Long-Lived States of N_2^-

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Stimulated by very recent mass spectrometric observations, we discuss the characteristics of possibly long-lived states of N_2^- and investigate the most promising candidates. Two N_2^- states are identified that exhibit lifetimes several orders of magnitude longer than the famous $^2\Pi_g$ resonance. [S0031-9007(98)05844-X]

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The N_2^- anion is one of the most studied metastable systems to be extensively investigated experimentally as well as theoretically (see, e.g., various articles in [1]). Its famous $^2\Pi_g$ resonance state represents *the* standard example for shape-type resonances and shows a lifetime of about 1.6×10^{-15} sec. In spite of the vast knowledge that has accumulated over the last decades, only recently a far longer lived N_2^- state has been observed in a mass spectrometer, implying a lifetime in excess of 10^{-5} sec [2,3]. In other words, there exists a resonance state of N_2^- that lives at least 10 orders of magnitude longer than the $^2\Pi_g$ resonance. In the following we will discuss possible candidates for this long-lived state and investigate their potential energy curves (PEC) and lifetimes.

Let us begin with some general considerations what a long-lived state of N_2^- has to look like. Since the addition of one electron to the ground state of N_2 gives rise to only short-lived shape resonances [4], one may assume that the observed N_2^- state is derived from an electronically excited neutral parent state. Indeed, it has been pointed out in [3] that in the mass spectrometrical experiments excited states of N_2 and N_2^- are likely to be produced. The excited N_2^- state must then exhibit long lifetimes with respect to autodetachment via one and two electron processes as well as with respect to dissociation. Owing to the latter requirement we restrict our investigations to states derived from the lowest excited states of the parent N_2. Moreover, in recent investigations of dianionic resonance states of atomic and molecular systems it has been established that systems consisting of a positively charged center and *n equivalent* electrons or ligands, respectively, promise especially long lifetimes [5,6]. Transferring these ideas to the N_2^- system, we add the extra electron to the same orbital ϕ^* the excited electron of the N_2 parent state occupies; therefore, the corresponding N_2^- states read

$$(N_2)^{-1}(\phi^*)^2,$$

where $(N_2)^{-1}$ denotes one hole in the N_2 ground state. By this means the resulting N_2^- states call to mind the picture of two equivalent electrons "bound" to a N_2^+ ion core.

We have examined various N_2^- states of the described type, but most have been found to possess purely dissociative potential curves and are consequently expected to show only short lifetimes. More promising candidates were the $^4\Pi_u$ and $^4\Sigma_g^-$ states that are derived from the N_2 states $A^3\Sigma_u^+$ and $B^3\Pi_g$, respectively. The associated electronic configurations are

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

$$^4\Sigma_g^-\text{: } (\text{core})^4(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^1(1\pi_u)^4(1\pi_g^*)^2,$$

i.e., in the $^4\Pi_u$ and $^4\Sigma_g^-$ state the holes are in the $1\pi_u$ and $2\sigma_g$ orbitals, respectively, and in both N_2^- states the lowest antibonding orbital $1\pi_g^*$ is doubly occupied. We concentrate here on the quartet states, where the two-electron autodetachment processes are spin forbidden.

The PEC of the anionic $^4\Pi_u$ and $^4\Sigma_g^-$ states and their associated N_2 parent states have been computed at the highly correlated coupled-cluster single-double and perturbative triple excitations level of theory [7] using the correlation consistent valence triple-z one particle basis set augmented with an $(spdf)$ set of diffuse functions (AUG-cc-pVTZ) [8,9], i.e., a $[5s4p3d2f]$ set of contracted gauss-type functions placed at both nuclei. Our results are displayed in Fig. 1. The equilibrium bond lengths of the two N_2 parent states are 1.2902 Å ($^3\Sigma_u^+$) and 1.2177 Å ($^3\Pi_g$), respectively, in correspondence with experimental

