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Long-lived high-spin sextet states of N_2^-

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Abstract

Motivated by recent mass spectrometric observations of N_2^- , we have examined several high-spin sextet states of this fundamental ion. Following a general construction principle for long-lived electronic states of small molecules, we have found a long-lived ${}^6\Sigma_u^+$ state of N_2^- that is stable with respect to direct single electron loss, as well as with respect to dissociation. All possible decay channels are spin forbidden and, therefore, this ${}^6\Sigma_u^+$ state is long-lived and observable in a mass spectrometer. Comparison is made with CO^- and general aspects of long-lived high-spin states of anions are stressed. (Int J Mass Spectrom 188 (1999) 199–204) © 1999 Elsevier Science B.V.

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1. Introduction

For a long time, N_2^- and the isoelectronic CO^- have been thought to possess only short-lived anionic resonance states. The energetically lowest state of N_2^- is the famous ${}^2\Pi_g$ resonance state, where the additional electron is added to the closed-shell ${}^1\Sigma_g^+$ ground state configuration of N_2 [1]. This resonance has become a textbook example for shape resonances over the years, and its lifetime is 1.6×10^{-15} s. In analogy, the isoelectronic CO^- possesses a ${}^2\Pi$ shape resonance state with a similar lifetime of 0.5×10^{-15} s. Although these lifetimes are too short to make possible the observation of these small anions in a mass spectrometer, N_2^- and CO^- ions have recently been detected by several groups. Middleton and Klein [2] and Gnaser [3] used sputtering techniques to

produce the negative ions; Mathur and co-workers [4] produced CO^- by intense field laser irradiation of CO_2 . All groups could clearly identify these negative ions in a mass spectrometer. The experimental results imply that the experimentally observed states of N_2^- and CO^- live at least *ten orders of magnitude* longer than the well examined ${}^2\Pi_g$ and ${}^2\Pi$ resonances of N_2^- and CO^- , respectively. Motivated by the experimental observation, we began searching for long-lived high-spin states of these fundamental anions.

In the following, we first briefly review our findings for quartet states of N_2^- [5] and CO^- [6]. Subsequently, we will present recent results for long-lived sextet states of CO^- [7]. Transferring these findings to the N_2^- system, we examine the energetically lowest ${}^6\Pi_g$ and ${}^6\Sigma_u^+$ sextet states of the fundamental N_2^- anion.

The investigations of several free stable dianions, such as ionic LiF_3^{2-} [8], BeF_4^{2-} [9] and covalent $C(C)_3^{2-}$ [10], $Si(C)_3^{2-}$ [11,12], have shown that they

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prefer a specific geometrical structure. These systems consist of a positively charged center atom and several *equivalent* negatively charged ligands. The structural pattern is ruled by the electrostatic forces present in the way that the electrostatic attraction between center atom and ligands exceeds the repulsion between the negatively charged ligands. As an extreme case of this electrostatic model, Sommerfeld et al. applied it to the smallest possible dianion, the fundamental H^{2-} system [13]. Here the electrons play the roles of the negatively charged ligands and the positively charged central atom is represented by a single proton. By this means they have found the 4S^0 ($2p^3$) state, which possesses three equivalent electrons surrounding one proton, forming the only known resonance state of H^{2-} with a lifetime of about 0.4×10^{-15} s. Many atomic anions have bound high-spin states, which also reflect the picture of equivalent electrons bound to a positively charged ion core, e.g. Be^- , B^- , C^- , etc [14]. In analogy to the quartet resonance state of H^{2-} , the bound 4S^0 state of the C^- anion, for example, can be seen as a C^{2+} ion core, where three equivalent $2p$ electrons are bound.

Adopting this general building principle for the molecular N_2^- system, one might expect that a long-lived electronic state should also possess “equivalent” valence electrons added to a positively charged N_2^+ ion core. Because of the nonspherical symmetry of small molecules in general, equivalent cannot mean really equivalent in this context, but rather “as equivalent as possible.” In the following we speak of equivalent electrons when we think about unpaired electrons of the *same spin* within the *same shell*.

