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Long-lived states of $N_2{}^-$: Formation, lifetimes, and identity

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Long-lived metastable states of $N_2{}^-$ are generated by sputtering surfaces of TiN or BN with keV Cs^+ ions. The lifetimes of the metastable ions have been measured at the storage ring ASTRID. Experimental investigations of the charge exchange of $N_2{}^+$ ions in alkali-metal vapor and theoretical calculations support the conclusion that the long-lived $N_2{}^-$ species are sextet states, originating from the attachment of an electron to a quintet state of the N_2 molecule. [S1050-2947(99)07911-1]

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I. INTRODUCTION

Atoms like He [1] and Be [2] or molecules like He_2 [3] are unable to form stable negative ions by attaching an electron to the ground state, but all three systems are able to form long-lived (μs-ms) negative ions by attaching an electron to an electronically excited state [4–6]. The conditions for the existence of such long-lived metastable states are usually as follows. Positive electron affinity with respect to the electronically excited state of the parent atom; forbidden radiative transitions; spin- or symmetry-forbidden autodetachment for at least one of the fine-structure components; stability with respect to dissociation and vertical electron detachment for molecular ions; and weak interaction with the electron continuum wave.

Negative ions of N_2 have been studied extensively [7–9] experimentally and theoretically over a long period of time to gain information about the structural and dynamic properties of these ions and their role in atmospheric processes. It is well established that the nitrogen molecule is unable to form a stable negative ion by attaching an electron to its ground state, but short-lived states of $N_2{}^-$ can be formed by scattering electrons on N_2. The short-lived species represent attachment of an electron to either the ground state or to an excited singlet state of molecular nitrogen. Until a few years ago, all the $N_2{}^-$ resonances which had been observed exhibited very short lifetimes (ps or shorter) with the well-known ${}^2\Pi_g$ resonance being described as a typical shape-type resonance [10]. In 1997, however, Gnaser [11] and Middleton and Klein [12] reported the observation of a much longer-lived $N_2{}^-$ ion. It was formed by sputtering surfaces of TiN or TiAlN. The efficiency for producing the long-lived $N_2{}^-$ ion was rather low with only one molecular negative ion being formed per 10^7 sputtered N atoms [11]. A lower limit for the lifetime of this long-lived $N_2{}^-$ ion could be estimated to be 10 μs, based on the time the ions used to pass from the ion source to the detection facility. Preliminary lifetime studies performed at a modified tandem accelerator have indicated that the lifetime may be much longer than 10 μs [13].

Stimulated by the mass-spectroscopic observations by Gnaser [11], Sommerfeld and Cederbaum performed *ab initio* calculations of quartet states of $N_2{}^-$, which could be potential candidates for the long-lived metastable state [14]. They proposed that the ${}^4\Pi_u$ state of $N_2{}^-$, formed by attaching an electron to the lowest-lying triplet state of N_2, ${}^3\Sigma_u^+$, was the most likely candidate to explain the experimental findings. The ${}^4\Pi_u$ state has the configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^3(1\pi_g)^2$, i.e., with a hole in the $1\pi_u$ orbital and with the antibonding $1\pi_g$ orbital being doubly occupied. The ${}^4\Pi_u$ state was found to be stable with respect to vertical autodetachment by 0.28 eV, but the calculated adiabatic electron detachment energy was negative, −0.11 eV. Since it is difficult to perform electron affinity calculations with very high accuracy for molecular systems with as many electrons as the $N_2{}^-$ ion possesses, it was proposed that zero-point corrections could change the sign of the adiabatic value, making the ${}^4\Pi_u$ state stable with respect to Coulomb-induced autodetachment. The only decay channel would then be the spin- and symmetry-forbidden autodetachment to the ground state of N_2, a process expected to happen on a μs-ms time scale.

