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# Are there Stable Excited Triplet States of $\text{NCS}^-/\text{CNS}^-$ and $\text{NCO}^-/\text{CNO}^-$ ?

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## Abstract

Highly correlated *ab initio* wave functions within the UCCSD(T)-F12 approach have been used to map portions of the potential energy surfaces (PESs) and to study the stability of the first excited triplet states of the  $\text{NCS}^-/\text{CNS}^-$  and  $\text{NCO}^-/\text{CNO}^-$  anions. These  $a^3\Pi$  states for linear geometries, or their  $^3A'$  and  $^3A''$  bent components, correlate with the lowest dissociation asymptote of  $\text{NCX}^-$  ( $X = \text{S}$  and  $\text{O}$ ) along the NC-X coordinates. The  $X^1\Sigma^+$  linear ground states of these anions are known to be stable with respect to dissociation to the  $X^2\Pi$  ground state of the corresponding neutral molecule with a rather large electron affinity (EA). The  $a^3\Pi$  state of the  $\text{NCS}^-$  anion is positioned below the  $X$  state of the neutral at long NC-S distances and its minimum of energy is found for bent geometries. The stability of its two components in bent geometries has been investigated, and it is found that some anionic forms are stable with respect to the  $X$  state of the neutral. The linear  $\text{CNS}^-$  and  $\text{CNO}^-$  isomers present a minimum only at long CN-X distances, located below the minimum of their corresponding neutral CNX ground states.

Keywords : Molecular anions, excited states, Potential energy functions

## Introduction

The molecular cyanate  $\text{NCO}^-$  and thiocyanate  $\text{NCS}^-$  anions are stable and well known in condensed phase, as reagents, substituents or ligands in molecular systems. Also in the gas phase, these anions are stable:  $\text{NCO}^-$  is one of the most stable anions of the interstellar medium, particularly in icy grains, and  $\text{NCS}^-$  should also be present even if it is less abundant. These two anionic systems are valence-isoelectronic with 16 valence electrons and consequently their electronic states have very similar properties. Both  $\text{NCS}^-$  and  $\text{NCO}^-$  anions have a stable linear ground state,  $X^1\Sigma^+$ , which has been studied theoretically and experimentally. The vibrational spectroscopy of these  $X^1\Sigma^+$  states has been examined in various alkali halide matrices,<sup>1,2</sup> and also in the gas phase under high resolution.<sup>3,4</sup> Their photoelectron spectra has also been studied,<sup>5</sup> providing an estimate of the adiabatic electron affinities,  $\text{EA}(\text{NCS}) = 3.537$  eV and  $\text{EA}(\text{NCO}) = 3.609$  eV. For

both molecular anions, extensive theoretical calculations have already been performed, providing structural and spectroscopic data of the electronic ground states. These calculations showed that the most stable form is the linear  $\text{NCX}^-$ , but another linear isomer  $\text{CNX}^-$  is also stable, which is analogous to the neutral cases. The minima of the  $X^1\Sigma^+$  states, and the isomerization path in  $^1A'$  symmetry between them, have been studied for both species:  $\text{CNO}^-$  is located 2.964 eV above  $\text{NCO}^-$  with an isomerization barrier close to 4.9 eV above  $\text{NCO}^-$  (MRCI/aV5Z calculations),<sup>6</sup> similarly  $\text{CNS}^-$  is found 1.565 eV above  $\text{NCS}^-$  with an isomerization barrier close to 2.7 eV above  $\text{NCS}^-$  (CCSD(T)/aVQZ calculations).<sup>7</sup> For both systems, the ground state of the anion is stable with respect to the neutral species all along the isomerization path. Interestingly, the energy difference between the minima of the two stable isomers of the negative forms is of the same order of magnitude as the energy difference between the corresponding isomers of the neutral molecules: the ground state minimum of  $\text{CNO}$  is located 2.74 eV above  $\text{NCO}$  (MRCI/aVQZ calculations),<sup>8</sup> with an  $\text{EA}(\text{CNO}) = 3.37$  eV, close to that of  $\text{NCO}$ , and the ground state minimum of  $\text{CNS}$  is found 1.29 eV above  $\text{NCS}$  (MRCI/aVQZ calculations),<sup>9</sup> with an  $\text{EA}(\text{CNS}) = 3.26$  eV.

In all previous theoretical studies, only the lowest electronic state of the negative species has been investigated. However, considering the large electron affinities of the  $X^2\Pi$  ground states of the neutrals for both systems, it seemed relevant to search for other stable electronic states. Since the overall lowest dissociation limit of  $\text{NCX}^-$  is located along the NC-X coordinate, corresponding to  $[\text{CN}^-(X^1\Sigma^+) + \text{X}(X^3\text{P})]$  with triplet spin, it seemed particularly appropriate to examine the behaviour of the lowest triplet states of the anions. Moreover, considering that the second stable isomers  $\text{CNX}^-$  dissociate to the same lowest limit but located higher in energy than  $\text{NCX}^-$ , it might also be probable to find stable triplet states for these isomers. Energetic data for both systems are discussed below.

## Computational details

Electronic structure calculations have been performed with the code MOLPRO<sup>10</sup> using highly correlated wave functions within the UCCSD(T)-F12a method.<sup>11,12</sup> Cuts through the full potential energy surfaces (PES) in linear and bent geometries have been determined for the singlet ground states and first triplet excited states of the negative ions, which have been positioned relative to the PES of the doublet ground states of the neutral molecules. The orbital basis sets used were the standard aug-cc-pVTZ basis sets (abbreviated aVTZ below) of Dunning and co-workers,<sup>13,14</sup> Such basis sets within the UCCSD(T)-F12a approach have been shown,<sup>12,15</sup> to yield as accurate results as conventional calculations with basis sets approaching aug-cc-pV5Z. Auxiliary basis sets required in the F12 procedure involved the cc-pVTZ/JKFIT sets of Weigend,<sup>16</sup> the aug-cc-pVTZ/MP2FIT sets of Weigend et al.,<sup>17</sup> and the aug-cc-pVTZ/OPTRI sets of Yousaf and Peterson.<sup>18</sup> A geminal exponent of 1.0 was used throughout. Since the UCCSD(T)-F12 approach is based on a single-determinantal description of the wave function, it can be very sensitive to the electron decoupling occurring along certain dissociation paths. In the present case, knowledge was needed of the dissociation path of the  $X^2\Pi$  state of neutral NCX along the NC–X coordinate into  $[\text{CN}(^2\Sigma^+) + \text{X}(^3\text{P})]$ . It was not possible to treat this with the UCCSD(T)-F12 approach and hence some additional calculations with the MRCI+Q/aV5Z method<sup>19</sup> were carried out to evaluate *in fine* this dissociation path.

