandinetti, Intern. J. Mass Spectrometry **237**, 243 (2004)
- [14] D.L. Cooper and S. Wilson, Molec. Phys. **41**, 161 (1981)
- [15] P. V. R. Schleyer, Adv. Mass. Spectrom. 287 (1985)
- [16] W. Koch and G. Frenking, J. Chem. Soc. Chem. Commun. 1095 (1986)
- [17] M.W. Wong, R.H. Nobes and L. Radom, J. Chem. Soc. Chem. Commun. 233 (1987)
- [18] G. Frenking and D. Cremer, Struct. Bonding (Berlin) **73**, 17 (1990)
- [19] G.A. Olah, G.K.S. Prakash and G. Rasul, Proc. Natl. Acad. Sci. USA **96**, 3493 (1999)
- [20] W. Eisfeld and J.S. Francisco, Proc. Natl. Acad. Sci. USA **99**, 15303 (2002)
- [21] E.R. Davidson, Intern. J. Quantum Chem. **8**, 61 (1974)
- [22] L. Meissner, Chem. Phys. Lett. **146**, 204 (1988)
- [23] A. Meunier and B. Levy, Intern. J. Quantum Chem. **16**, 955 (1979)

- 1 [24] J. Karwowski and I. Shavitt, in Handbook of Molecular Physics and Quantum Chemistry, volume 2,
2 Molecular Electronic Structure, ed: S. Wilson, P.F. Bernath and R. McWeeny, chapter 18, John Wiley,
3 Chichester (2003)
- 4 [25] S. Wilson, Electron correlation in molecules, Dover, New York (2007)
- 5 [26] J.A. Pople, Rev. Mod. Phys. **71**, 1267 (1999)
- 6 [27] W.J. Hehre, L. Radom, P. von Schleyer, J.A. Pople: *Ab initio Molecular Orbital Theory*, John Wiley,
7 Chichester (1986)
- 8 [28] L.A. Curtiss, K. Raghavachari, P.C. Redfern, V. Rassolov, J.A. Pople, J. Chem. Phys. **109**, 7764 (1998)
- 9 [29] L.A. Curtiss, P.C. Redfern, K. Raghavachari, V. Rassolov, J.A. Pople, J. Chem. Phys. **110**, 4703 (1999)
- 10 [30] D.R. Lide (ed.), CRC Handbook of Chemistry and Physics, 74th edition, CRC Press, Boca Raton
11 (1993)
- 12 [31] J.P. Toennies and A.F. Vilesov, Angew. Chem. Int. Ed. **43** 2662 (2004)
- 13 [32] J.J. Manley, Nature **115**, 337 (1925)
- 14 [33] R. Heller, J. Chem. Phys. **9**, 154 (1941)
- 15 [34] T. Weiske and H. Schwarz, Angew. Chem. Int. Ed. **31** 183 (1992)
- 16 [35] M. Saunders, H.A. Jiménez-Vázquez, R.J. Cross and R.J. Poreda, Science **259**, 1428 (1993)
- 17 [36] G. Frenking, W. Koch, J. Gauss and D. Cremer, J. Am. Chem. Soc. **110**, 8007 (1988)
- 18 [37] P. Antonioti, N. Bronzolino and F. Grandinetti, J. Phys. Chem. A **107**, 2974 (2003)
- 19 [38] S. Wilson, Adv. Chem. Phys. (1987)
- 20 [39] S. Wilson, in Handbook of Molecular Physics and Quantum Chemistry, volume 2, Molecular Electronic
21 Structure, ed: S. Wilson, P.F. Bernath and R. McWeeny, chapter 28, John Wiley, Chichester (2003)
- 22 [40] P.P. Bera, K.W. Sattelmeyer, M. Saunders, H.F. Schaefer, and P.R. Schleyer, "Mindless Chemistry",
23 J. Phys. Chem. A **110**, 4287 (2006)
- 24 [41] G. Karlström, R. Lindh, P.-A. Malmqvist, B. O. Roos, U. Ryde, V. Veryazov, P.-O. Widmark, M.
25 Cossi, B. Schimmelpfennig, P. Neogrady, L. Seijo, Computational Material Science, **28**, 222 (2003)
- 26 [42] <http://www.cmbi.ru.nl/molden/molden.html>
- 27 [43] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery,
28 Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci,
29 M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R.
30 Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E.