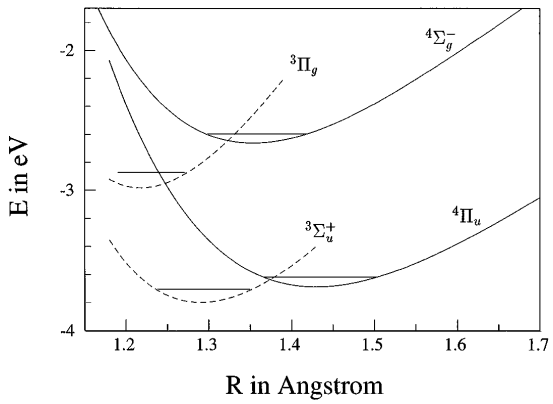

FIG. 1. Potential energy curves of the $A^3\Sigma_u^+$ and $B^3\Pi_g$ states of N_2 (dashed lines) and the associated $^4\Pi_u$ and $^4\Sigma_g^-$ states of N_2^- (full lines). The lowest vibrational level of each potential curve is indicated.

and other *ab initio* data (see, e.g., [10]). In the anionic states the excess electron occupies the antibonding π_g^* orbital, and consequently the bond lengths are found to be distinctly longer, 1.4298 Å ($^4\Pi_u$) and 1.3540 Å ($^4\Sigma_g^-$), respectively. Regarding the electronic stability, both anionic states are found to be stable with respect to vertical autodetachment by 0.28 and 0.20 eV, respectively, but the adiabatic electron detachment energies are negative, -0.11 and -0.32 eV, respectively. Since all these values are close to zero, the zero-point correction can play an important role; but before we discuss our findings in detail let us introduce some notation. We refer to the energy difference between the minima of the neutral and the associated anionic PEC as ΔE_0 and to the corresponding zero-point corrected quantity, i.e., to the difference between the lowest vibrational levels of the associated potential curves as ΔE_e. The latter will be called binding energy of the anion throughout the paper.

It is, in general, extremely difficult to compute accurate binding energies of atomic or small molecular anions [11]. At the employed level of theory the errors are expected to be less than a few tenths of an eV, but changes of this size decide on the very stability of the investigated species. Especially for the $^4\Pi_u$ state the binding energy is very close to zero ($\Delta E_e = -0.08$ eV, $\Delta E_0 = -0.11$ eV), and we expect both anionic states to be further stabilized at even higher theoretical levels and more extended basis sets. For example, the addition of a second $(spdf)$ set of diffuse functions to the AUG-cc-pVTZ basis set yields a slightly less negative ΔE_0 (-0.098 eV). Moreover, the bond length of the anionic state is increased by 0.002 Å, whereas that of the $^3\Sigma_u^+$ parent state is virtually unchanged. Thus, despite using the large AUG-cc-pVTZ basis the neutral states are still clearly favored by the basis set. On the other hand, in the anionic states the number of electrons is by one larger than in the corresponding neutral species, and, thus, there is more correlation energy in the former. Hence, our results can be viewed as a "lower bound" to ΔE_e. Nevertheless, we can conclude only that the binding energy of the $^4\Pi_u$ state is close to zero, but we cannot decide on its sign. Far more costly computations would be needed to settle this issue and we doubt that presently any practical method is able to accomplish this task.

So far we have established two excited N_2^- states that are stable with respect to dissociation and vertical electron loss. For both states decay via two-electron processes is spin *and* symmetry forbidden, and we expect the corresponding lifetimes to be sufficiently long for all practical purposes. Regarding adiabatic electron loss we cannot draw any final conclusions, since the associated energy differences are in the order of or less than 0.1 eV, respectively, which is beyond the accuracy of any presently available method. Especially the $^4\Pi_u$ state is found to be at the threshold of stability, and we expect it to be further stabilized if higher theoretical levels are employed. Thus, the N_2^- $^4\Pi_u$ state is very likely to possess a long lifetime and may consequently be invoked to explain the recent experiments [2,3].