## Potential Energy Surfaces

### Dissociation limits of $\text{NC-X}^-/\text{CN-X}^-$ and molecular correlations

Due to the large EA of CN (3.862 eV)<sup>20</sup> compared to that of CS (0.205 eV),<sup>21</sup> NS (1.194 eV)<sup>21</sup> and NO (0.026 eV),<sup>22</sup> the lowest dissociation limits of the  $\text{NCX}^-$  molecular anions correspond to the breaking of the C-X bond and formation of  $[\text{CN}^- + \text{X}]$ . The molecular states and the energies associated with these dissociation limits are given in Table 1. The energies are given relative to the

lowest dissociation limit of the neutral NCX species along the NC-X coordinate, i.e., [CN( $X^2\Sigma^+$ ) + X( $X^3P$ )]. Considering these energy values, it is clear that the lowest asymptote of the anionic species corresponds to the triplet states. For both X=O and S, it lies 3.862 eV below the dissociation asymptote of the neutral, corresponding to the EA of the CN fragment. A total of at least four anionic asymptotes lie below that of the neutral.

Three factors are important in discussing the possible stability of the excited triplet states of  $\text{NCX}^-/\text{CNX}^-$  relative to the ground states of the neutrals. The first is the relative position of the neutral and anion minima; the EAs have been calculated as the difference between the minima of the  $X^1\Sigma^+$  ground state of the anion and the  $X^2\Pi$  ground state of the neutral,  $\text{EA}(\text{NCS}) = 3.57$  eV and  $\text{EA}(\text{NCO}) = 3.70$  eV. These can be compared to the experimental adiabatic values of 3.537 eV (NCS) and 3.609 eV (NCO). The second factor is the position of the singlet dissociation asymptote of the anion, i.e., the dissociation limit of the ground state of the anion with respect to that of the triplet. In the case of  $\text{NCS}^-$  the singlet asymptote lies only 1.15 eV above the triplet one. In the case of  $\text{NCO}^-$  the singlet asymptote is higher, 1.96 eV above the triplet. The third factor is the dissociation energy  $D_0$  of the  $X^1\Sigma^+$  state of  $\text{NCX}^-$  along the NC-X coordinate calculated from the sum of separate CCSD(T)-F12a calculations on  $\text{CN}^-$  and X. In the case of  $\text{NCS}^-$  this energy has been calculated to be equal to 4.16 eV in good agreement with a previously calculated value of 3.89 eV,<sup>7</sup> while in the case of  $\text{NCO}^-$  the  $D_0$  value has been determined to be 5.67 eV.

From these two data we can conclude that the triplet dissociation asymptote of  $\text{NCS}^-$  lies approximately only 0.59 eV above the minimum of the  $X^2\Pi$  ground state of NCS, but for  $\text{NCO}^-$  the triplet asymptote lies approximately 2.0 eV above the minimum of the  $X^2\Pi$  ground state of NCO. As a consequence it is certainly more probable to find a stable excited triplet state for  $\text{NCS}^-$  than for  $\text{NCO}^-$ . Both systems have, however, been explored.

A similar analysis for the less stable  $\text{CNX}^-$  isomers gives for the  $\text{CNS}^-$  system a position for the triplet dissociation limit of approximately 1.10 eV below the minimum of the  $X^2\Pi$  ground state of CNS, and for  $\text{CNO}^-$  at 0.94 eV below the minimum of the  $X^2\Pi$  ground state of CNO. For both systems, it is possible to find a stable triplet state of the anion.

## Potential Energy Surfaces of $\text{NCS}^-/\text{CNS}^-$

Figure 1 shows cuts of the PESs along the NC-S coordinate calculated at the UCCSD(T)-F12a/aVTZ level of theory for the  $X^1\Sigma^+$  electronic ground state and first excited states of  $\text{NCS}^-$ , together with the  $X^2\Pi$  ground state of the neutral NCS and its  $^4\Sigma^-$  first excited state. For the anion, the parts of the curves corresponding to an unstable situation with respect to the neutral have been plotted with dashed lines. These cuts are constructed for linear geometries and fixed  $R_{\text{NC}} = 2.22$  bohr, which is the equilibrium bond length in the CN molecule and corresponds to an averaged value in the anion and neutral triatomic systems. The energy of the  $[\text{NC} (X^2\Sigma^+) + \text{S} (X^3\text{P})]$  dissociation asymptote is taken as the zero of energy. For all geometries reported here, the  $X^1\Sigma^+$  state of  $\text{NCS}^-$ , which is known to be linear, is stable relative to the  $X^2\Pi$  ground state of NCS. The excited  $a^3\Pi$  state of  $\text{NCS}^-$  crosses these two electronic states at relatively short distances in regards to the neutral and at a long distance in the case of the anion ground state. The crossing with the  $X^1\Sigma^+$  state of the anion occurs at  $R_{\text{CS}} = 5.28$  bohr, with an energy of 3.68 eV above the minimum of the  $X^1\Sigma^+$  state. The spin-orbit interaction matrix element between these states at the crossing point has been calculated<sup>25</sup> (MRCI/aV5Z) to be equal to  $125 \text{ cm}^{-1}$ , giving a transition dipole moment of 0.41 a.u., which should allow an efficient predissociation of the  $X^1\Sigma^+$  state by the triplet. The crossing of the  $a^3\Pi$  state with the  $X^2\Pi$  state of the neutral occurs at  $R_{\text{CS}} = 3.6$  bohr, with an energy of only 0.64 eV above the minimum of the  $X^2\Pi$  state. For  $R_{\text{CS}}$  distances longer than 3.6 bohr, the  $a^3\Pi$  state of  $\text{NCS}^-$  is stable with respect to the neutral and it presents a linear minimum for  $R_{\text{CS}} = 4.8$  bohr, located 0.1 eV below the absolute minimum of the  $X^2\Pi$  state.

For bent geometries, the two Renner-Teller components of the  $a^3\Pi$  state of  $\text{NCS}^-$  and those of the  $X^2\Pi$  state of NCS have been considered. In Figure 2 the cuts along the bending coordinate of these four states for a fixed value of  $R_{\text{NC}} = 2.22$  bohr and different values of the  $R_{\text{CS}}$  distance are plotted. It clearly appears in Figure 2 that the triplet states are always located below the doublet states of the neutral for nearly all bent geometries, at least for  $R_{\text{CS}} \leq 3.4$  bohr. The absolute minimum of the  $^3A'$  state, which is the lowest bent component, has been calculated to be only 0.11 eV below the energy of the  $X^2\Pi$  state of the neutral (see Table 2). This implies that even

in the molecular region, providing that the system is bent, the excited triplet state of the anion can be stable with respect to the neutral. Since the energy stabilisation is very small, additional calculations at the MRCI+Q/aV5Z level have been performed to compare the absolute minimum energy of the  $X^2\Pi$  state of the neutral and the absolute minimum energy of this bent  $^3A'$  state of the anion. In these calculations the  $X^2\Pi$  state is calculated to lie 0.05 eV below the  $^3A'$  state of the anion. The order of the states is reversed compared to the UCCSD(T)-F12 results, however these energy differences are very small, attesting the proximity of the states.