31 Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann,
32 O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth,
33 P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas,
34 D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S.
35 Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin,
36 D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B.
37 Johnson, W. Chen, M.W. Wong, C. Gonzalez, and J.A. Pople, GAUSSIAN 03, Gaussian, Inc., Wallingford
38 CT, 2004.
- 39 [44] T.J. Lee, J.E. Rice, G.E. Scuseria and H.F. Schaefer, Theor. Chim. Acta **75**, 81 (1989)
- 40 [45] T.J. Lee and P.R. Taylor, Int. J. Quantum Chem. **23**, 199 (1989)
- 41 [46] T.H. Dunning, Jr. J. Chem. Phys. **90**, 1007 (1989)
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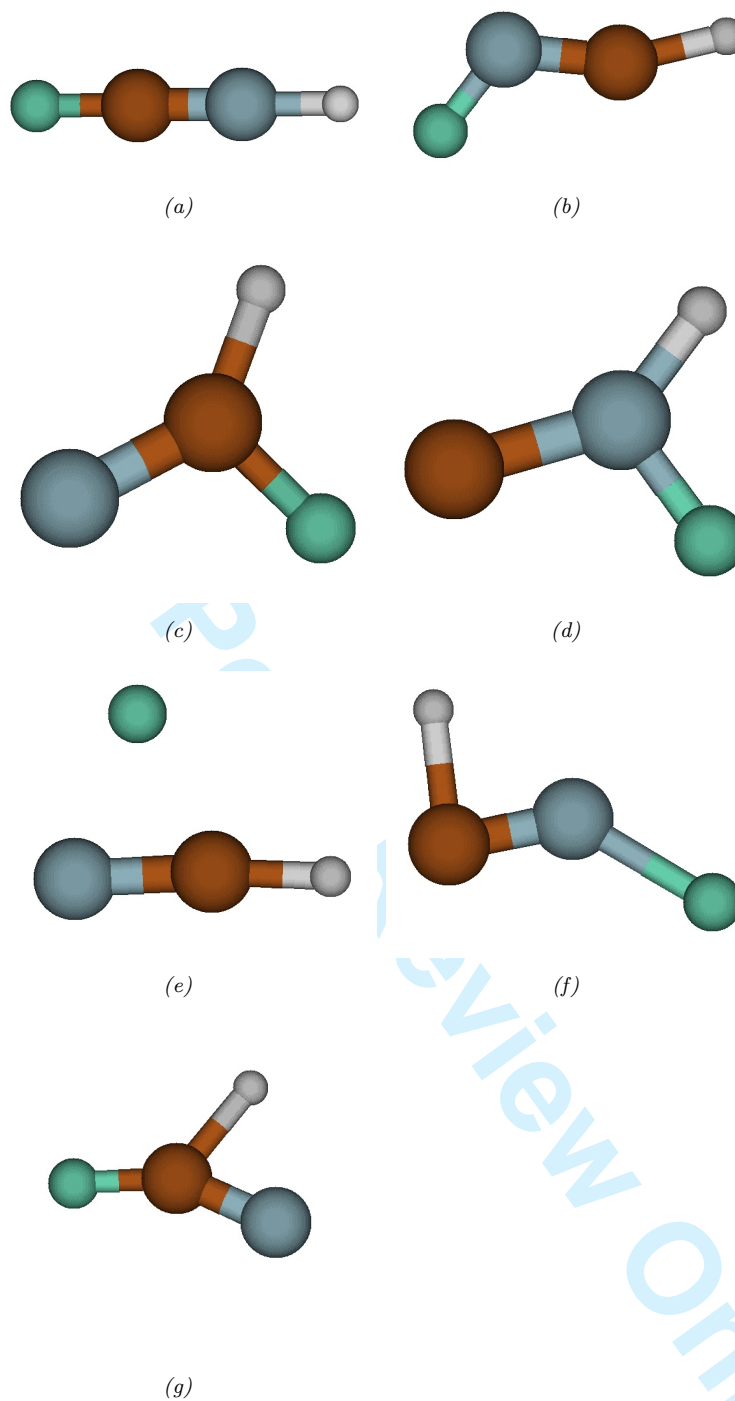


Figure 1. Geometries of stationary points on the potential energy surface of the HeCNH²⁺ dication: (a) linear *L*: HeCNH²⁺; (b) non-linear *N*: HeNCH²⁺; (c) trigonal pyramidal *T1*: NCHeH²⁺; (d) trigonal pyramidal *T2*: CNHeH²⁺; (e) transition state *TS1*: (HCN...He)²⁺; (f) transition state *TS2*: HCNHe²⁺; (g) transition state *TS3*: HCNHe²⁺.

