The electronic spectra of CaN_2^+ and $Ca(N_2)_2^+$

Luis Rodriguez-Santiago

Departament de Química

Universitat Autónoma de Barcelona

08193 Bellaterra, Barcelona, Spain

Charles W. Bauschlicher, Jr.

Mail Stop 230-3

NASA Ames Research Center

Moffett Field, CA 94035

Abstract

The ground and low-lying electronic states of CaN_2^+ are studied at several levels of theory. The results for the $X^2\Sigma^+$ state and the excited $(2)^2\Pi$ state, arising from occupying the Ca $4p$ orbital, are in good agreement with experiment. The analogous states of $Ca(N_2)_2^+$ are studied using the same theoretical approaches, and predictions are made as to the changes caused by the addition of the second N_2 ligand.

I. INTRODUCTION

Understanding the metal-ligand (M-L) interaction is very important. One novel approach is to study the electronic spectra of ML_n^+ systems, thus making it is possible to study the changes in the bonding that arise when the electronic state of the metal is changed. That is, one can study the bonding between a metal s orbital and the

ligand, then excite the metal atom to study the bonding of a metal p orbital with ligand. This can be repeated for multiple ligands to help understand the ligand-ligand interactions, as well as, help understand how the metal-ligand interaction varies with the number of ligands. The changes in bonding and geometry with increasing numbers of ligands can also contribute to our understanding of solvation.

The ML_n^+ systems containing alkaline-earth cations have attracted considerable attention since they have strong s to p transitions, which make the experiments tractable[1-5]. This experimental interest, along with the fact that the alkaline-earths are much easier than transition metals to treat accurately, has resulted in computational studies[6,7] of these systems.

Pullins et $al.$ have recently studied[5] the CaN_2^+ system. They observed the $(2)^2\Pi(4p) \leftarrow X^2\Sigma^+(4s)$ transition, where the character of the open-shell Ca orbital is given in parentheses. They were able to determine the excitation energy, the binding energies of both states, geometries, and some vibrational frequencies. This experimental work supplies an excellent calibration for theory. It is of special interest to see how well density functional theory (DFT) does on these systems. After calibrating theory for the CaN_2^+ system, theory can then be applied to the system with two N_2 ligands to make predictions of the changes caused by the second ligand. In this manuscript, we report on such calculations for CaN_2^+ and $Ca(N_2)_2^+$.

II. COMPUTATIONAL METHODS

The systems are studied using several methods. Hartree-Fock (HF) is the simplest approach and it does not include any electron correlation; we use both the spin-restricted (R) and spin-unrestricted (U) approaches for the open-shell systems. Electron correlation is added to the RHF reference using the coupled cluster singles and doubles approach[8], including the effect of connected triples determined using

perturbation theory[9], CCSD(T). The CCSD(T) calculations are performed using the restricted open-shell approach[10,11]. The Ca $1s - 2p$ and nitrogen $1s$ orbitals are not correlated at the CCSD(T) level. To treat higher states of the same symmetry, we use the complete-active-space self-consistent-field (CASSCF) or state-averaged (SA) CASSCF approaches. To compute the vibrational frequencies, the CASSCF approach is used, with the optimization performed for a single specific state. There is only one active electron in these calculations, so for the lowest state of each symmetry, these CASSCF calculations are equivalent to HF calculations. In the SA-CASSCF calculations, the active space consists of the Ca $3d$, $4s$, and $4p$ orbitals. Since there is only one electron in the active space, these are essentially SA-HF calculations. Electron correlation is included using the multireference configuration interaction (MRCI) approach. The SA-CASSCF configurations of the appropriate symmetry are used as references. Internal contraction[12] (IC) is used to limit the size of the calculation. The importance of higher excitations is estimated using the multireference analog of the Davidson correction. As for the CCSD(T) calculations, the Ca $1s - 2p$ and nitrogen $1s$ orbitals are not correlated at the ICMRCI level. DFT is the simplest approach that includes electron correlation; in general, we use the hybrid[13] B3LYP[14] functional, but the BP86 functional[15,16] is also tried for one state.

