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Possible long-lived quartet resonance states of CO^{-*}

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Abstract. Two states of CO^- which are expected to live longer than the well-known $^2\Pi$ shape resonance are examined and the results obtained are compared with the analogous states of the isoelectronic N_2^- system. The $^4\Sigma^-$ and $^4\Pi$ states are found to be stable with respect to dissociation. The latter state is also stable with respect to single-electron loss to its parent neutral state. The lifetime of this state is supposed to be long, but not necessarily long enough to allow detection in a mass spectrometer.

Key words: Resonance states – Carbon monoxide – Ab initio calculations – Anionic systems

N_2^- and CO^- are two of the most studied metastable anionic systems in the literature (see, for example, various articles in [1]). The $^2\Pi_g$ resonance state of the N_2^- system is the standard example for shape-type resonances. This resonance has a lifetime of about 1.6×10^{-15} s. Carbon monoxide is isoelectronic with nitrogen and is a weakly polar molecule with a dipole moment of about 0.1 Debye. As with N_2^-, a low-energy shape resonance of $^2\Pi$ configuration exists. Because the potential parameters of CO^- are very similar to those of N_2^-, it is not surprising that this resonance state has a similar lifetime of about 0.5×10^{-15} s. Motivated by recent mass spectrometric observation of a long-lived N_2^- state with a lifetime in excess of 10^{-5} s [2, 3], Sommerfeld and Cederbaum [4] examined several quartet states of the N_2^- system. They predict the anionic states $^4\Pi_u$ and $^4\Sigma_g^-$ to be the first known long-lived N_2^- states that exist significantly longer than the famous $^2\Pi_g$ shape resonance. As a "lower limit", the lifetime of the $^4\Pi_u$ state has been computed to be at least 2×10^{-12} s, but it could be markedly longer.

In this work we transfer the results for the N_2^- system of [4] to the isoelectronic CO^- anion. As with the observation of N_2^-, CO^- has also been detected in a mass spectrometer. Middleton and Klein [2] and Gnaser [3] used sputtering techniques to produce the negative ions, while Mathur et al. [5] produced CO^- by intense-field laser irradiation of CO_2. We examine the potential energy curves (PECs) of the $^4\Sigma^-$ and $^4\Pi$ states of CO^- and compare our results with the analogous N_2^- states.

We begin with some general considerations of why the above-mentioned electronic states are supposed to be good candidates to represent long-lived anionic states. Because the addition of an electron to the ground states of N_2 and CO leads only to short-lived resonances, one needs to concentrate on excited electronic states of the parent neutral systems. Another very important aspect is that examination of various long-lived dianionic and anionic systems has established a favorable geometrical pattern. Negatively charged systems that consist of a positively charged center and n equivalent electrons or negatively charged ligands have long lifetimes or in favorable cases are electronically stable [6, 7]. The transfer of these ideas to the CO^- system has the consequence that the added electron should be equivalent to the excited electron of the parent neutral CO state, i.e., both electrons should occupy the same orbital. From this point of view, the states examined can be seen as made up of a positively charged core CO^+ to which two equivalent electrons are added. In general such electronic states can be expressed as

$$(CO)^{-1}(\phi^*)^2 \ .$$

The excited anionic states should be examined to determine whether they exhibit long lifetimes with respect to electron detachment via one- and two-electron processes as well as with respect to dissociation. Following this general scheme many electronic states are possible, but most of them possess purely dissociative potential curves, which implies only very short lifetimes. The most promising states that fulfill the latter

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* Dedicated to Prof. Dr. Wilfried Meyer on the occasion of his 60th birthday

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two criteria are the $^4\Pi$ and $^4\Sigma^-$ states of CO$^-$, which are derived from the neutral parent states $^3\Sigma^+$ and $^3\Pi$, respectively. The electronic configurations of the anionic states are

$$\begin{aligned} &^4\Pi: (\mathrm{core})^4(1\sigma)^2(2\sigma)^2(1\pi)^3(3\sigma)^2(1\pi^*)^2 \\ &^4\Sigma^-: (\mathrm{core})^4(1\sigma)^2(2\sigma)^2(1\pi)^4(3\sigma)^1(1\pi^*)^2 \ . \end{aligned} \qquad ()$$

In the $^4\Pi$ state the hole is in the 1π orbital and the excited as well as the additional electron occupy the antibonding $1\pi^*$ orbital. In the $^4\Sigma^-$ state the $1\pi^*$ orbital is also doubly occupied, but the hole is located in the 3σ orbital.