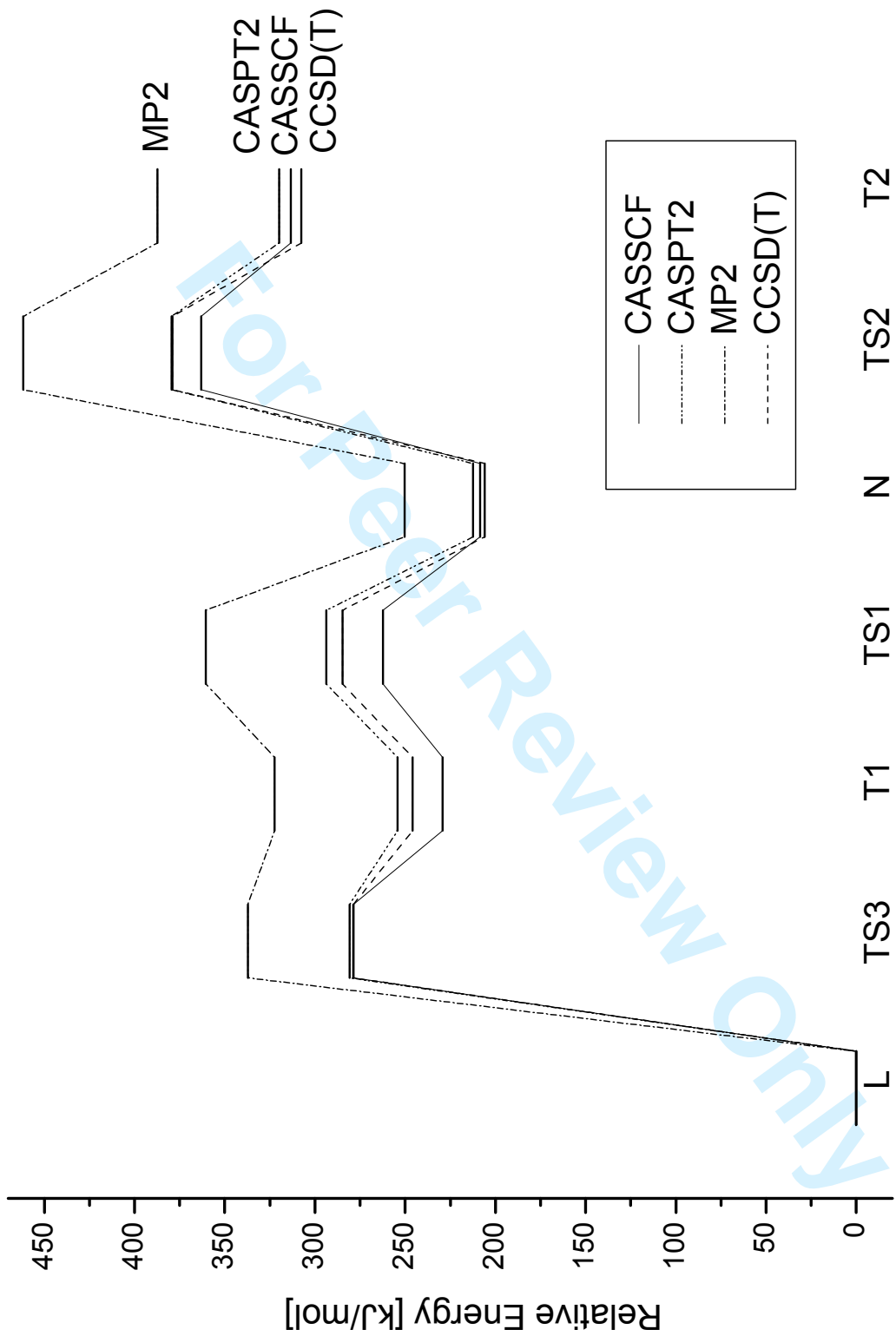
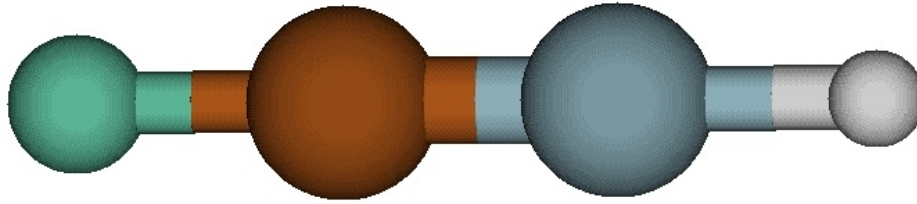


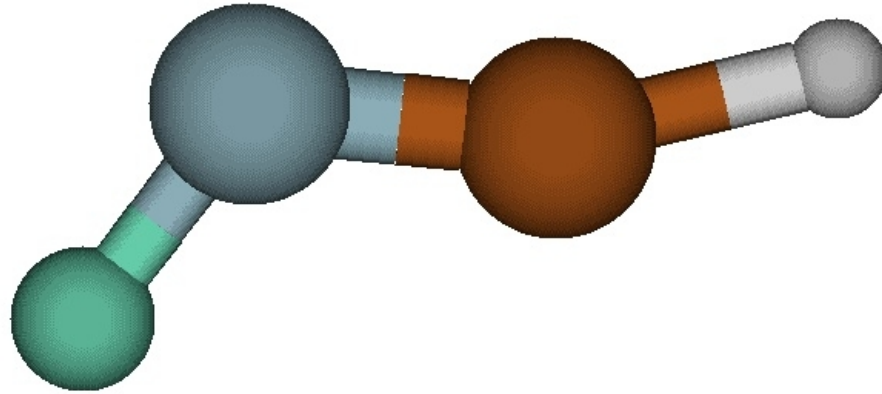
Figure 2. Reaction path connecting the minima and transition structures shown in Figure 1. Energies are given in kJ mol^{-1} .