The theoretical work by Sommerfeld and Cederbaum [14] initiated the present study, a joint experimental and theoretical investigation of the properties of the long-lived $N_2{}^-$ ions, to gain more information about their formation, lifetime, and identity. The experimental part has been focusing on the possible production of the long-lived $N_2{}^-$ ions, either from $N_2{}^+$ ions undergoing charge exchange in alkali-metal vapor or by sputtering surfaces of the nitrogen-containing materials TiN, BN, and NaN_3. In addition, lifetimes have been determined by means of a time-of-flight technique, utilizing the storage ring ASTRID at Aarhus University [15]. The theoretical part has been dealing with calculations of binding energies of $N_2{}^-$ quartet states, using an alternative calculation method to the one applied by Sommerfeld and

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Cederbaum [14], and finally as a consequence of the experimental results reported here, a study of $N_2{}^-$ sextet states which may be formed by attaching an electron to quintet states of molecular nitrogen.

II. EXPERIMENTAL APPROACH

The experimental investigations were performed partly at the Aarhus Storage Ring Denmark (ASTRID) and partly at the Aarhus EN tandem accelerator. ASTRID and the experimental setup used at this facility for measurements of lifetimes have been described before [4,16]. Therefore, only the main parts will be mentioned here. The ring, which is 40 m in circumference, has two 45° bending magnets in each corner, followed by four quadrupole magnets on the straight sections. The $N_2{}^-$ ions were injected into the ring from a 200 keV accelerator. Two different types of ion sources were applied to investigate the production of long-lived $N_2{}^-$ ions: a sputter ion source loaded with the nitrogen-containing compounds TiN, BN, and NaN_3 or a plasma-type ion source [17]. In the former, the surfaces of the solid nitrogen-containing compounds were sputtered with 2 keV Cs^+ ions; the negative ions produced were accelerated, mass- and charge-state analyzed before being injected into the storage ring. In the plasma-type ion source, electron bombardment of molecular nitrogen was utilized to generate intense beams of $N_2{}^+$ in its ground state. The mass- and charge-state analyzed positive ions were passed through a cell containing alkali-metal vapor (potassium), with the purpose of generating negatively charged, molecular nitrogen ions by the charge-exchange process. The negative ions were finally injected as a pulsed beam into the ring. At the tandem accelerator, only the sputter ion source was applied.

The tandem accelerator has been used to investigate the composition of the negative ions formed having a mass very close to 28 amu. In addition to $N_2{}^-$, it was expected that Si^- would be present, the latter as an impurity formed by sputtering of pump-oil deposits on the solid samples. Additional impurities with masses close to 28, such as CO^- or AlH^-, have been observed by Gnaser [11]. He applied thin films of TiAlN on a WC substrate as sputter targets, which proved to contain an appreciable amount of C and O as replacements for N. These impurities have not been observed in the present study. The relative mass resolution at the tandem is approximately 1500, making it difficult to secure a complete separation of these impurities from $N_2{}^-$ and Si^-. Application of the stripping technique available at the tandem accelerator followed by mass analysis at masses 12 (C), 16 (O), and 27 (Al) allows, however, an unambiguous analysis of the species with masses close to 28. After stripping the $N_2{}^-$ ion for some of its electrons, leading to Coulomb explosion of the molecule, the ratios between N and Si were determined for the following combinations of ions: (N^{4+},Si^{8+}), (N^{3+},Si^{6+}), and (N^{2+},Si^{4+}).

At the storage ring the negative ion beam intensity was measured as a function of time by monitoring neutral particles produced by detachment from the $N_2{}^-$ or Si^- ions, by means of a neutral particle detector installed in a chamber behind one of the bending magnets. The average rest-gas pressure in the ring was in the range of 3×10^{-11} mbar, with H_2 being the dominant rest-gas component. Measurements of lifetimes in the range from ~50 μs to fractions of seconds are possible at ASTRID. The lower limit is determined by the revolution time, the upper limit being controlled by the collisionally induced destruction of the negative ions caused by the rest gas. Negative ions with binding energies similar to Si^- [1.389 52(2) eV for the ^4S ground state [18]] will be destroyed by the rest gas, resulting in a mean lifetime of 1–5 s. The experimental conditions for the injected mass 28 ion beam ($N_2{}^-$ or Si^-) can be varied as far as beam energy, beam intensity, or rest-gas pressure are concerned.