Sommerfeld and Cederbaum have examined several quartet states of N_2^- [5] and discussed the two energetically lowest states $4\Sigma_g^-$ and $4\Pi_u$ in detail (Fig. 1). In view of the fact that the addition of an electron to the ground state configuration of N_2 gives rise to only short-lived resonance states, they have focused on quartet states, which can be generated from the singly excited N_2 states $3\Sigma_u^+$ and $3\Pi_g$. The additional electron is added to the $1\pi_g$ orbital, where the excited electron resides also. The resulting quartet states can then be understood as two equivalent $1\pi_g$ electrons bound to a N_2^+ ion core. The examined $4\Sigma_g^-$ and $4\Pi_u$

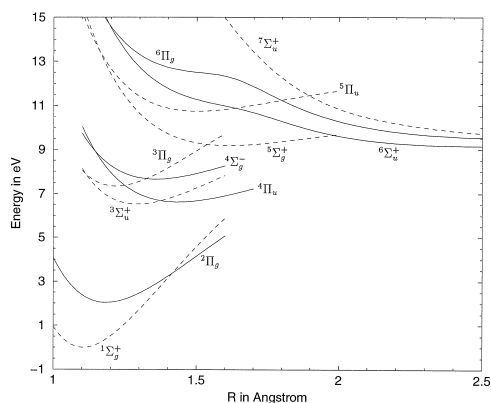


Fig. 1. Overview of the energetically lowest electronic states of N_2^- (solid lines) of doublet, quartet, and sextet multiplicity is given. These states are compared with their neutral parent states of odd spin multiplicity (dashed lines). All potential energy curves are calculated at the CCSD(T) level using an AUG-cc-pVTZ basis set. The minimum energy of the N_2 ground state $1\Sigma_g^+$ has been set to zero.

states possess holes in the $3\sigma_g$ or $1\pi_u$ orbital, respectively, of the electronic ground state configuration of neutral N_2 . These anionic states were predicted to live significantly longer than the famous $2\Pi_g$ shape resonance (Fig. 1). As a lower bound, the lifetime of the $4\Pi_u$ state was computed to be 2×10^{-12} s, but arguments for a markedly longer lifetime were given.

We have examined the analogous 4Π and $4\Sigma^-$ states of the isoelectronic CO^- anion [6], and have obtained similar results. Both states have been found to be long-lived, making them possible candidates for observation in a mass spectrometer, but the observed long-lived state has not yet been unambiguously identified.

Summarizing the results for the quartet states of N_2^- and CO^- , the application of the geometrical principle that has been found for free stable molecular dianions to these fundamental anions has been successful. For both systems far longer-lived states than the famous $2\Pi_g$ and 2Π resonance states of N_2^- and CO^- , respectively, have been found. Nevertheless, the unambiguous identification of the experimentally observed long-lived anionic state of N_2^- still remains to be done.

In a recent publication we have investigated long-lived high-spin sextet states of the CO^- anion [7]. The

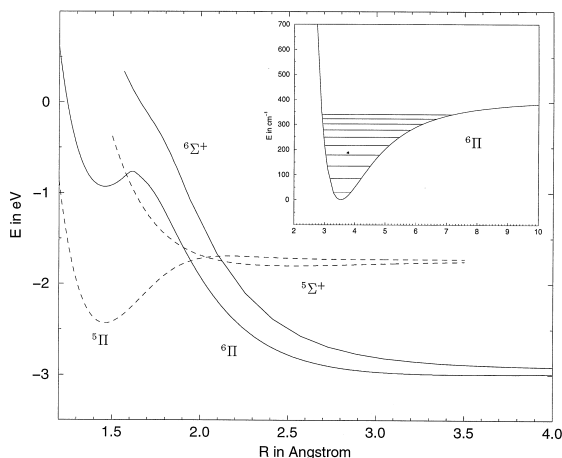


Fig. 2. Potential energy curves of the high-spin sextet states ${}^6\Sigma^+$ and ${}^6\Pi$ of CO^- are compared with those of their respective neutral parent states ${}^5\Pi$ and ${}^5\Sigma^+$. The vibrational levels of the second shallow minimum of the ${}^6\Pi$ state (see inset) at a bond length of 3.5 Å have been found to be long-lived. The ${}^6\Pi$ state is predicted to be observable in a mass spectrometer. The zero point of the energy is arbitrarily chosen.