As a first step, the PEC of the anionic $^4\Pi$ and $^4\Sigma^-$ states and the parent CO states have been computed at the independent-particle level using the standard self-consistent field (SCF) restricted open-shell Hartree-Fock (ROHF) technique. Within these calculations the [5*s*4*p*3*d*2*f*] aug-cc-pVTZ one-particle basis set [8] built into the ACES2 package of programs [9] has been used, and the results are displayed in Fig. 1. Based on these calculations, the PECs have also been computed at the highly correlated coupled-cluster single-double and perturbative triple excitation [CCSD(T)] [10] level of theory. The CCSD(T) results are depicted in Fig. 2.

Let us briefly compare the PECs obtained by the ROHF calculations with those obtained by the CCSD(T) calculations. At the independent-particle level both quartet states are clearly unstable with respect to instant electron loss because both PECs are energetically higher than the curves of the corresponding parent states. The minima of the $^4\Sigma^-$ and $^4\Pi$ states lie about 0.7 and 0.4 eV above their parent triplet states, respectively. At the correlated level of CCSD(T) the energy difference between the minima of the quartet $^4\Sigma^-$ state and its corresponding parent decreases to 0.32 eV. The $^4\Pi$ state of CO$^-$ becomes stable with respect to its parent $^3\Sigma^+$ state, i.e., the PEC of the quartet $^4\Pi$ state slides down below the curve of the parent triplet state. It is worth mentioning that the $^4\Pi$ state is stabilized by about 0.6 eV, while the $^4\Sigma^-$ state shows a stabilization of only about 0.4 eV. In summary, the quartet states examined are clearly stabilized if correlation is regarded. By definition the large differences between the results of the ROHF and the correlated CCSD(T) calculations imply that correlation plays an important role in the binding process of the additional electron. In the following, we therefore focus only on the results of the CCSD(T) calculations.

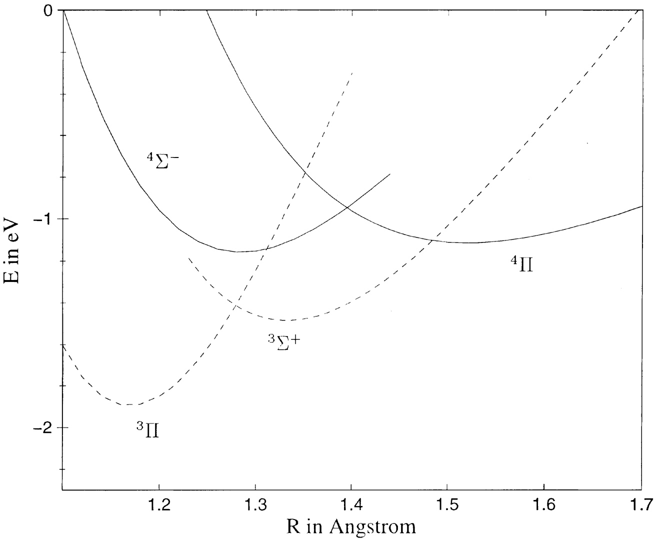

Fig. 1. Potential energy curves of the $^3\Pi$ and $^3\Sigma^+$ states of CO (*dashed lines*) and the corresponding $^4\Sigma^-$ and $^4\Pi$ states of CO$^-$ (*full lines*) at the single-particle level of ROHF. The zero point of the energy scale is arbitrarily chosen because only relative energies are of interest