III. THEORETICAL CALCULATIONS

A. Calculations of quartet states

A many-body perturbation method for general model spaces [19], previously successfully applied to calculate the electron affinities for atoms like Ar and Ca [20], has been utilized to predict the properties of quartet states belonging to the $N_2{}^-$ ion. Starting with Hartree-Fock optimized molecular orbitals for the $A\ ^2\Pi_u$ state of $N_2{}^+$ with leading configuration $(3\sigma_g)^2(1\pi_u)^3$, the potential-energy curves for the $A\ ^3\Sigma_u^+$ and $B\ ^3\Pi_g$ states of N_2 were calculated around their respective minima. The leading configurations of these states are $(3\sigma_g)^2(1\pi_u)^3(1\pi_g)^1$ and $(3\sigma_g)^1(1\pi_u)^4(1\pi_g)^1$, respectively. The potential-energy curve for the $A\ ^3\Sigma_u^+$ state was obtained with single-reference many-body perturbation theory, complete to third order. A rather extensive basis set of atomic Slater orbitals was used, comprising 22 orbitals of σ symmetry, 14 of π symmetry, and 8 of δ symmetry. Several diffuse $2s$, $2p$, and $3d$ atomic orbitals were included in the basis set. In the case of the $B\ ^3\Pi_g$ state, single-reference perturbation theory turned out to be inadequate and, in addition to the leading configuration given above, the three excited configurations $(3\sigma_g)^1(1\pi_u)^2(1\pi_g)^3$, $(2\sigma_u)^1(3\sigma_g)^2(1\pi_u)^3(1\pi_g)^2$, and $(2\sigma_g)^1(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^1$ had to be included. Due to the technical complexity of the multireference method, the perturbation expansion had to be terminated after the second order in this case.

The $^4\Pi_u$ and $^4\Sigma_g^-$ states of $N_2{}^-$ with the leading configurations $(3\sigma_g)^2(1\pi_u)^3(1\pi_g)^2$ and $(3\sigma_g)^1(1\pi_u)^4(1\pi_g)^2$, respectively, were handled with the same basis of atomic Slater orbitals as in the neutral case. Hartree-Fock optimized molecular orbitals for the $^4\Sigma_g^-$ state were used for the perturbation expansion in both cases. For the $^4\Pi_u$ state, a single-reference expansion was found to be adequate, whereas a multireference method had to be used for the $^4\Sigma_g^-$ state, with the two excited configurations $(3\sigma_g)^1(1\pi_u)^2(1\pi_g)^4$ and $(2\sigma_u)^1(3\sigma_g)^2(1\pi_u)^3(1\pi_g)^3$ added to the leading one.

B. Calculations of sextet states

The two lowest-lying sextet states of $N_2{}^-$ are $^6\Pi_g$ with the configuration $(3\sigma_g)^1(1\pi_u)^3(1\pi_g)^2(3\sigma_u)^1$ and $^6\Sigma_u^+$ with the configuration $(1\pi_u)^2(1\pi_g)^2(3\sigma_u)^1$. These states are obtained from the doubly excited $^5\Pi_u$ and $^5\Sigma_g^+$ states of N_2 by attachment of an electron to the $3\sigma_u$ orbital. Both of the anion states dissociate into $N(^4S)+N^-(^3P)$. The $^5\Sigma_g^+$ state dissociates into the ground-state atoms $N(^4S)+N(^4S)$

and the $^5\Pi_u$ state into the excited channel $N(^4S)+N(^2D)$. Since the $^5\Pi_u$ state has a significantly higher energy than the remaining considered states, it will not be discussed further.

The potential-energy curves of the quintet and sextet states were examined using the *augmented* correlation-consistent polarized valence triple-zeta (AUG-CCP VTZ) basis set [21] and the complete active space self-consistent field (CASSCF) method [22] with the valence electrons distributed in an active orbital space comprising the $2s$, $2p$, and $3p$ orbitals of each atom. The CASSCF method can be applied to all regions of a potential-energy curve, but does not produce very accurate results, as the method does not include dynamic correlation. The lack of dynamic correlation has been compensated for by adjusting the potential-energy curves, so that the asymptotic energy separations are in agreement with experiment. To obtain the quantitative correct results from *ab initio* calculations, one must use a more extensive correlation method and a significantly larger basis set.