Figure 3 shows the cuts of the PESs along the CN-S coordinate calculated at the UCCSD(T)-F12a/aVTZ level of theory for the  $X^1\Sigma^+$  electronic ground state and first excited states of  $CNS^-$ , together with the  $X^2\Pi$  ground state of the neutral CNS and its  $^4\Sigma^-$  first excited state. As in Figure 1 these cuts are constructed for linear geometries and fixed  $R_{NC} = 2.22$  bohr. As for the lowest energy isomer, the linear  $X^1\Sigma^+$  state of  $CNS^-$  is stable relative to the linear  $X^2\Pi$  state of neutral CNS. As expected from the energetic data given above, the  $a^3\Pi$  state at long  $R_{NS}$  distances is much lower in energy with respect to the  $X^1\Sigma^+$  and  $X^2\Pi$  states of this isomer than in the  $NCS^-$  case.

The  $a^3\Pi$  state crosses these two states, for  $R_{NS} = 4.78$  bohr and an energy of 2.15 eV above the minimum of the  $X^1\Sigma^+$  and for  $R_{NS} = 3.35$  bohr and an energy of 0.28 eV above the minimum of the  $X^2\Pi$  state. A predissociation of the  $X^1\Sigma^+$  state of  $CNS^-$  by the triplet can occur under the same condition as for the other isomer. For  $R_{NS}$  distances longer than 3.35 bohr, the  $a^3\Pi$  state of  $CNS^-$  is stable with respect to the neutral and it presents a swallow minimum for  $R_{NS} = 4.8$  bohr, located 1.11 eV below the minimum of the  $X^2\Pi$  state of neutral CNS. The triplet state is thus stable at long distance.

A study has also been done in bent geometries for the  $a^3\Pi$  state of the  $CNS^-$  isomer, but contrary to the  $NCS^-$  isomer, this state does not present a minimum for bent geometries. Consequently it lies always higher than the  $X^2\Pi$  state of the neutral in the molecular region for bent geometries.

## Potential Energy Surfaces of $\text{NCO}^-/\text{CNO}^-$

Figure 4 plots cuts of the PESs along the NC-O coordinate, calculated at the UCCSD(T)-F12a/aVTZ level of theory, for the  $X^1\Sigma^+$  electronic ground state and the first excited states of  $\text{NCO}^-$ , together with the  $X^2\Pi$  ground state of the neutral NCO and its  $^4\Sigma^-$  first excited state. These cuts are constructed for linear geometries and fixed  $R_{\text{NC}} = 2.22$  bohr, as for the  $\text{NCS}^-$  system. The energy of the  $[\text{NC} (X^2\Sigma^+) + \text{O} (X^3\text{P})]$  dissociation asymptote is taken as zero of energy. For all geometries reported here the linear  $X^1\Sigma^+$  state of  $\text{NCO}^-$  is stable relative to the linear  $X^2\Pi$  state of NCO. The first  $a^3\Pi$  state of  $\text{NCO}^-$  crosses these two electronic states at relatively long distances - 3.0 bohr for the  $X^2\Pi$  state at an energy of 2.28 eV above the minimum of the  $X^2\Pi$  state and 4.18 bohr for the  $X^1\Sigma^+$  state with an energy of 5.28 eV above the minimum of the  $X^1\Sigma^+$  state. The spin-orbit interaction between the  $X^1\Sigma^+$  and the  $a^3\Pi$  states at the distance of the crossing has been calculated (MRCI/aV5Z) to be equal to  $74 \text{ cm}^{-1}$ , giving a transition dipole moment of 0.43 a.u., which should allow an efficient predissociation of the  $X^1\Sigma^+$  state by the triplet. For  $R_{\text{CO}}$  longer than 3.0 bohr, the  $a^3\Pi$  state of  $\text{NCO}^-$  is stable with respect to the neutral. As discussed in a previous section, the triplet state of  $\text{NCO}^-$  lies higher than that of  $\text{NCS}^-$  with respect to the ground state of the corresponding neutral. The  $a^3\Pi$  state of  $\text{NCO}^-$  also presents a linear minimum for  $R_{\text{CO}} = 4.2$  bohr, located 1.56 eV above the absolute minimum of the  $X^2\Pi$  state.

Figure 5 shows cuts of the PESs along the CN-O coordinate, calculated at the UCCSD(T)-F12a/aVTZ level of theory, for the  $X^1\Sigma^+$  electronic ground state and the first excited states of  $\text{CNO}^-$ , together with the  $X^2\Pi$  ground state of the neutral CNO and its  $^4\Sigma^-$  first excited state. These cuts are also constructed for linear geometries and fixed  $R_{\text{NC}} = 2.22$  bohr. As for the other isomer, the linear  $X^1\Sigma^+$  state of  $\text{CNO}^-$  is stable relative to the linear  $X^2\Pi$  state of CNO. As expected from the energetic data given above, the  $a^3\Pi$  state at long  $R_{\text{NO}}$  distance is much lower in energy with respect to its  $X^1\Sigma^+$  and  $X^2\Pi$  states than for the other isomer.

The  $a^3\Pi$  state crosses these two states at  $R_{\text{NO}} = 2.8$  bohr and an energy of 1.04 eV above the minimum of the  $X^2\Pi$  state and for  $R_{\text{NO}} = 3.75$  bohr and an energy of 2.40 eV above the minimum of the  $X^1\Sigma^+$ . As for the other isomer, the  $X^1\Sigma^+$  state of the anion can be predissociated by the

triplet. For  $R_{NO}$  distances longer than 2.8 bohr, the  $a^3\Pi$  state of  $CNO^-$  is stable with respect to the neutral CNO and it presents a shallow minimum for  $R_{NO} = 4.5$  bohr, located 0.92 eV below the minimum of the  $X^2\Pi$  state of the neutral.

For bent geometries, the two Renner-Teller components of the  $a^3\Pi$  state of  $NCO^-$  and of the  $X^2\Pi$  state of NCO have been considered. Figure 6 plots cuts along the bending coordinate of these four states for a fixed value of  $R_{NC} = 2.22$  bohr and for different values of the C-O distance. It clearly appears in Figure 6 that the triplet states are located below the doublet states of the neutral for bent geometries. However the absolute minimum of energy of the  $^3A'$  state (see Table 3) is located 0.81 eV above the absolute minimum of the  $X^2\Pi$  state of NCO and consequently the anion cannot be considered as a stable species. For  $CNO^-$ , as for  $CNS^-$ , the  $a^3\Pi$  state has a global linear minimum and does not present additional minima upon bending.