Three basis sets are used in this work. Basis set A consists of the 6-31G* nitrogen set[17] and the $(12s\ 8p\ 5d)/[8s\ 6p\ 3d]$ modified[18] Ca basis set of Roos *et al.*[19]. This Ca set has been described in detail previously[20]. In basis set B, the nitrogen set is improved to 6-311+G(2df). For Ca, the two most diffuse p functions are replaced by five functions (0.224, 0.112, 0.056, 0.028, and 0.014) and two f functions are added (0.2 and 0.07). Basis set C consists of the correlation-consistent polarized-valence triple zeta (cc-pVTZ) set[21] for nitrogen and the $(12s\ 15p\ 9d\ 5f\ 2g)/[8s\ 7p\ 7d\ 5f\ 2g]$ Ca set developed by Partridge[22]. This set is sufficiently flexible to describe the ground and low-lying states of Ca and Ca$^+$ and to allow $3s3p$ correlation. Only the spherical

harmonic components of the basis sets are used.

Basis set C is used in all of the RHF/CCSD(T) and SA-CASSCF/ICMRCI calculations. Unless otherwise noted, basis set A is used in the B3LYP, UHF, and CASSCF calculations.

The frequencies are computed at the B3LYP, UHF, and CASSCF levels of theory using analytic second derivatives. The ICMRCI+Q harmonic frequencies are computed using only energies. The UHF and DFT calculations are performed using Gaussian 94[23]. The SA-CASSCF, CCSD(T), and ICMRCI calculations are performed using MOLPRO 96[24]. The CASSCF frequency calculations are performed with DALTON[25]. The ICMRCI+Q vibrational frequencies are computed using SPECTRO[26].

III. RESULTS AND DISCUSSION

In Table I, we compare the Ca^+ excitation energies with experiment[27]. The CCSD(T) $^2D - ^2S$ separation is in very good agreement with experiment, being only 70 cm^{-1} too small. The error in the $^2P - ^2S$ separation is somewhat larger (384 cm^{-1}), but still acceptable. The errors at the ICMRCI level are larger than at the CCSD(T) level. The +Q correction reduces the error, with the $^2D - ^2S$ separation having a smaller error than at the CCSD(T) level. The error in the $^2P - ^2S$ separation is reduced, but it is still larger than at the CCSD(T) level. The relatively small errors at the ICMRCI and ICMRCI+Q levels are encouraging as these methods can treat multiple states of the same symmetry. We should note that the ICMRCI and ICMRCI+Q values in Table I are for a supermolecule calculation, Ca^+—N_2, since this should be more representative of the errors in the molecular systems. If only Ca^+ is treated, the errors in the ICMRCI calculations are reduced by about 200 cm^{-1}. The errors in the B3LYP approach are much larger than for the traditional approaches, with the B3LYP results being only qualitatively correct. In fact, the B3LYP results

4

are no better than the UHF results (15905 and 23500 cm^{-1}) using the same basis set.