If—despite the expected stabilization—ΔE_e is slightly negative, the $^4\Pi_u$ state can, nevertheless, exhibit a long lifetime, since its bond length is notably longer than that of its neutral parent, and, consequently, the Franck-Condon factor for the detachment process will be small. In other words, the region in coordinate space where electron detachment is possible and the region experienced in the zero-point motion of the $^4\Pi_u$ state barely overlap (Fig. 1). We have, consequently, studied the lifetime τ of the $^4\Pi_u$ state in dependence of ΔE_e. For positive ΔE_e electron loss is obviously not possible, and $\tau = \infty$. For negative ΔE_e, however, the vibrational state is turned into a resonance and in the following we aim at giving a lower bound for its lifetime provided our *ab initio* data were correct. Moreover, our study will reveal for which values of $\Delta E_e < 0$ the detection in a mass spectrometer is still possible. In the subsequent paragraphs we will outline the theoretical background needed to compute the detachment lifetime τ and discuss the results for the $^4\Pi_u$ state.

It is well known that resonances can be viewed as discrete states embedded in and interacting with a continuum [12–15]. This interaction converts the discrete state into a resonance, and the vibrational motion in the resonance state is described by an energy-dependent *nonlocal* complex potential [16,17]

$$\mathcal{V}_n = V_d + \Delta(E - H_0, R) - \tfrac{1}{2} i\Gamma(E - H_0, R), \quad (1)$$

where V_d is the potential for the vibrational motion in the discrete state that acquires a width $\Gamma(E, R)$ and is shifted by $\Delta(E, R)$. E is the kinetic energy of the incident electron (the energy of the target is chosen to be 0), H_0 is the Hamiltonian describing the vibrational motion of the target state and, thus, the width and the shift are not simply functions of E and R, but depend on the nuclear kinetic energy operator.

Instead of the nonlocal potential $\mathcal{V}_n$, the approximation of a *local* complex potential

$$\mathcal{V}_l = V_d + \Delta(R) - \tfrac{1}{2} i\Gamma(R), \quad (2)$$

which depends on the internuclear distance R only, has been introduced [18–19]. The local approximation clearly breaks down close to threshold, but so far direct comparisons of local and nonlocal potentials are rare [21], and to our best knowledge the threshold behavior of a single vibrational resonance has not been studied for realistic systems.

Let us return to the $^4\Pi_u$ N_2^- state and the quantities characterizing its vibrational motion. V_d is just the potential curve shown in Fig. 1. The level shift functions $\Delta(E, R)$ and $\Delta(R)$ are expected to be small and negative at threshold [20,21]. Thus, the level shift will only slightly stabilize the resonance state, and we will neglect it subsequently. The local width function $\Gamma(R)$ has been computed employing the complex absorbing potential (CAP) method. This

method has been described in [22] and allows us to compute the lifetimes of electron scattering resonance states in the fixed-nuclei picture. A CAP can, in principle, be used in conjunction with any theoretical method [23], and our CAP calculations for the $^4\Pi_u$ state have been performed at a static-exchange-like level. That is, only the two π_g^* electrons have been treated explicitly, whereas the N_2^+ ion core has been frozen. At this level the lifetime is expected to be considerably underestimated, since the core of the target cannot adapt to the incoming projectile. Our results for the local width function are shown in the upper panel of Fig. 2, where the R value for $\Gamma(R) = 0$ has been taken as the crossing point R_c of the $^4\Pi_u$ and $^3\Sigma_u^+$ potential energy curves in Fig. 1.

From the local width function $\Gamma(R)$ we have obtained an energy-dependent width function $\Gamma(E)$ that was then used in our nonlocal calculations