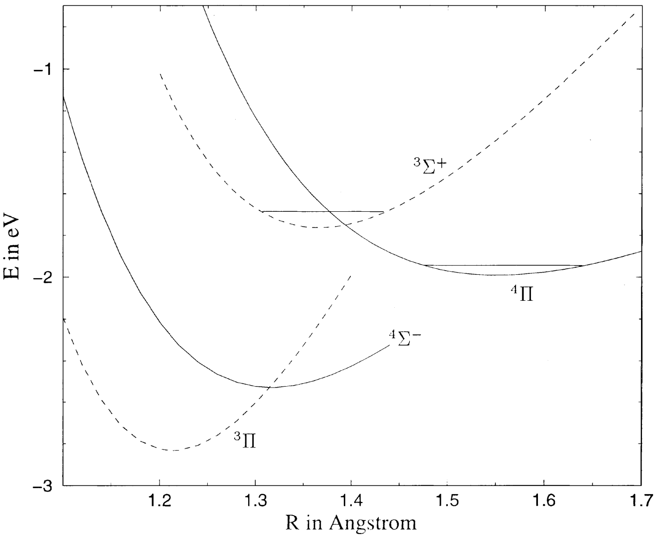

Fig. 2. Potential energy curves of the $^3\Pi$ and $^3\Sigma^+$ states of CO (*dashed lines*) and the corresponding $^4\Sigma^-$ and $^4\Pi$ states of CO$^-$ (*full lines*) at the level of CCSD(T). The zero-point correction is indicated for the $^3\Sigma^+$ and $^4\Pi$ states. The zero point of the energy scale is arbitrarily chosen because only relative energies are of interest

We first turn to the $^4\Sigma^-$ state, which is derived from the $^3\Pi$ state of neutral CO. The equilibrium bond length of the $^3\Pi$ state is 1.2134 Å and agrees with experimental and other theoretical data [11,12]. Since the additional electron in the $^4\Sigma^-$ state occupies the antibonding $1\pi^*$ orbital, the bond length is elongated by about 0.1 Å to 1.3159 Å. Regarding the electronic stability, we first note that this state possesses only a tiny positive vertical electron detachment energy of 0.01 eV at the minimum of its PEC. Not surprisingly, the adiabatic electron detachment energy (EDE), which is the more relevant quantity and is defined as the energy difference between the minima of the parent and the resonance states, is clearly negative. The EDE has a value of −0.30 eV. The $^4\Sigma^-$ anionic state examined is thus unstable with respect to electron detachment to its parent $^3\Pi$ state. The calculation of the lifetime of the $^4\Sigma^-$ resonance state will be the subject of future work. Although we might expect this state to live longer than the well-known $^2\Pi$ shape resonance of CO, its lifetime is most probably not long enough to allow its observation in a mass spectrometer. This observation should only be possible if our calculation has a relative error of ≥ 0.30 eV such that the EDE of the $^4\Sigma^-$ state becomes positive.

The second CO^- state of interest is the $^4\Pi$ state, which is generated by attaching an electron to the excited $^3\Sigma^+$ state of neutral CO. The additional electron occupies the antibonding $1\pi^*$ orbital and, therefore, the bond length increases by about 0.2 Å from 1.3660 Å in the $^3\Sigma^+$ state to 1.5511 Å in the $^4\Pi$ state. Taking electronic stability into account, the $^4\Pi$ state is found to be stable with respect to vertical single-electron loss. The vertical EDE has a value of $+0.66$ eV. In contrast to the above-mentioned analogous $^4\Pi_u$ state of the nitrogen anion, which is on the verge of stability, the $^4\Pi$ state of CO^- is stable with respect to adiabatic electron detachment regarding its parent $^3\Sigma^+$ state. The adiabatic EDE is clearly positive by $+0.23$ eV. If we include vibrational zero-point corrections, the adiabatic EDE increases slightly to 0.26 eV. Using the harmonic approximation to calculate the vibrational levels of the $^4\Pi$ state, three vibrational levels are found to lie below the PEC of the parent $^3\Sigma^+$ state of neutral CO. In conclusion, the $^4\Pi$ state of CO^- is stable with respect to vertical and adiabatic direct electron detachment, i.e., detachment to its parent neutral state, as well as with respect to dissociation.