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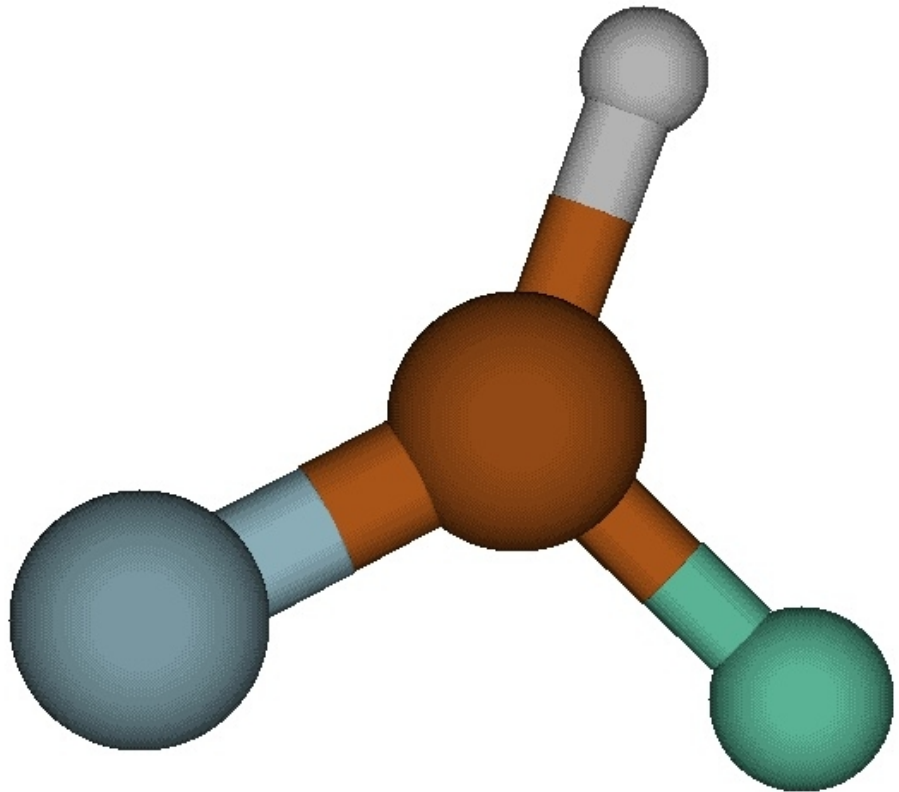
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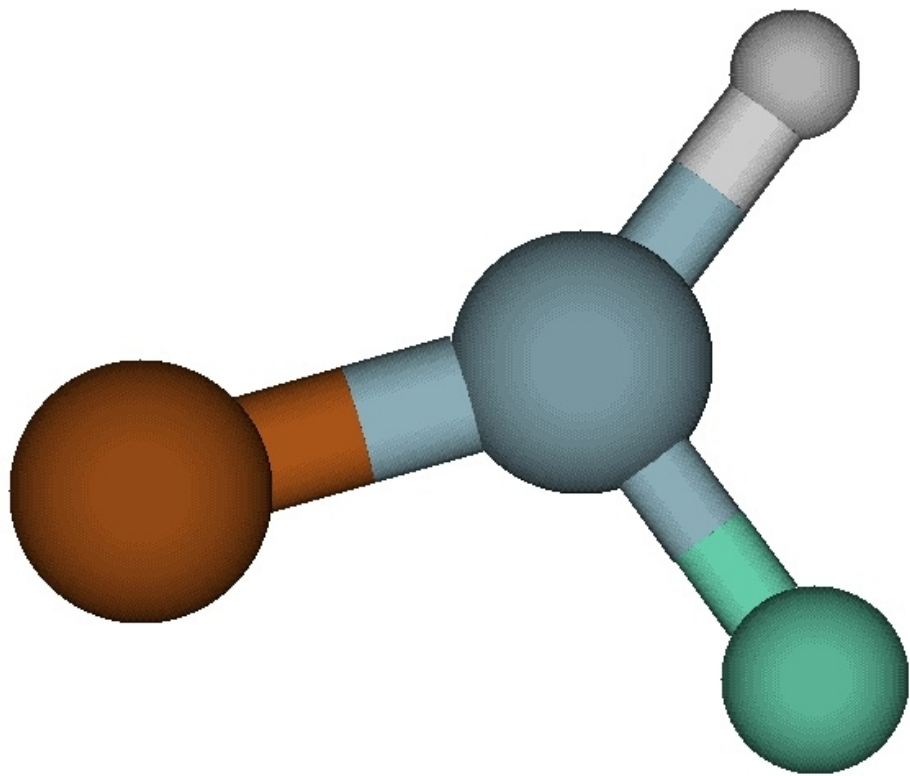