## Conclusions

In the present study we have shown that, at the UCCSD(T)-F12a/aVTZ level, the  $NCS^-$  anion presents a second stable electronic state which is found in  $^3A'$  symmetry with a minimum energy 0.11 eV below the absolute minimum of the  $X^2\Pi$  ground state of the neutral NCS. MRCI+Q/aV5Z calculations, performed for these states, give the minimum of the  $X^2\Pi$  ground state of the neutral 0.05 eV below that of the triplet of the anion and could not confirm that the triplet state of  $NCS^-$  is stable relative to the neutral NCS, however the energy difference is so small that only experimental or higher level electronic structure calculations can provide a definitive answer. For  $NCO^-$  it was not possible to find a stable triplet state, neither at long distance nor in the molecular region. Both  $CNX^-$  isomers present a minimum at long distance and are stable with respect to the neutral CNX. If the anion  $CNX^-$  is produced by collision of  $CN^-$  with  $X(^3P)$ , it is possible to form these two anions in a triplet state. However since the crossing of the triplet with the singlet ground state of  $CNX^-$  occurs in the region of these minima, the spin-orbit coupling can efficiently depopulate the triplet to form the singlet  $X^1\Sigma^+$  state of the anion. Such a process can also happen with the triplet

state of  $\text{NCS}^-$ .

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## Figures caption:

Figure 1: Linear cuts of the PES (UCCSD(T)-F12/aVTZ) for the  $X^1\Sigma^+$  and first excited states of  $\text{NCS}^-$  and for the  $X^2\Pi$  and  $^4\Sigma^-$  states of  $\text{NCS}$ . The  $R_{CN}$  distance was fixed to 2.22 bohr.

Figure 2: Cuts of the bending PESs of the lowest two states of  $\text{NCS}^-$  and  $\text{NCS}$ . The  $R_{CN}$  distance was fixed to 2.22 bohr.

Figure 3: Linear cuts of the PES (UCCSD(T)-F12/aVTZ) for the  $X^1\Sigma^+$  and first excited states of  $\text{CNS}^-$  and for the  $X^2\Pi$  and  $^4\Sigma^-$  states of  $\text{CNS}$ . The  $R_{CN}$  distance was fixed to 2.22 bohr.

Figure 4: Linear cuts of the PES (UCCSD(T)-F12/aVTZ) for the  $X^1\Sigma^+$  and first excited states of  $\text{NCO}^-$  and for the  $X^2\Pi$  and  $^4\Sigma^-$  states of  $\text{NCO}$ . The  $R_{CN}$  distance was fixed to 2.22 bohr.

Figure 5: Linear cuts of the PES (UCCSD(T)-F12/aVTZ) for the  $X^1\Sigma^+$  and first excited states of  $\text{CNO}^-$  and for the  $X^2\Pi$  and  $^4\Sigma^-$  states of  $\text{CNO}$ . The  $R_{CN}$  distance was fixed to 2.22 bohr..

Figure 6: Cuts of the bending PESs of two lowest states of  $\text{NCO}^-$  and  $\text{NCO}$ . The  $R_{CN}$  distance was fixed to 2.22 bohr.

Figure 1: Linear cuts of the PES (UCCSD(T)-F12/aVTZ) for the  $X^1\Sigma^+$  and first excited states of  $\text{NCS}^-$  and for the  $X^2\Pi$  and  $^4\Sigma^-$  states of  $\text{NCS}$ . The  $R_{\text{CN}}$  distance was fixed to 2.22 bohr.

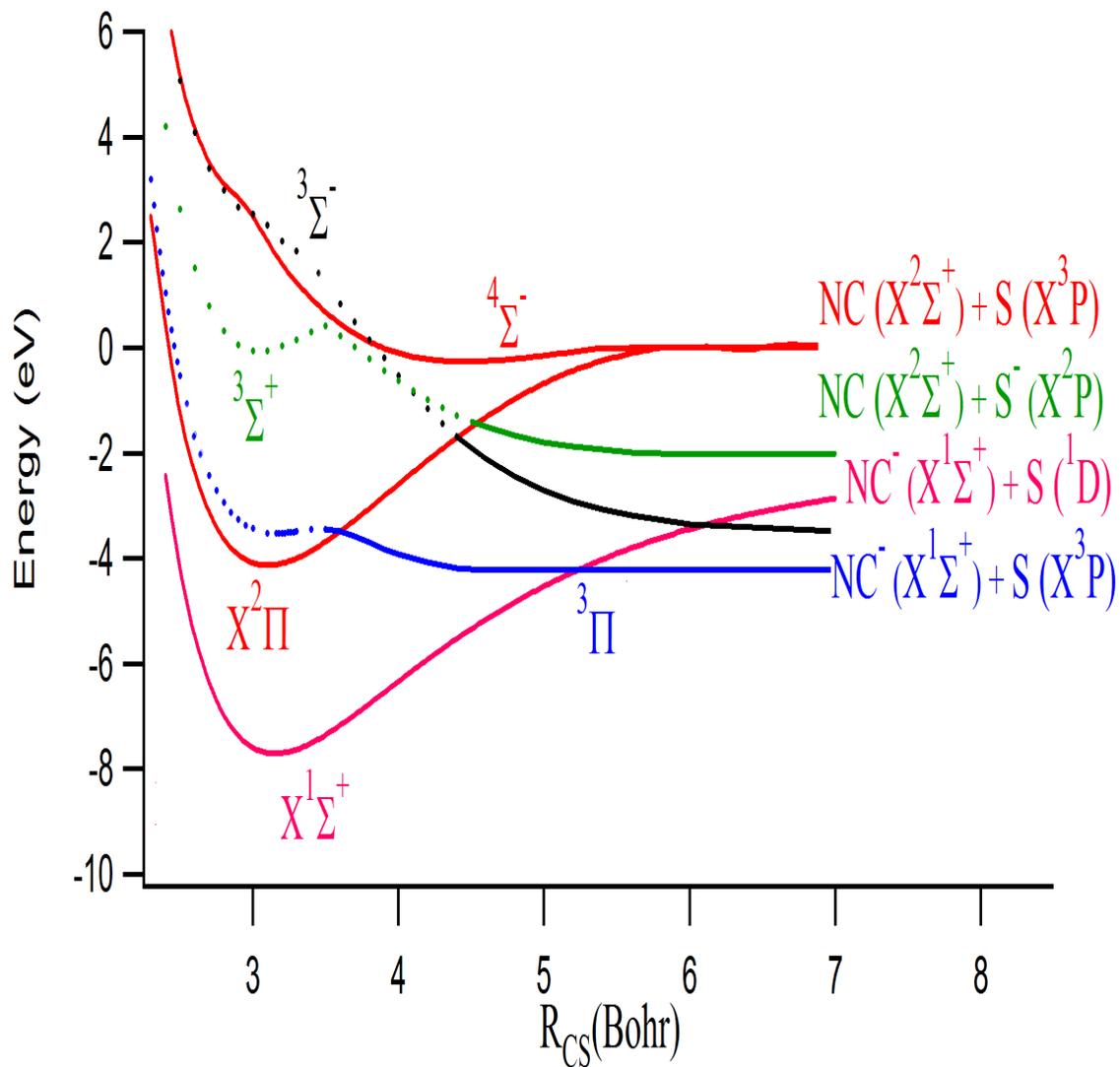


Figure 2: Cuts of the bending PESs of the lowest two states of  $\text{NCS}^-$  and  $\text{NCS}$ . The  $R_{\text{CN}}$  distance was fixed to 2.22 bohr.