Before we compare our results for CO^- with those for N_2^-, let us briefly recall the findings for the latter system. The long-lived N_2^- states are the $^4\Sigma_g^-$ and the $^4\Pi_u$ states. They are derived from the neutral parent states $^3\Pi_g$ and $^3\Sigma_u^+$, respectively. The corresponding PECs are depicted in Fig. 3. Whereas the $^4\Sigma_g^-$ state exhibits a clearly negative adiabatic EDE of -0.32 eV with respect to the neutral parent $^3\Pi_g$ state, the adiabatic EDE of the $^4\Pi_u$ state with respect to its parent $^3\Sigma_u^+$ state is found to be very close to zero but still slightly negative by 0.11 eV. The stability of the $^4\Pi_u$ state is slightly increased by a shift of 0.03 eV due to zero-point corrections. Additional stabilizing energy shifts are expected with a more extended calculation of electron correlation effects and with the inclusion of bound-continuum interactions in the anion. At the present level of theory both anionic states examined have negative single-electron detachment energies and represent shape resonance states. For this reason, the lifetime of the $^4\Pi_u$ state has been computed and found to be at least 2×10^{-12} s [4]. The complex absorbing potential (CAP) method, which is discussed elsewhere, has been used [13, 14]. As discussed in Ref. [4] in some detail, the above-mentioned energy shifts are expected to prolong this lifetime substantially. This $^4\Pi_u$ state represents the first known long-lived anionic nitrogen state.

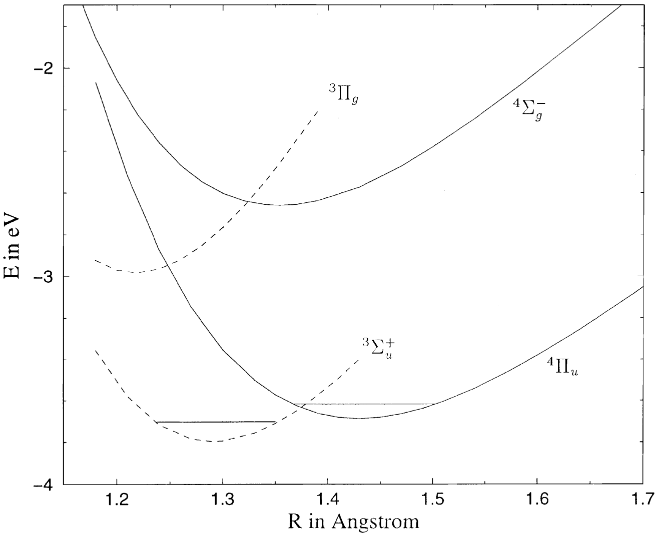

Fig. 3. Potential energy curves of the $A^3\Sigma_u^+$ and $B^3\Pi_g$ states of N_2 (*dashed lines*) and the corresponding $^4\Pi_u$ and $^4\Sigma_g^-$ states of N_2^- (*full lines*) at the correlated level of CCSD(T). The zero-point correction is indicated for the $A^3\Sigma_u^+$ and $^4\Pi_u$ states. The results are from Ref. [4]. The zero point of the energy scale is arbitrarily chosen because only relative energies are of interest

Comparing the results for CO^- with those for N_2^-, there are similarities as well as differences. First of all, the overall shapes of the corresponding PECs are very similar. For example, the curvature of the $^4\Pi$ curve of CO^- is nearly equivalent to the curvature of the $^4\Pi_u$ curve of N_2^-. Also the relative geometries of the examined CO^- states compared with their corresponding parent neutral states are strongly related to the relative geometries of the nitrogen system. As mentioned earlier, the potential parameters of CO^- are very similar to those of N_2^-. One major difference between CO and N_2 is in the energetic ordering of the parent $^3\Pi$ and $^3\Sigma^+$ states in CO, which is the reverse of that of the related $^3\Pi_g$ and $^3\Sigma_u^+$ states in N_2. In N_2, $^3\Sigma_u^+$ is the triplet ground state and lies energetically lower than the $^3\Pi_g$ state, whereas in CO the analogous $^3\Sigma^+$ state is higher in energy than the $^3\Pi$ triplet ground state. This is well-documented in the literature [12]. The ordering of anionic states follows that of their parent states. It is $^4\Pi_u$ and $^4\Sigma_g^-$ in the nitrogen anion compared with $^4\Sigma^-$ and $^4\Pi$ in the carbon monoxide anion. We note that this might be guessed even at the single-particle level of Hartree-Fock theory where the energetic order of the lowest σ and π orbitals is reversed in N_2 and CO.