One could argue that an active space comprising only the valence orbitals $2s$ and $2p$ should be sufficient to give the essential features of the potential-energy curves. For the anion states this choice is problematic considering that the dissociation limit contains both a neutral and a negatively charged atom. The $2p$ wave functions should be more diffuse for the negatively charged atom than for the neutral. If, however, only a pair of p orbitals is occupied, the $D_{\infty h}$ symmetry of the molecule enforces the $2p$ orbitals of the two atoms to be identical. This problem may be bypassed by reducing the symmetry to $C_{\infty v}$, but a more satisfying approach is to keep the correct symmetry and include a second set of p orbitals in the active space. In accordance with the discussion above, one finds that the CASSCF method produces erratic energies for the anion at long internuclear distances unless the symmetry is lowered to $C_{\infty v}$.

IV. RESULTS

A. Production of long-lived N_2^- ions

The charge-exchange experiments, starting with intense beams of N_2^+ (more than 50 μA) and passing the positive ion beam through a cell containing alkali-metal vapor, showed no evidence of the formation of long-lived, negative molecular nitrogen ions. The upper limit for production of long-lived N_2^- ions from N_2^+ ions could be estimated to be $\sim 5\times 10^{-10}$. This result is in good agreement with previous investigations by Bae *et al.* [23], but in contradiction with those of Hiraoka *et al.* [24], who reported the observation of small quantities of metastable N_2^-, which they proposed could originate from the $^4\Pi_u$ state, provided at least one vibrational level was located below the lowest triplet state, $A\ ^3\Sigma_u^+$, of N_2.

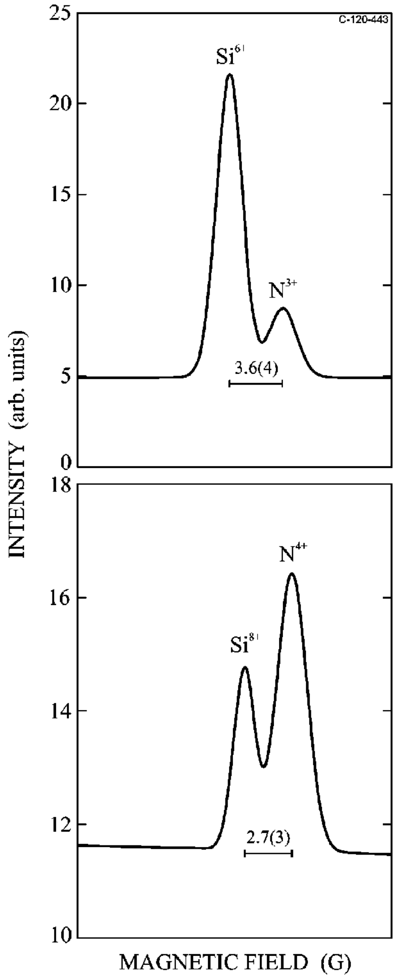

FIG. 1. Accelerator mass spectrum of mass 28 produced from sputtering of TiN at terminal voltage 5.1 MeV. Upper section: The two peaks are separated by 3.6(4) G by the analyzing magnet compared to a calculated mass difference of 3.4 G. Lower section: The two peaks are separated by 2.7(3) G compared to a calculated mass difference of 2.9 G.