guiding idea is that an increase in the number of equivalent electrons should lead to a larger lifetime of the anionic system. According to the geometrical principle described above, the sextet states ${}^6\Pi$ and ${}^6\Sigma^+$ (Fig. 2) correspond to three equivalent electrons bound to a CO^{2+} ion core. The examined sextet states of CO^- possess the maximum number of equivalent electrons that is possible without occupying a new energetically unfavourable shell. Employing high level ab initio methods we have found that the ${}^6\Sigma^+$ state is completely repulsive and dissociates directly into C^- and O fragments. In contrast, the potential energy curve of the ${}^6\Pi$ state has two wells, one with a deep and one with a shallow minimum at 1.460 and 3.501 Å, respectively (Fig. 2). Only vibrational states of the shallow minimum are stable with respect to both dissociation and direct single electron emissions: at the shallow well the neutral parent ${}^5\Pi$ state lies energetically above the ${}^6\Pi$ anionic state (see Fig. 2). All other decay channels for this state are spin-forbidden and, therefore, slow. For this reason, the ${}^6\Pi$ state of CO^- is long-lived, and exhibits a lifetime compatible with mass spectrometer detection.

2. Methods, results, and discussion

In this contribution we report our results for analogous sextet states of the N_2^- system. We have investigated various sextet states of N_2^- , which reflect the picture of three equivalent valence electrons bound to a N_2^{2+} ion. Most of these states have purely dissociative potential curves and consequently can be excluded as possible candidates for the observed long-lived states. More promising candidates are the energetically lowest states of sextet multiplicity ${}^6\Sigma_u^+$ and ${}^6\Pi_g$ of which the latter is the sextet ground state. The associated electronic configurations are

$${}^6\Pi_g: (\text{core})^4(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^1(1\pi_u)^3(1\pi_g)^2(3\sigma_u)^1,$$

$${}^6\Sigma_u^+: (\text{core})^4(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^2(1\pi_g)^2(3\sigma_u)^1$$

These states can be derived from the doubly excited neutral parent states ${}^5\Pi_u$ and ${}^5\Sigma_g^+$ by adding the additional electron into the $3\sigma_u$ orbital.

The potential energy curves (PECs) of the anionic ${}^6\Pi_g$ and ${}^6\Sigma_u^+$ states and their corresponding N_2 parent states have been computed at the highly correlated coupled-cluster single-double and perturbative triple excitations [CCSD(T)] level of theory [15], using the correlation consistent valence triple- ζ one particle basis set augmented with a (*spdf*) set of diffuse functions (AUG-cc-pVTZ) [16,17], i.e. a [*5s4p3d2f*] set of contracted Gauss-type functions placed at both nuclei.

For a better understanding of the overall situation, we have depicted in Fig. 1 the PECs of the above sextet states together with the low lying quartet and doublet anionic states. In addition, the PECs of the low lying states of various multiplicities of neutral N_2 are shown. For consistency, all states have been computed using CCSD(T) and the basis set described above. In Fig. 3 we show the PECs of the sextet states and of their parent neutral states on a more detailed energy scale and extending to larger internuclear distances than in Fig. 1.