$$\Gamma(E) = \Gamma\big(R(E)\big)\,, \tag{3}$$

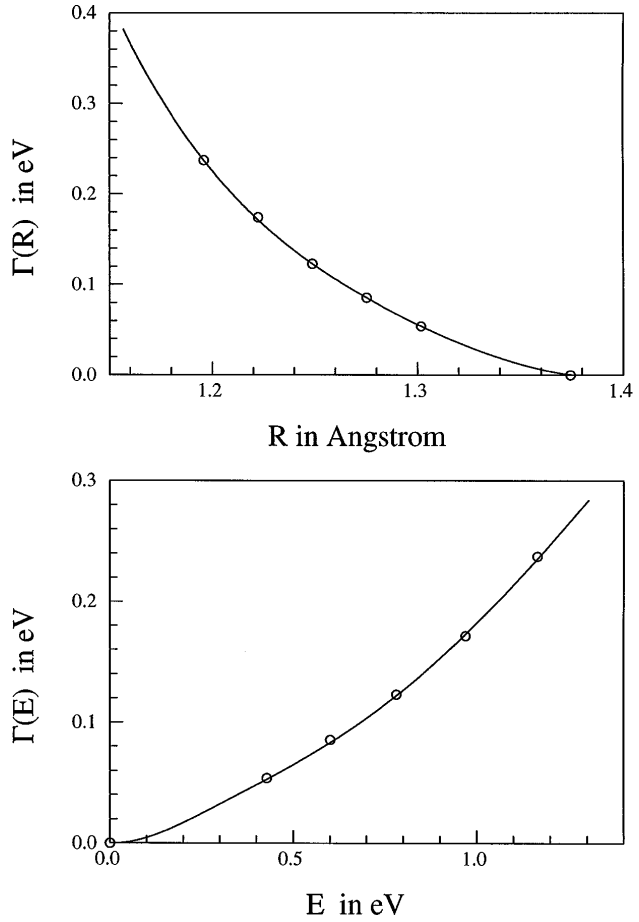

FIG. 2. In the upper panel the local width function $\Gamma(R)$ of the $^4\Pi_u$ state is shown. The value for $\Gamma(R) = 0$ has been taken as the crossing point of the $^3\Sigma_u^+$ N_2 and the $^4\Pi_u$ N_2^- state (Fig. 1) and the continuous line represents a cubic spline. In the lower panel the associated energy-dependent width function $\Gamma(E)$ is displayed. Here the continuous line represents the fit to an analytic form that exhibits the correct threshold behavior.

where $R(E) < R_c$ corresponds to the nuclear distance where the energy gap between the neutral and anionic PEC equals E. The $\Gamma(E)$ values obtained in this way have then been fitted to an analytic expression given in [21] that exhibits the correct threshold behavior

$$\Gamma(E) \propto E^{5/2} \quad \text{for } E \to 0\,. \tag{4}$$

The obtained energy-dependent width function is shown in the lower panel of Fig. 2. Clearly, $\Gamma(E)$ is only an approximation to the width function in Eq. (1) that depends also on R. However, one may expect the R dependence of $\Gamma(E, R)$ to be much weaker than its E dependence [20,21], and in the present context $\Gamma(E, R)$ is needed to close to threshold where the E dependence is expected to dominate in any case. The latter fact is reflected by the small R range ($<$0.3 Å), where $\Gamma(R) > 0$ and that is experienced in the zero-point motion.

Having established a local and a nonlocal width function, we now turn to the vibrational motion described by $\mathcal{V}_l$ and $\mathcal{V}_n$. In the local calculations a standard discrete variable representation (DVR) of the vibrational wave function has been used [24]. For the nonlocal calculations the eigenfunctions of the $^3\Sigma_u^+$ parent state have been computed first (using the DVR), and the wave function of the anionic state has been expanded in these eigenfunctions to facilitate the evaluation of the matrix elements $\Gamma(E - H_0)$. The lifetime of the vibrational levels is then obtained from the imaginary parts of the respective eigenvalues. This procedure has been repeated for different ΔE_e values, i.e., the N_2^- potential energy curve has been shifted vertically, which entails a corresponding shift in the $\Gamma(R)$ and $\Gamma(E)$ functions. The results for the ΔE_e dependent lifetimes τ_l (local) and τ_n (nonlocal) are displayed in Fig. 3. As expected, only the nonlocal lifetime exhibits the correct threshold behavior $\tau_n \to \infty$ for $\Delta E_e \to 0$. In contrast, τ_l tends to a constant corresponding to the imaginary potential that even for $\Delta E_e = 0$ is experienced by the exponentially vanishing tail of the vibrational wave function.