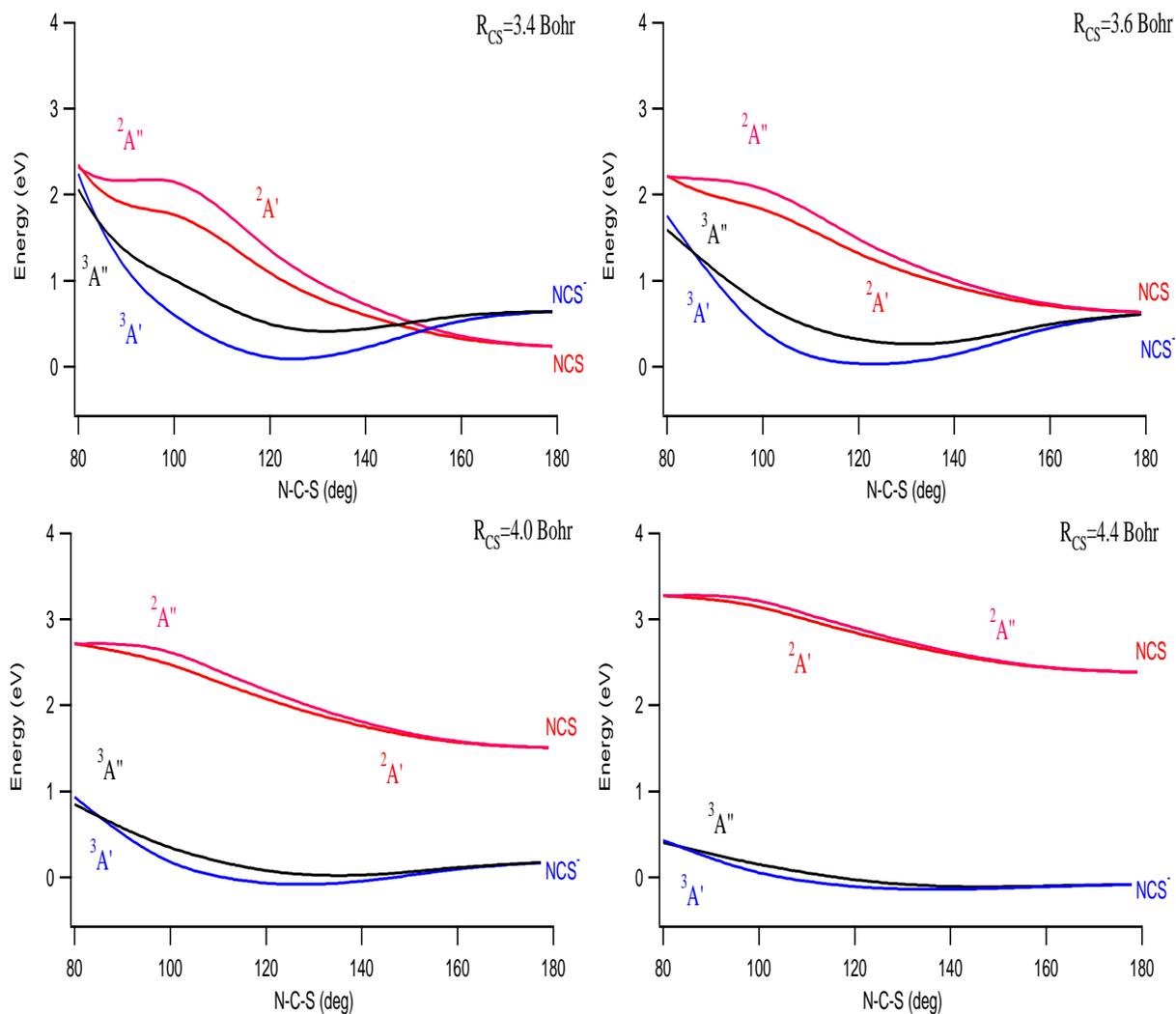


Figure 3: Linear cuts of the PES (UCCSD(T)-F12/aVTZ) for the  $X^1\Sigma^+$  and first excited states of  $\text{CNS}^-$  and for the  $X^2\Pi$  and  $^4\Sigma^-$  states of  $\text{CNS}$ . The  $R_{\text{CN}}$  distance was fixed to 2.22 bohr.