It is well known that the CCSD(T) approach uses a single determinant reference function and therefore fails to describe dissociation processes with multiconfigurational character. Since this is the case for the

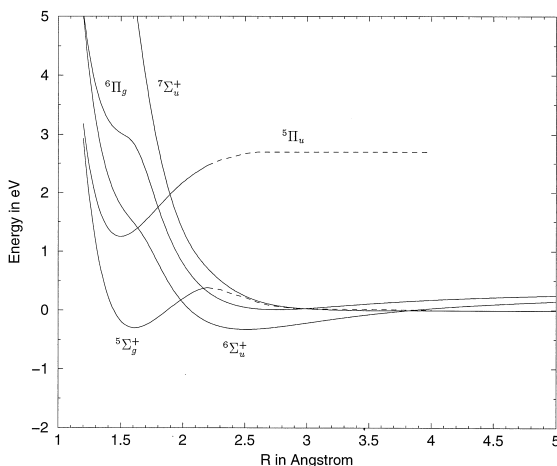


Fig. 3. Potential energy curves of the sextet states ${}^6\Pi_g$ and ${}^6\Sigma_u^+$ of N_2^- are compared with those of their respective neutral parent states ${}^5\Pi_u$ and ${}^5\Sigma_g^+$ and that of the ${}^7\Sigma_u^+$ state of neutral N_2 which is parent state to both anionic states. All curves are calculated at the CCSD(T) level of theory (solid lines). Due to their multiconfigurational character of the dissociation process of the PECs of the neutral quintet states have been extrapolated (dashed lines) for bond lengths longer than 2.2 Å according to the multiconfigurational MRDCI results of Bauschlicher and co-workers [18] (see text). The zero point of the energy corresponds to the dissociation limit into two ground state N (4S) atoms.

neutral parent states ${}^5\Sigma_g^+$ and ${}^5\Pi_u$, we have used the CCSD(T) method only in the region of the corresponding minima and for the calculation of the dissociation limits. For larger bond lengths we have extrapolated the potential energy curves of the neutral quintet states of N_2 according to the results of the multireference double configuration interaction (MRDCI) calculations of Bauschlicher and co-workers [18]. This problem does not occur for the ${}^6\Pi_u$ and ${}^6\Sigma_g^+$ states of N_2^- and the ${}^7\Sigma_u^+$ state of N_2 , because these states represent high spin cases which maintain their single configurational character through the dissociation limit, and, for this reason, are well described by the CCSD(T) approach.

The equilibrium bond length of the neutral parent states ${}^5\Pi_u$ and ${}^5\Sigma_g^+$ have been calculated to be 1.493 and 1.604 Å, respectively (Fig. 3). This is in good agreement with the multireference results of Bauschlicher and co-workers [18] who obtained 1.497 (${}^5\Pi_u$) and 1.611 Å (${}^5\Sigma_g^+$). These authors have found that the

quintet ground state ${}^5\Sigma_g^+$ dissociates into two ground state N (4S) atoms and the ${}^5\Pi_u$ state dissociates into one N (4S) and one N (2D) atom. Since the additional electron occupies the antibonding $3\sigma_u$ orbital in the anionic states, the equilibrium bond lengths are found to be markedly longer compared with the parent quintet states. They are 2.744 and 2.495 Å for the ${}^6\Pi_g$ state and the sextet ground state ${}^6\Sigma_u^+$, respectively. Dissociation here leads to a ground state N (4S) atom and a (hypothetical) N^- (3P) ion. In reality, however, the nitrogen atom does not possess a bound anionic state. The coupled cluster method simulates a shape resonance of the N^- (3P) ion in the dissociation limits of the anionic sextet N_2^- states, i.e. at internuclear distances greater than 3.8 Å (3 Å) where the ${}^6\Sigma_u^+$ (${}^6\Pi_g$) sextet state crosses its parent neutral states (see Fig. 3). This does not affect the interpretation of the results.

Interestingly, the neutral ${}^7\Sigma_u^+$ state is a parent state to both anionic sextet states. The ${}^6\Pi_g$ state gets into the ${}^7\Sigma_u^+$ state by direct single electron emission from the $1\pi_u$ orbital, and the ${}^6\Sigma_u^+$ state by emission from the $3\sigma_g$ orbital. The multireference results of Bauschlicher and co-workers for the essentially repulsive ${}^7\Sigma_u^+$ state are perfectly reproduced by our CCSD(T) calculations (Fig. 3).