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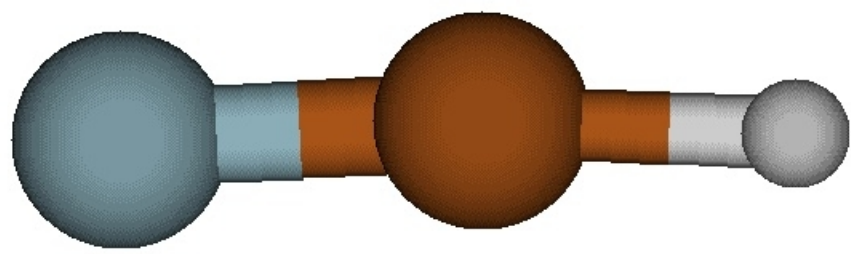
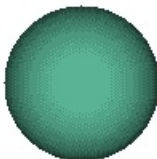
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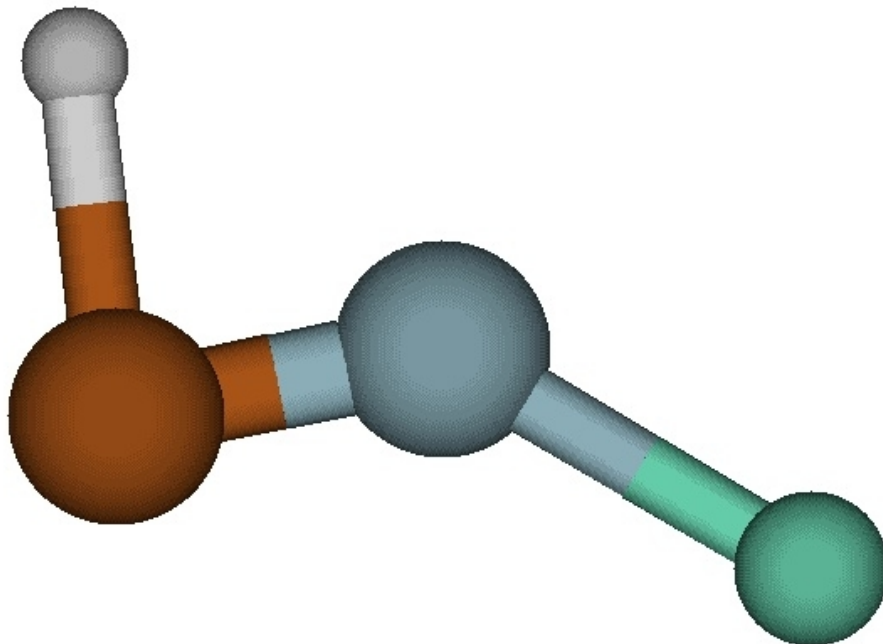