The yield of long-lived N_2^- ions produced from TiN and BN was roughly the same, whereas no N_2^- formation was observed by sputtering of NaN_3. These three compounds were selected for the sputtering experiments since they exhibit different environments for the N atoms in the solid targets. TiN has a NaCl structure and may be regarded as cubic close-packed arrangements of Ti atoms with N atoms in the octahedral holes. The nitrogen atoms thus have two types of neighbors: N and Ti atoms. BN has a graphitelike structure with B and N atoms alternating in the layer, but the structure differs from graphite in having the hexagons directly under one another (B under N). Thus a N atom will always have a different type of atom, in this case a B atom, as its nearest neighbor, contrary to TiN. In NaN_3, the N_3^- ion is linear. By heating NaN_3, N_2 will be generated. If it is important for the formation of a long-lived N_2^- ion that a molecular precursor is present in the solid phase—TiN and NaN_3 have neighboring N atoms—then the production of long-lived N_2^- ions would be expected to be favored by applying these two substances for sputtering. If, on the other hand, the long-lived N_2^- ion is generated via interaction between two sputtered N atoms and the Cs coated surface in the ion source, then it may be expected that TiN and BN can act as suitable sputtering materials, whereas NaN_3 may be less effective. Figure 1 illustrates the relative yields of N^{n+} and Si^{2n+} ($n=3$ and 4) measured at the tandem accelerator after stripping of the 5.1 MeV N_2^- ions. The +4 charge state was favored for both N and Si at the selected accelerator voltage. The ratios N^{4+} to Si^{8+}, N^{3+} to Si^{6+}, and N^{2+} to Si^{4+} were measured to be 2, 0.2, and 0.04, respectively. Detailed analysis was performed at the tandem accelerator to secure that the N-containing peaks (N^{4+}, N^{3+}, and N^{2+}) did

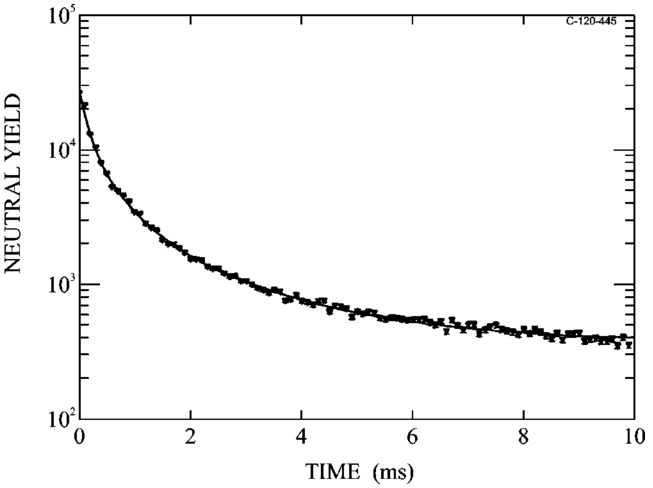

FIG. 2. Semilogarithmic plot of the neutral particle signal (N_2 and Si) as a function of time after injection of a 100 keV N_2^- beam. The solid curve represents a fit to four exponentials.

originate from N_2^- and not from other N-containing molecules with mass 28, such as $^{14}N^{13}CH$ or $^{14}N^{12}CH_2$, but there was no indication of such a contamination.

B. Lifetime data

An ~25 pA beam of N_2^- ions, generated by sputtering TiN, was used for the lifetime measurements. Since the tandem accelerator investigation had shown the mass 28 yield to be a mixture of N_2^- and Si^-, a reference measurement was performed using a pure Si^- beam produced by sputtering a pure Si surface. Si^- is known to possess three stable terms belonging to the $3p^3$ configuration ^4S, ^2D, and ^2P, with binding energies of 1.389 521 (20), 0.527 234(25), and 0.029(5) eV, respectively [18,25]. The investigation of the lifetime of the Si^- beam showed the presence of a short-lived component, fitted to 2.0(2) ms, with the stated uncertainty reflecting the span of lifetimes obtained when disregarding data points from the first few round trips in the storage ring. In addition, a long-lived component (1–5 s) was present. Such a long-lived component can be attributed to the strongly bound ^4S and ^2D states undergoing electron detachment due to collisions with the rest gases, whereas the short-lived component can be assigned to the weakly bound ^2P state. Previous studies of weakly bound states of negative atomic ions, such as Ca^- [26], Sr^- [27], and Ba^- [28], exhibiting binding energies in the range from 24 meV [26] to 144 meV [28], have shown that such states will appear as decay components with lifetimes in the range 0.5–10 ms.

A typical decay curve obtained with the N_2^- beam is shown in Fig. 2 on a semilogarithmic scale, illustrating a number of not clearly resolvable lifetime components. In fitting the data, two of the components were fixed at the values dictated by the Si^- decay curve. The minimum number of exponentials required to give a reasonable fit to the decay curve for the N_2^- beam is four, meaning that at least two different components which can be attributed to N_2^- are present. Due to the very rapid initial decay, only the first three data points can be disregarded, which is just on the edge of influence from initial state effects (such as slit scattering). The results obtained for the two components attributed to N_2^- are 120(15) and 515(25) μs, respectively, with the uncertainty representing one standard deviation. These results are independent of varying the lifetimes for the Si^- components within the ranges of 1.8–2.2 ms and 1–5 s, since these longer-lived components have a negligible influence on the lifetime determination of the shorter-lived components.