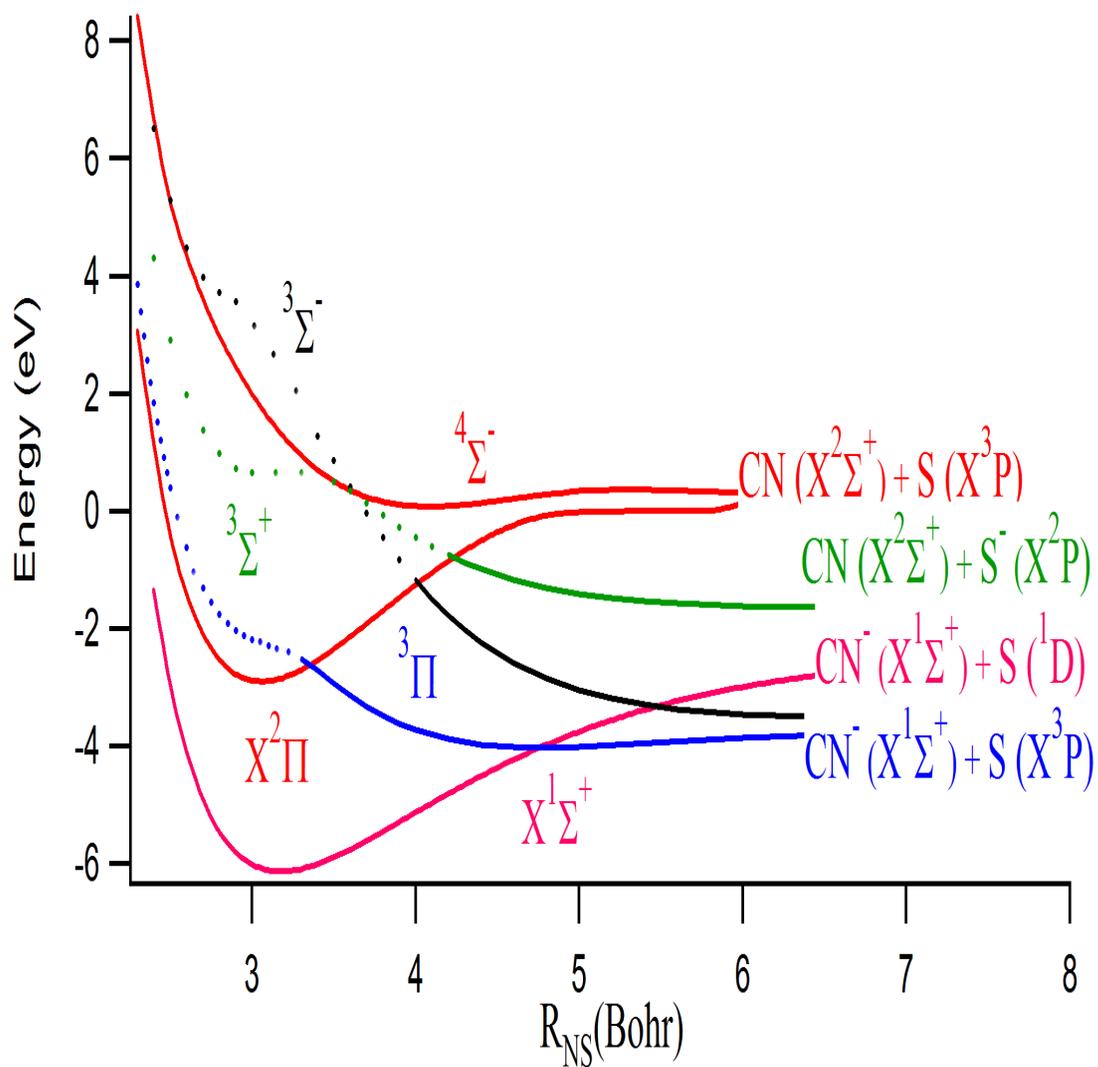


Figure 4: Linear cuts of the PES (UCCSD(T)-F12/aVTZ) for the  $X^1\Sigma^+$  and first excited states of  $\text{NCO}^-$  and for the  $X^2\Pi$  and  $4\Sigma^-$  states of  $\text{NCO}$ . The  $R_{\text{CN}}$  distance was fixed to 2.22 bohr.

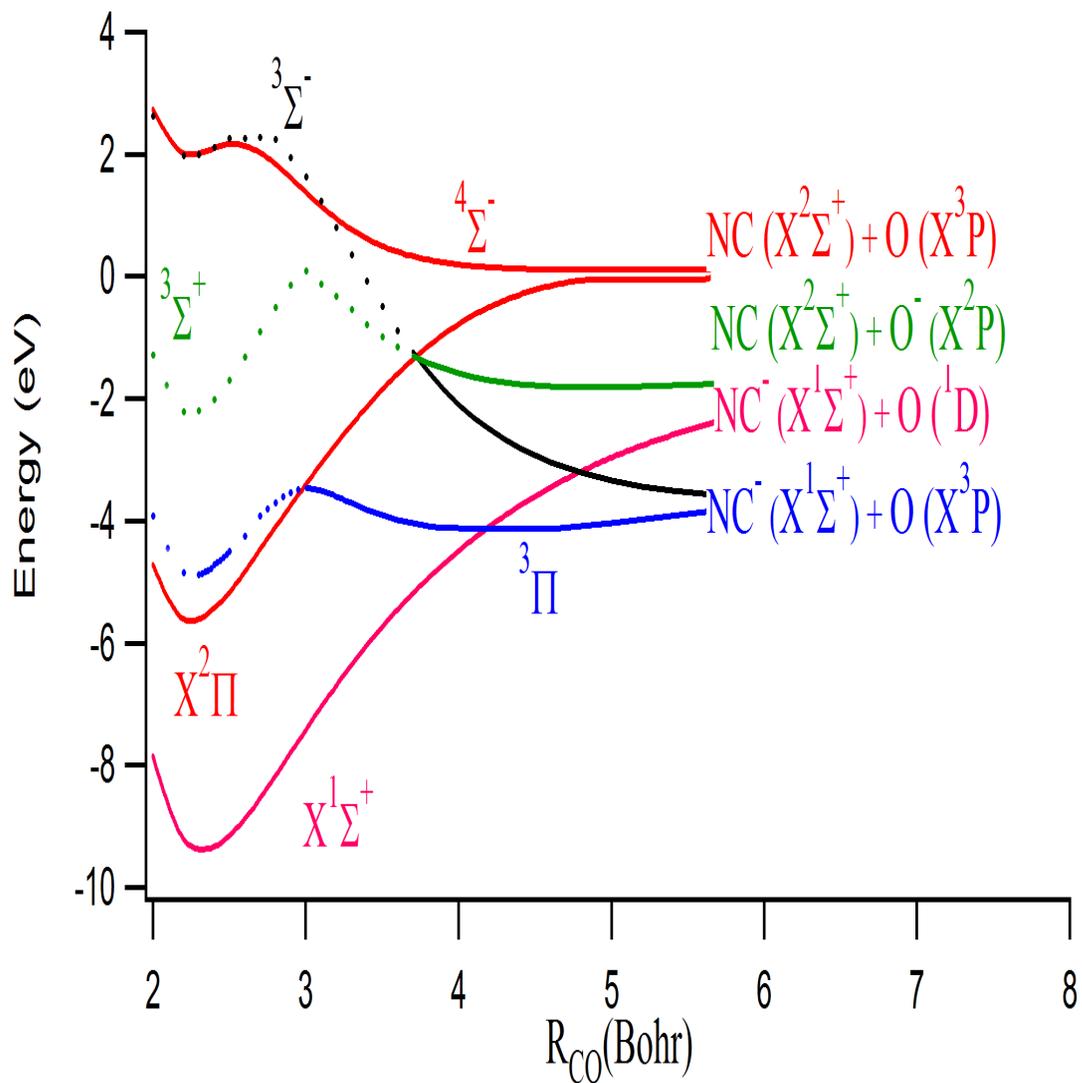


Figure 5: Linear cuts of the PES (UCCSD(T)-F12/aVTZ) for the  $X^1\Sigma^+$  and first excited states of  $\text{CNO}^-$  and for the  $X^2\Pi$  and  $4\Sigma^-$  states of  $\text{CNO}$ . The  $R_{\text{CN}}$  distance was fixed to 2.22 bohr.