The change of the energetic order of the parent and the anionic states in CO has consequences regarding the lifetime of the anionic $^4\Pi$ state of CO^- compared with the $^4\Pi_u$ state of N_2^-. Taking a look at the $^4\Pi_u$ state of N_2^-, this state possesses only two possible decay channels. These are the direct channel by single-electron loss to the parent $^3\Sigma_u^+$ state, denoted as $^4\Pi_u \rightarrow {}^3\Sigma_u^+$, and the indirect decay channel into the $^1\Sigma_g^+$ ground state of N_2, $^4\Pi_u \rightarrow {}^1\Sigma_g^+$. This $^4\Pi_u \rightarrow {}^1\Sigma_g^+$ is spin- and symmetry-forbidden. It combines single-electron loss with a spin-forbidden $\alpha\pi^* \rightarrow \beta\pi$ transition, which is known to be very slow. The $^4\Pi_u \rightarrow {}^1\Sigma_g^+$ channel can thus be neglected for our purposes, and the $^4\Pi_u \rightarrow {}^3\Sigma_u^+$ is the only lifetime-determining process of the $^4\Pi_u$ decay.

In contrast to N_2, there are several other decay possibilities for the $^4\Pi$ state of CO^-. The $^3\Pi$ and the $^4\Sigma^-$ states are energetically lower than the $^4\Pi$ state and, therefore, there are four possible decay channels for this state of CO^-. Decay into different states of neutral CO which possess the same configuration but different spatial symmetry, e.g., the $^3\Sigma^-$ and the $^3\Delta$ states, need not to be considered because they lie higher in energy than the $^3\Sigma^+$ state [12]. First, there is the possibility of direct decay by single-electron loss into the $^3\Sigma^+$ parent state, abbreviated as $^4\Pi \rightarrow {}^3\Sigma^+$. The second possibility is via the optical transition $^4\Pi \rightarrow {}^4\Sigma^-$ and subsequent electron loss. The decay $^4\Pi \rightarrow {}^3\Pi$ represents the third possible channel. The fourth and last decomposition channel is the decay into the ground state of CO, $^4\Pi \rightarrow {}^1\Sigma^+$.

We will first discuss single-electron loss of the $^4\Pi$ state. This decay is represented by the $^4\Pi \rightarrow {}^3\Sigma^+$ channel described above. As we have seen in the description of our results, the $^4\Pi$ state of CO^- is adiabatically stable with respect to single-electron loss because the quartet $^4\Pi$ state is energetically lower than the triplet $^3\Sigma^+$ state of neutral CO (see Fig. 2). Consequently, the direct decomposition channel by simple electron loss is closed.

The second decay path is via the $^4\Pi \rightarrow {}^4\Sigma^-$ transition, which is dipole allowed and therefore optically possible. For several reasons this decomposition channel is supposed to be slow. On the one hand, those electron transitions from the vibrational ground state of the $^4\Pi$ state to the vibrationally excited states of the $^4\Sigma^-$ state, which are favored by Franck-Condon factors, are slow because of the small energy differences involved. On the other hand, the probability of a transition into low-lying vibrational states of the $^4\Sigma^-$ state is decreased by unfavorable Franck-Condon factors. To get an idea of the lifetime of this process, we compare this $^4\Pi \rightarrow {}^4\Sigma^-$ transition with the analogous transition between the parent states $^3\Pi \rightarrow {}^3\Sigma^+$. In both cases, an electron is de-excited from the 3σ orbital to the 1π orbital. The latter electronic transition between the parent states in their vibrational ground states is known to exhibit a lifetime of 6.5×10^{-5} s [11]. The analogous transition $^4\Pi \rightarrow {}^4\Sigma^-$ between the anionic states is supposed to possess a lifetime of the same magnitude. Once the transition to the $^4\Sigma^-$ state takes place, a decay of this state by direct electron loss to the parent $^3\Pi$ state of CO is possible. In conclusion, the decay of the $^4\Pi$ state via the transition $^4\Pi \rightarrow {}^4\Sigma^-$ is supposed to be slow and is therefore not a lifetime-determining process of the $^4\Pi$ state.