Let us first discuss the ${}^6\Pi_g$ anionic state. This state is found to be stable with respect to vertical electron emission. The vertical electron detachment energy is about 3.8 eV with respect to its neutral parent ${}^5\Pi_u$ state and 0.06 eV with respect to the neutral parent ${}^7\Sigma_u^+$ state. Also the adiabatic electron detachment energy of the ${}^6\Pi_g$ state is positive with respect to the ${}^5\Pi_u$ state and accounts to 1.15 eV. However, the minimum of the PEC of the ${}^6\Pi_g$ is energetically above the dissociating tail of that of the ${}^7\Sigma_u^+$ parent neutral state and thus can decay by direct single electron emission out of the $1\pi_u$ orbital. There exists another decay channel for the ${}^6\Pi_g$ state, namely via an optical $1\pi_u \rightarrow 3\sigma_g$ transition from the ${}^6\Pi_g$ to the energetically lower ${}^6\Sigma_u^+$ state (see the electronic configurations of these states given previously). Such dipole-allowed single electron radiative transitions are fast, and for this reason, the ${}^6\Pi_g$ state of N_2^- is expected to be short-lived and not observable in a mass spectrometer.

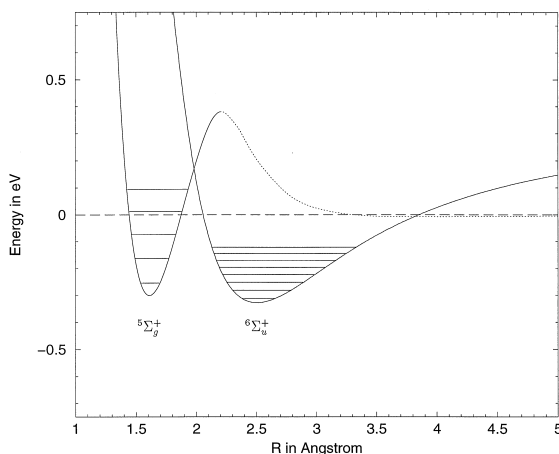


Fig. 4. Comparison of the ${}^6\Sigma_u^+$ state of N_2^- with the corresponding neutral parent ${}^5\Sigma_g^+$ state. The two lowest vibrational levels of the anionic ${}^6\Sigma_u^+$ state are energetically below the lowest vibrational level of the neutral quintet state. The zero point of the energy corresponds to the dissociation limit into two ground state N (4S) atoms of the neutral parent states ${}^5\Sigma_g^+$ and ${}^7\Sigma_u^+$.

Also, the ${}^6\Sigma_u^+$ state is found to be stable with respect to vertical electron emission. Both neutral parent states lie about 0.8 eV above the minimum of the ${}^6\Sigma_u^+$ state. As can be seen from Fig. 3, the well of this anionic state is located energetically below the parent ${}^7\Sigma_u^+$ state and the anion cannot decay into the latter neutral state. The situation is more delicate for the ${}^5\Sigma_g^+$ state. On the one hand, the minima of the anion and the neutral ${}^5\Sigma_g^+$ parent state are at considerable different internuclear distances, and this suppresses a possible decay of the anion due to unfavourable Franck–Condon factors. On the other hand, the energies of the minima differ only by 0.02 eV according to our calculations. For a more definite conclusion, we have to consider zero point corrections for both states. Therefore, we have calculated the vibrational energy levels of the neutral ${}^5\Sigma_g^+$ and the anionic ${}^6\Sigma_u^+$ states by using a standard discrete variable representation (DVR) of the vibrational wave function [19]. As one can see in Fig. 4, two vibrational levels of the anionic ${}^6\Sigma_u^+$ state lie energetically lower than the vibrational ground state of the neutral ${}^5\Sigma_g^+$ minimum. The energy difference between the respective vibrational ground states is 0.05 eV. This means that the two lowest vibrational states of the

${}^6\Sigma_u^+$ minimum are stable with respect to direct single electron emission. From our experience with negative ions (see, e.g. [5]) we expect the anionic state to be further stabilized at even higher theoretical levels and more extended basis sets.