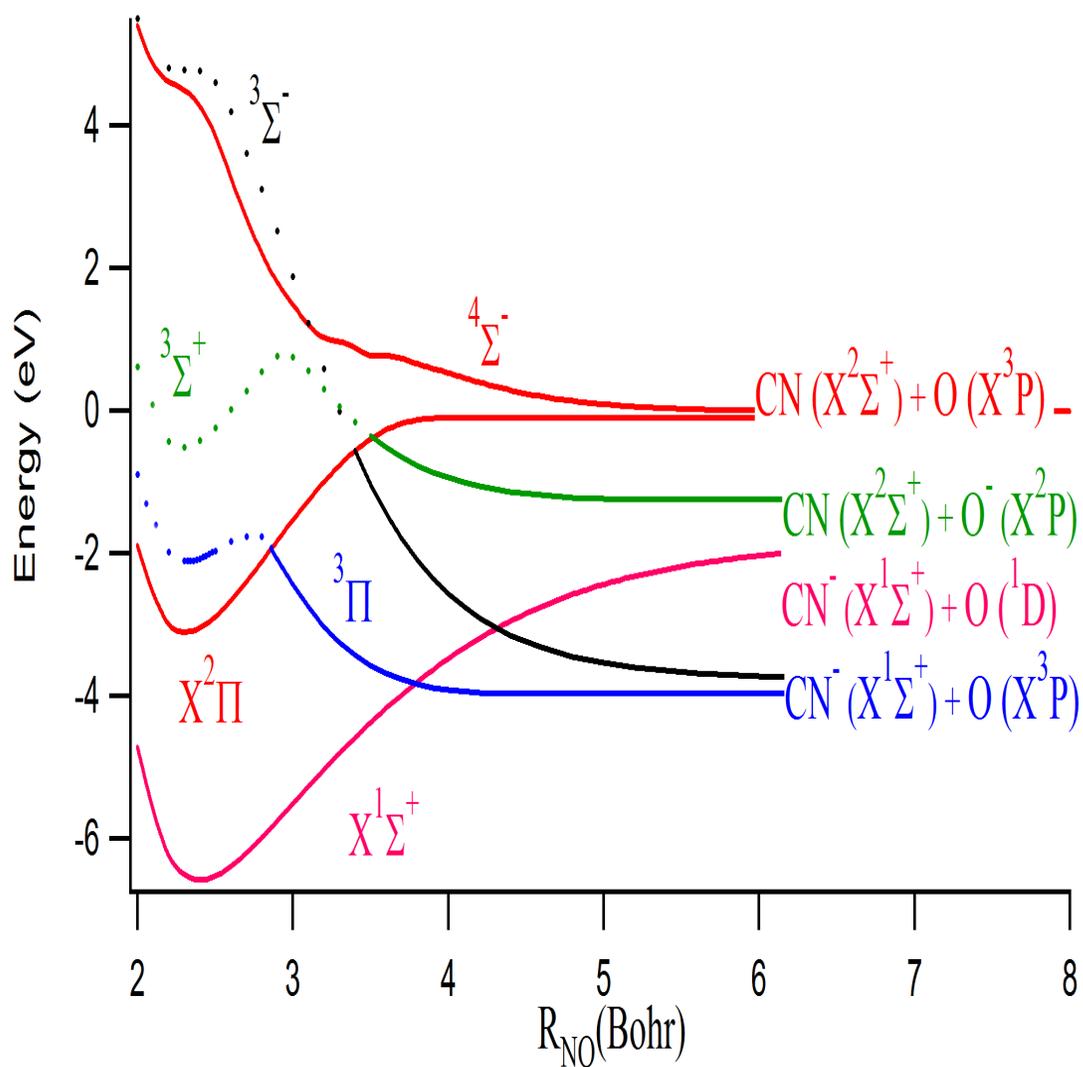
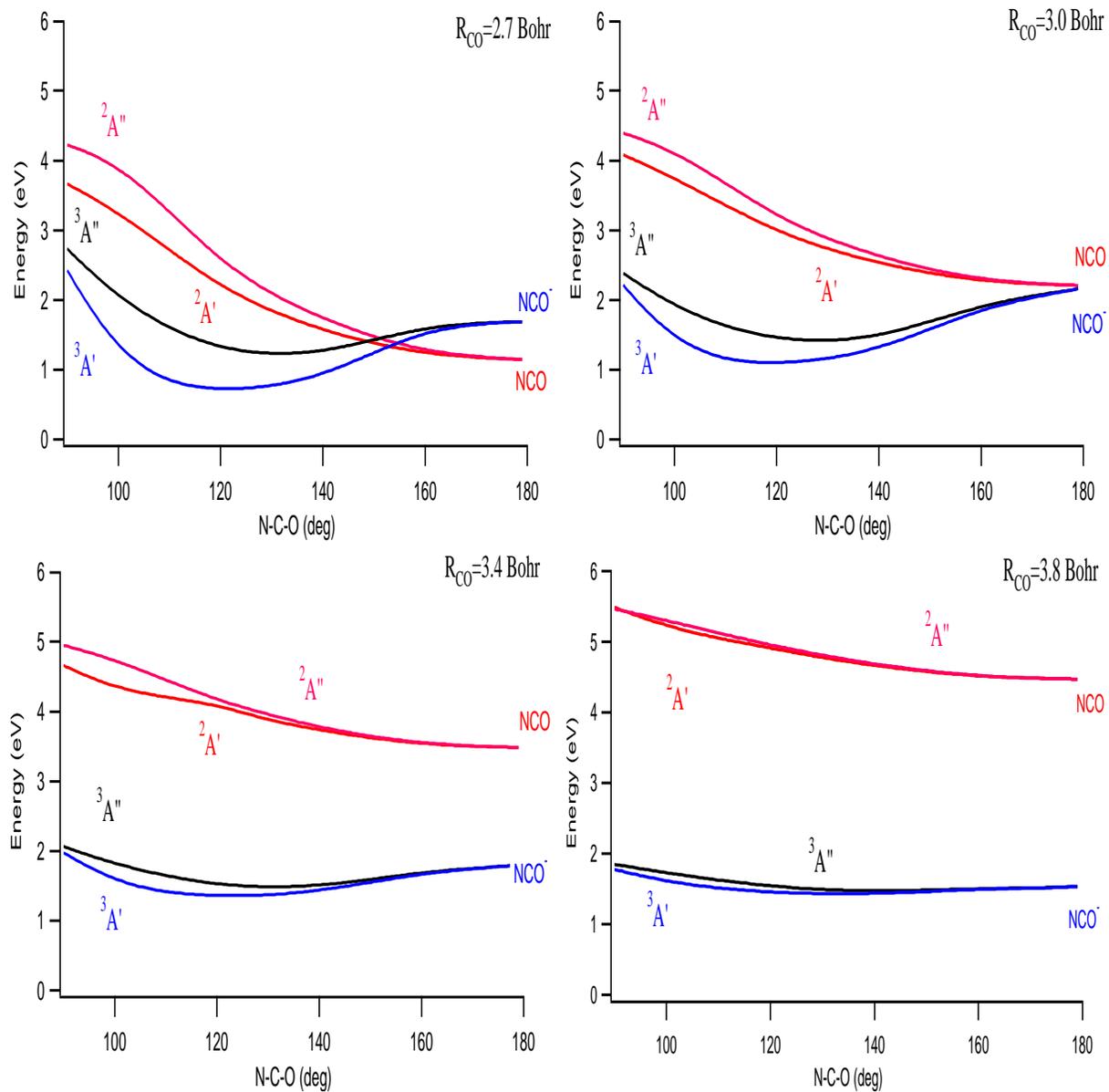


Figure 6: Cuts of the bending PESs of two lowest states of  $\text{NCO}^-$  and  $\text{NCO}$ . The  $R_{\text{CN}}$  distance was fixed to 2.22 bohr.