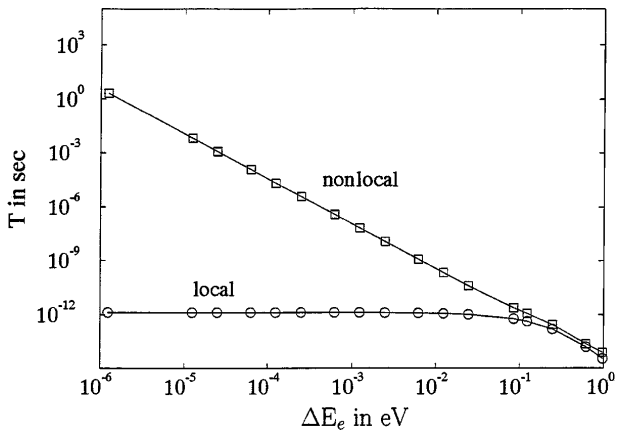

FIG. 3. ΔE_e dependent lifetimes of the lowest vibrational level of the $^4\Pi_u$ state. Note the logarithmic scales.

Nevertheless, for values of $\Delta E_e > 0.2$ eV, which can still be considered to be close to threshold, both the local and nonlocal approaches yield lifetimes of the same order of magnitude. Thus, even if only one or two vibrational states of the neutral parent are accessible the local approximation can provide reasonable lifetimes. In the present context, however, only the nonlocal theory provides an adequate description.

Taking the binding energy obtained from our *ab initio* calculations ($\Delta E_e = 0.08$ eV ≈ 690 cm^{-1}), we find a lifetime of $\tau_n \approx 2 \times 10^{-12}$ sec. This lifetime is far longer than that of the famous $^2\Pi_g$ resonance state but clearly too short to allow the detection in a mass spectrometer. Remember, however, that the ΔE_e value from the *ab initio* calculations, the neglect of the level shift Δ, and the theoretical level at which the local width function has been obtained lead to a very conservative estimate of the lifetime. As discussed above, at higher levels of electron structure theory, we expect a considerable decrease in the width function for fixed nuclei as well as a stabilizing shift of the anionic PEC of the order of 0.1 eV. Our findings show that even if this shift is not sufficient to change the sign of ΔE_e, the $^4\Pi_u$ state of N_2^- may still live a long time on a mass spectrometric time scale.

In this communication we have investigated long-lived states of the N_2^- anion. Employing high level *ab initio* methods, we have found the $^4\Pi_u$ and $^4\Sigma_g^-$ states, which can be derived from the $^3\Sigma_u^+$ and $^3\Pi_g$ parent states of N_2, to be stable with respect to dissociation and vertical electron autodetachment. For both anionic states, decay by deexcitation followed by electron detachment is spin as well as symmetry forbidden; thus, we expect both states to exhibit long lifetimes with respect to two-electron decay processes. Regarding adiabatic electron loss, both states have been found to be unstable, but especially the $^4\Pi_u$ state is on the verge of stability. Higher theoretical levels are expected to stabilize the anionic states further, but presently we cannot draw any final conclusions. Since the relevant energy differences are tiny, far more elaborate methods are needed to decide this issue. Consequently, we have calculated the dependence of the autodetachment lifetime of the $^4\Pi_u$ state on its binding energy.

Both local and nonlocal complex potentials have been used to describe the vibrational motion of the anionic $^4\Pi_u$ state. It is known that the local approximation does not show the right threshold behavior, but it, nevertheless, yields acceptable lifetimes down to an energy difference of $\Delta E_e \approx 0.2$ eV, i.e., down to energies where only one or two vibrational states of the neutral parent are accessible. For the $^4\Pi_u$ state ΔE_e is less than 0.1 eV, and, thus, only the nonlocal width function accounts for an adequate description. Using the ΔE_e value obtained from our *ab initio* calculations and the width function $\Gamma(E)$ computed at a static-exchange-like level of theory, the lifetime of the $^4\Pi_u$ state is about 2×10^{-12} sec. This value represents a lower bound to the lifetime, hence, the $^4\Pi_u$ state lives far longer than any N_2^- states known so far in the literature. Moreover, our findings show that a stabilizing shift of the anionic PEC, which is expected if higher theoretical levels are employed, will lead to a lifetime sufficiently long to allow detection in a mass spectrometer. From our findings and the experience with small anions, we conclude that the $^4\Pi_u$ state is by far the most likely candidate to have been observed in the recent experiments [2,3].

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