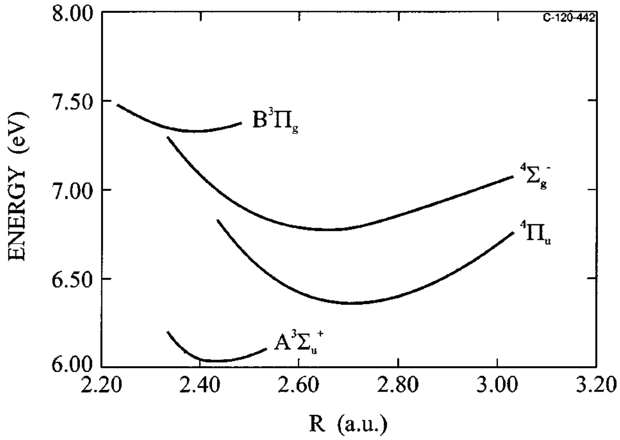

FIG. 3. Potential-energy curves for the $^4\Pi_u$ and the $^4\Sigma_g^-$ states of N_2^- and the associated $^3\Sigma_u^+$ and $^3\Pi_g$ parent states of N_2.

C. Calculations of quartet states

The fact that the long-lived N_2^- ions can only be formed in a sputter process and not by charge exchange of N_2^+ ions provides evidence against a long-lived quartet state of N_2^-, which has as a parent a triplet state of N_2. This observation has initiated calculations of the potential-energy curves associated with the $^4\Pi_u$ and $^4\Sigma_g^-$ states of N_2^-, using a different calculation method from that applied by Sommerfeld and Cederbaum [14]. Figure 3 shows the result of the calculations.

The energies are calculated with reference to a computed third-order many-body energy of the N_2 ground state at the internuclear distance $R = 2.068$ a.u. For the $A\ ^3\Sigma_u^+$ state of N_2, a minimum in the energy is calculated to be 6.04 eV at

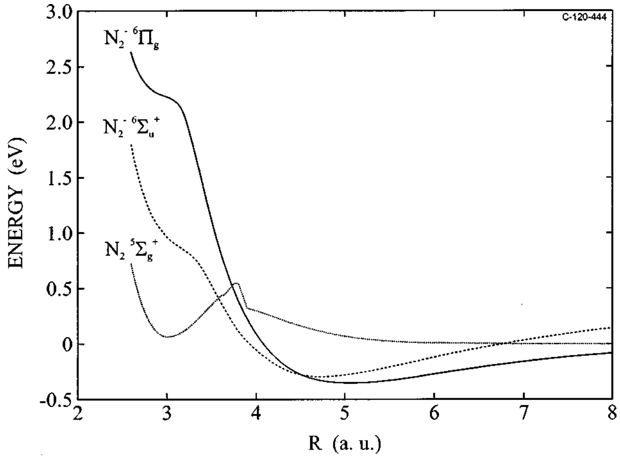

FIG. 4. Potential-energy curves for the $^6\Sigma_u^+$ and $^6\Pi_g$ states of N_2^- and the associated $^5\Sigma_g^+$ state of N_2.

$R=2.43$ a.u. in good agreement with the experimental values of 6.17 eV and 2.431 a.u. [7]. For the $B\ ^3\Pi_g$ state of N_2, the computed excitation energy at the minimum at $R=2.38$ a.u. is 7.31 eV, which should be compared with the experimental values of 2.294 a.u. and 7.35 eV [7]. The energetic lowest-lying negative-ion state, $^4\Pi_u$, exhibits a minimum at $R=2.73$ a.u. of 6.36 eV and thereby a negative adiabatic electron affinity with respect to the $A\ ^3\Sigma_u^+$ neutral parent state of 0.32 eV. For the higher-lying $^4\Sigma_g^-$ state, the computed minimum energy is 6.77 eV at $R=2.65$ a.u., which yields a positive adiabatic electron affinity of 0.54 eV with respect to the $B\ ^3\Pi_g$ parent state. The $^4\Sigma_g^-$ state will, however, be unstable with regard to autodetachment to the lowest-lying triplet state with a lifetime estimated by a many-body method to be only 2×10^{-15} s [19]. Hence, the computed properties for the lowest-lying quartet states of N_2^- do not support the proposal [14] that a quartet state most likely could explain the existence of the long-lived N_2^- ions.