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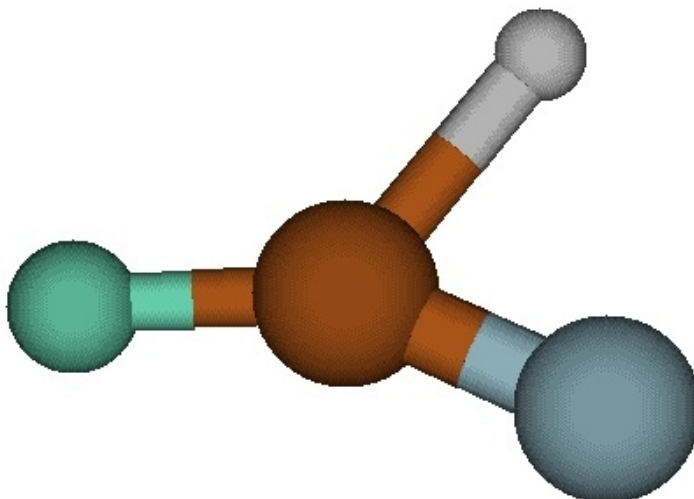
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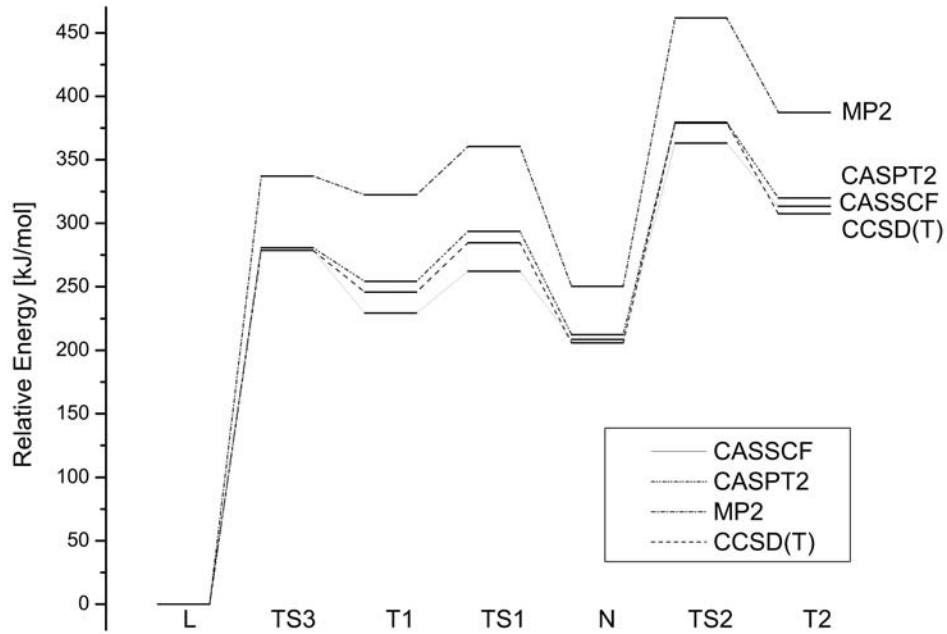
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