In the third possible decay channel, the $^4\Pi \rightarrow {}^3\Pi$ decomposition, the decay is a two-electron process. In this process an electron is de-excited from the 3σ to the 1π orbital and the energy released is used to eject an electron from the $1\pi^*$ orbital into the continuum. Both transitions involve a change of angular momentum. Alternatively, an electron can be de-excited from the $1\pi^*$ to the 1π orbital followed by ejection of an electron from the 3σ orbital. The $1\pi^* \rightarrow 1\pi$ transition is spin-forbidden. In general, such processes are known to be slow. In the present case, this decay is further suppressed by unfavorable Franck-Condon factors: the $^4\Pi$ and the $^3\Pi$ PECs are strongly separated from each other (see Fig. 2). We conclude that the decay along the $^4\Pi \rightarrow {}^3\Pi$ channel can be considered to be slow.

By analogy to the N_2^- system the decay into the $^1\Sigma^+$ ground state of CO is also possible. Because this $^4\Pi \rightarrow {}^1\Sigma^+$ transition is double-spin-forbidden as discussed above for N_2^-, this decomposition channel should play a negligible role in determining the lifetime of the $^4\Pi$ state of CO^-.

In summary, we were able to show that the decay via direct single-electron loss is impossible for the $^4\Pi$ state of CO^-. Furthermore, all other decay channels are connected with slow processes. Of these decay channels the decay via the two-electron process (the $^4\Pi \rightarrow {}^3\Pi$ channel) is the only Coulombic decay and should be the lifetime-determining channel of the $^4\Pi$ Feshbach resonance. Computation of this process is necessary before we can definitely predict this state to be observable in a mass spectrometer.

We now take a closer look at the vertical and adiabatic EDEs of the anionic $^4\Pi$ resonance state of CO^- with respect to its parent neutral $^3\Sigma^+$ state and compare them with the corresponding data for nitrogen. The $^4\Pi_u$ state of N_2^- has a vertical and adiabatic EDE of 0.28 and -0.11 eV, respectively, whereas both values are clearly positive for the $^4\Pi$ state of CO^-: 0.66 and 0.23 eV, respectively. Hence, this state is stabilized in the anionic CO system. Why is the $^4\Pi$ state of CO^- stabilized compared with the isoelectronic $^4\Pi_u$ state of N_2^-?

We propose that this trend can be explained with the help of the dipole moment of CO. In contrast to N_2, which does not have a dipole moment at all, CO possesses a small moment of about 0.1 D in the ground state. Going to the excited state of interest, the dipole moment increases to about 1.4 D [11]. Because it is well-known that a strong dipole can bind an excess electron [15–18], we assume that the dipole moment of the parent excited $^3\Sigma^+$ state might play a role in the stabilization of the anionic state.

In this communication we have investigated long-lived states of the CO^- anion. Employing high-level ab initio methods, the $^4\Pi$ and $^4\Sigma^-$ states have been found to be stable with respect to dissociation and vertical electron loss. Only the $^4\Pi$ state is found to be stable with respect to adiabatic electron loss to its parent neutral state, which is the $^3\Sigma^+$ state. Although the lifetime of the $^4\Pi$ state has not been calculated in detail, a qualitative estimation of the lifetime contributions of the remaining decay channels explains why this $^4\Pi$ state exhibits a long lifetime. More calculations are necessary before this candidate can be predicted as sufficiently long-lived to be observable in a mass spectrometer. In contrast to the $^4\Pi$ state, the $^4\Sigma^-$ can be observed in a mass spectrometer only if the present calculation computes its EDE with an error of at least 0.3 eV smaller. Although such an error is unlikely, it cannot a priori be excluded. Finally, we would like to mention that higher spin states of CO^- and N_2^- (e.g., sextets) could, in principle, also be good candidates to be observed in a mass spectrometer.

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