D. Calculations of sextet states

Figure 4 shows the potential-energy curves for the $^6\Sigma_u^+$ and $^6\Pi_g$ states of N_2^- and the $^5\Sigma_g^+$ state of N_2. As mentioned above, the potential curves for the anion were adjusted to give the correct asymptotic energy difference, corresponding to an electron affinity of $N(^3P)$ of -0.07 eV [29]. The asymptotic energy of the quintet state has been set to zero. Both sextet states exhibit minima in the potential-energy curves and these minima are below the minimum electronic energy of the quintet state, which near 4 a.u. exhibits a complicated behavior (probably an avoided crossing). The sextet states are thus predicted to be stable with respect to dissociation and electron detachment. The equilibrium distance and dissociation energy of the $^6\Sigma_u^+$ state are predicted to be 4.7 a.u. and 0.30 eV, respectively, whereas the $^6\Pi_g$ state is predicted to have an equilibrium geometry of 5.0 a.u. and a dissociation energy of 0.35 eV. At the current level of approximation it is not possible to establish which of the two sextet states has the lowest energy. The limited accuracy is evident from the calculation on the quintet state, which is predicted to be slightly unstable.

Using a variational calculation on the vibrational states, one obtains a harmonic frequency of about 0.03 eV for each of the sextet states, indicating that the lowest-lying sextet state may have a significant number of vibrational states that will be stable with respect to dissociation as well as with respect to electron detachment. A more accurate calculation including dynamic correlation and a larger basis set will favor the above equilibrium geometries and further stabilize the anion states with respect to dissociation.

V. DISCUSSION

The present investigation has shown that long-lived metastable N_2^- ions can be formed by sputtering substances like TiN or BN, but not from N_2^+ ions via charge-exchange processes. This provides evidence against a long-lived quartet state of N_2^-, which has a parent triplet state of N_2, as supported by our calculations. The calculated potential-energy curves for two sextet states, on the other hand, exhibit the properties expected for a long-lived metastable state, in particular positive adiabatic electron affinity and spin-forbidden autodetachment to lower-lying triplet or singlet states of N_2. The two electronic sextet states could account for the measured lifetimes, which should most likely be regarded as average values over some of the vibrational states. Presented with our experimental results, Dreuw and Cederbaum have performed a similar theoretical study of possible long-lived sextet states of N_2^- [30]. The two independent calculations have reached the same conclusion, that sextet states may account for the observed long-lived N_2^- ions.

The formation of the long-lived N_2^- ions is assumed to take place via the interaction between two sputtered $N(^4S)$ atoms, forming a quintet state of the N_2 molecule, which is able to bind an extra electron under the conditions present in the sputter ion source (Cs vapor). Snowdon and Heiland have performed optical emission studies of sputtered nitrogen implanted in silicon [31]. They explain the observed Lewis-Rayleigh afterglow by the recombination of two $N(^4S)$ atoms leading to the formation of N_2 in the $^5\Sigma_g$ state, followed by stabilization at the surface and formation of the $B\ ^3\Pi_g$ state of N_2. The stabilization could, however, under the influence of a strong electron donating substance such as Cs vapor, probably also lead to the formation of a N_2^- ion in a sextet state.

Sputtering of solid substances as a method to produce negative atomic ions is well established and routinely applied in many laboratories performing accelerator mass spectrometry or exploring the structural and dynamic properties of negative ions, but it is also well suited for production of negatively charged molecular and cluster ions. The present study indicates that some of these molecular negative ions are formed in long-living high-spin states, constituting a group of molecular systems so far rather unexplored.

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