Of course, there are states of N_2^- of lower spin multiplicity than sextet, e.g. ${}^4\Pi_u$, ${}^4\Sigma_g^-$, and ${}^2\Pi_g$ (Fig. 1), that are lower in energy than ${}^6\Sigma_u^+$, and radiative decay into these electronic states is in principle possible. But since all these decay channels are spin-forbidden, they are slow, and do not need to be considered when discussing a lifetime of 10^{-4} – 10^{-5} s. For example, the radiative lifetime for the spin-forbidden transition $a^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ in He_2 has been theoretically as well as experimentally determined to be 10–20 s [20,21]. The same is true for decay via electron emission into energetically low lying states of neutral N_2 , e.g. ${}^3\Sigma_g^+$, ${}^3\Pi_u$, and ${}^1\Sigma_g^+$ (Fig. 1). All these decay channels combine single electron emission with a spin-forbidden deexcitation of an inner-valence electron. In view of these findings the ${}^6\Sigma_u^+$ state is the most likely candidate to be the observed long-lived N_2^- species.

Let us finally compare the long-lived ${}^6\Sigma_u^+$ state of N_2^- with the long-lived ${}^6\Pi$ state of CO^- . As is well known, the energetical order of the $3\sigma_g$ (5σ) and $1\pi_u$ (1π) molecular orbitals is reversed at the level of self-consistent field theory when going from N_2 to CO . Correspondingly, the sextet ground state of these molecules changes from Σ to Π symmetry. As discussed in a recent publication [7], the stable vibrational states of the electronic ${}^6\Pi$ state of CO^- can be explained as a loosely bound complex of a C^- (${}^4S^0$) ion and an O (3P) atom at an equilibrium distance of 3.5 Å (Fig. 2). The binding of the complex can be nicely described by a simple electrostatic point charge model polarizing the oxygen atom. The electronic stability of the ${}^6\Pi$ state can then be rationalized by the positive electron affinity of the carbon atom.

This explanation does not apply to the long-lived ${}^6\Sigma_u^+$ state of the N_2^- system, because a nitrogen atom does not have a bound anionic state. As soon as the bond of the N_2^- system is fully destroyed, the additional electron is free. In Fig. 3 we can see that this is the case at a bond length of about 3.8 Å, when the

${}^6\Sigma_u^+$ PEC crosses the curve of the neutral parent ${}^7\Sigma_u^+$ state. We note that the equilibrium internuclear distance of the N_2^- system is by as much as 1 Å shorter than that of CO^- . This indicates that an electrostatic model analogous to the CO^- case may not be adequate for N_2^- . If one should wish to consider such a model at all, one could argue that the interaction of the polarized neutral N with the resonance N^- state stabilizes the latter.

In this article, we have investigated long-lived high-spin sextet states of the fundamental N_2^- ion. We have applied a general construction principle for long-lived anionic states of small molecules. The idea is that such states should possess several “equivalent” valence electrons bound to a positively charged ion core. Employing the CCSD(T) method using a standard AUG-cc-pVTZ basis set, we have found that the ${}^6\Sigma_u^+$ ground state possesses a minimum at an internuclear distance of 2.495 Å. To establish the electronic stability of this state, we considered the decay into its neutral parent states via direct single electron emission. These decay channels are found to be closed for the two lowest vibrational levels of the anionic ${}^6\Sigma_u^+$ state. All other decay possibilities of this state are spin forbidden and, therefore, should be slow. In conclusion, we predict that the ${}^6\Sigma_u^+$ state of N_2^- is long-lived, having a lifetime large enough to make observation in a mass spectrometer possible.

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