## Tables caption:

Table 1: Dissociation limits of  $[\text{N,C,S}]^-$  and  $[\text{N,C,O}]^-$ .

Table 2: Calculated (UCCSD(T)-F12a) bond lengths and absolute energies of the minima of the relevant states of  $\text{NCS}^-/\text{NCS}$  and  $\text{CNS}^-/\text{CNS}$ .

Table 3: Calculated (UCCSD(T)-F12a) bond lengths and absolute energies of the minima of the relevant states of  $\text{NCO}^-/\text{NCO}$  and  $\text{CNO}^-/\text{CNO}$ .

**Table 1: Dissociation limits of  $[\text{N,C,S}]^-$  and  $[\text{N,C,O}]^-$**

Dissociated states	Molecular states	$\Delta E^a(\text{eV})$
$\text{CN}(X^2\Sigma^+) + S(^3P)$	$(2,4)\Pi, \Sigma^-$	0.0
$\text{CN}(A^2\Pi) + S(^2P)$	$(1,3)\Sigma^+, \Sigma^-, \Pi, \Delta$	-0.93
$\text{CN}(X^2\Sigma^+) + S(^2P)$	$(1,3)\Sigma^+, \Pi$	-2.07
$\text{CN}^-(X^1\Sigma^+) + S(^1D)$	$(1)\Sigma^+, \Pi, \Delta$	-2.72
$\text{CN}^-(X^1\Sigma^+) + S(^3P)$	$(3)\Sigma^-, \Pi$	-3.86
$\text{CN}(X^2\Sigma^+) + O(^3P)$	$(2,4)\Pi, \Sigma^-$	0.0
$\text{CN}(A^2\Pi) + O(^2P)$	$(1,3)\Sigma^+, \Sigma^-, \Pi, \Delta$	-0.31
$\text{CN}(X^2\Sigma^+) + O(^2P)$	$(1,3)\Sigma^+, \Pi$	-1.46
$\text{CN}^-(X^1\Sigma^+) + O(^1D)$	$(1)\Sigma^+, \Pi, \Delta$	-1.89
$\text{CN}^-(X^1\Sigma^+) + O(^3P)$	$(3)\Sigma^-, \Pi$	-3.86

<sup>a</sup> Energy values are given relative to the  $\text{CN}(X^2\Sigma^+) + \text{X}(X^3P)$  asymptote, they are deduced from the experimental data given below.

Experimental values :  $S(^1D) : E = 1.14 \text{ eV}$  ;  $S(^2P) : E = 2.07 \text{ eV}$ <sup>23</sup>

$O(^1D) : E = 1.96 \text{ eV}$  ;  $O(^2P) : E = 1.46 \text{ eV}$ <sup>23</sup>

$E A_e(\text{CN}) = 3.86 \text{ eV}$ <sup>20</sup> ;  $\text{CN}(A^2\Pi) : E = 1.15 \text{ eV}$ <sup>24</sup>

**Table 2: Calculated (UCCSD(T)-F12a) bond lengths and absolute energies of the minima of the relevant states of NCS<sup>-</sup>/NCS and CNS<sup>-</sup>/CNS**

<i>State</i>	<i>E (hartree)</i>	<i>R<sub>CN</sub> (bohr)</i>	<i>R<sub>CS</sub> (bohr)</i>	<i>θ</i>
<i>NCS</i> ( <sup>2</sup> Π)	-490.432006	2.229	3.102	180
	-490.429993 <sup>a</sup>	2.229	3.102	180
<i>NCS</i> <sup>-</sup> ( <i>X</i> <sup>1</sup> Σ <sup>+</sup> )	-490.563316	2.228	3.163	180
<i>NCS</i> <sup>-</sup> ( <sup>3</sup> Π)	-490.435624	2.22	4.80	180
<i>NCS</i> <sup>-</sup> ( <sup>3</sup> A')	-490.436003	2.22	4.55	143
	-490.428000 <sup>a</sup>	2.22 <sup>a</sup>	4.52 <sup>a</sup>	140 <sup>a</sup>
<i>State</i>	<i>E (hartree)</i>	<i>R<sub>CN</sub> (bohr)</i>	<i>R<sub>NS</sub> (bohr)</i>	<i>θ</i>
<i>CNS</i> ( <sup>2</sup> Π)	-490.386060	2.23	3.06	180
<i>CNS</i> <sup>-</sup> ( <i>X</i> <sup>1</sup> Σ <sup>+</sup> )	-490.504550	2.23	3.19	180
<i>CNS</i> <sup>-</sup> ( <sup>3</sup> Π)	-490.426979	2.22	4.80	180

<sup>a</sup> Calculations MRCI+Q-aV5Z.

The dissociation limit of the *a*<sup>3</sup>Π state is calculated E = -490.411455 *hartree*

**Table 3: Calculated (UCCSD(T)-F12a) bond lengths and absolute energies of the minima of the relevant states of NCO<sup>-</sup>/NCO and CNO<sup>-</sup>/CNO**

<i>State</i>	<i>E (hartree)</i>	<i>R<sub>CN</sub> (bohr)</i>	<i>R<sub>CO</sub> (bohr)</i>	<i>θ</i>
<i>NCO</i> ( <sup>2</sup> Π)	-167.815181	2.323	2.226	180
<i>NCO</i> <sup>-</sup> ( <i>X</i> <sup>1</sup> Σ <sup>+</sup> )	-167.951357	2.254	2.323	180
<i>NCO</i> <sup>-</sup> ( <sup>3</sup> Π)	-167.757840	2.22	4.20	180
<i>NCO</i> <sup>-</sup> ( <sup>3</sup> A')	-167.785347	2.22	2.70	120
<i>State</i>	<i>E (hartree)</i>	<i>R<sub>CN</sub> (bohr)</i>	<i>R<sub>NO</sub> (bohr)</i>	<i>θ</i>
<i>CNO</i> ( <sup>2</sup> Π)	-167.716307	2.29	2.30	180
<i>CNO</i> <sup>-</sup> ( <i>X</i> <sup>1</sup> Σ <sup>+</sup> )	-167.842386	2.24	2.40	180
<i>CNO</i> <sup>-</sup> ( <sup>3</sup> Π)	-167.750275	2.22	4.50	180

The dissociation limit of the *a*<sup>3</sup>Π state is calculated E = -167.743350 *hartree*