We next consider CaN$_2^+$. The leading term in the electrostatic bonding is charge-quadrupole, which favors a linear system. The interaction of the Ca$^+$ $^2S(4s^1)$ ground state with N$_2$ leads to the $^2\Sigma^+$ ground state of CaN$_2^+$. The Ca–N$_2$ repulsion is reduced by polarization of the Ca $4s$ orbital away from the N$_2$ molecule; this involves both sp and $sd\sigma$ hybridization. The Mulliken populations show essentially the same population of the $4p\sigma$ and $3d\sigma$ orbitals. A plot of the open-shell orbital (not shown) is also consistent with an orbital that is neither a pure $sd\sigma$ nor a pure sp hybrid orbital. In Table II the B3LYP and ICMRCI geometries are given. The N-N distance in CaN$_2^+$ is slightly shorter than for free N$_2$, at both levels of theory. The ICMRCI values are in reasonable agreement with those deduced by Pullins et $al.$[5], r(Ca-N)=2.745±0.065 and r(N-N)=1.146±0.1 Å. The biggest difference is that the computed results show a contraction in the N-N distance, while the experiment has been interpreted as showing an expansion. However, both theory and experiment agree that the change in the N-N distance is small. The B3LYP frequencies confirm that this structure corresponds to a minimum—see Table III. The B3LYP Ca-N stretching frequency of 164 cm^{-1} is in good agreement with the experimental value of 171.8 cm^{-1}. The UHF and ICMRCI+Q results have larger errors. The B3LYP approach predicts that the N-N stretching frequency increases relative to free N$_2$, while the UHF suggests that it shifts down slightly. The ICMRCI+Q result supports the B3LYP approach, however, all of the shifts are small.

The Ca$^+$–N$_2$ binding energy is given in Table IV. The computed values are in reasonable agreement with each other. The CCSD(T) value is expected to be the most accurate. Combining this value with the B3LYP frequencies reported in Table III yields a D_0 value of 6.23 kcal/mol, which is in acceptable agreement with the best estimate of 5.0±1.4 kcal/mol made by Pullins et $al.$ Using the CCSD(T) optimized bond length for free N$_2$, instead of the B3LYP value, reduces D_0 by 0.2 kcal/mol.

We consider 6.0 kcal/mol as a lower bound, because optimizing the CaN_2^+ geometry at the CCSD(T) level will increase the D_0 value. Therefore, it appears that the true value must lie near the upper limit of the experimental range.

The $^2D(3d)$ state of Ca^+ plus N_2 will yield a $^2\Pi(3d)$ state, where promoting the Ca $4s$ electron to the $3d\pi$ orbital reduces the Ca–N_2 repulsion and allows Ca donation to the N_2 π^* orbital. Thus the Ca-N_2 bonding in this state should be much stronger than in the ground state. An inspection of Table II and IV confirms this expectation. The Ca^+-N_2 binding energy is much larger and Ca-N distance is significantly smaller than for the ground state. The larger binding energy means that the $^2\Pi - ^2\Sigma^+$ excitation energy is smaller than the Ca^+ $^2D - ^2S$ separation—see Table I. The vibrational frequencies also show the stronger interaction; the Ca-N stretching frequency has increased relative to the ground state and the Ca to N_2 π^* donation has reduced the N-N stretching frequency by almost 400 cm^{-1}. This state is not observed in experiment. At the SA-CASSCF level, the transition moment for $^2\Pi(3d) \leftarrow X^2\Sigma^+(4s)$ is 16.5 times smaller than for the $(2)^2\Pi \leftarrow X^2\Sigma^+$ transition observed in experiment. The small moment coupled with the transition energy means that this state might be difficult to observe.

Exciting the $4s$ electron to the $3d\delta$ orbital, to form the $^2\Delta$ state, decreases the Ca-N_2 repulsion, just as in the $^2\Pi(3d)$ state. However, N_2 has no orbitals of the correct symmetry to accept Ca donation from the $3d\delta$ orbital. Thus it is not surprising to find a binding energy for this state that is between those of the $^2\Sigma^+$ and $^2\Pi(3d)$ states.

Exciting the $4s$ electron to the $3d\sigma$ orbital will produce a $^2\Sigma^+$ state. With the valence electron in the σ space and no Ca electrons to donate to the N_2, we expected this state to be more weakly bound than the $^2\Delta$ state. This expectation is confirmed at the SA-CASSCF level, where the $(2)^2\Sigma^+$ state is found to be about 5 kcal/mol above the $^2\Delta$ state. We do not consider the $(2)^2\Sigma^+$ state further.

Exciting the $X^2\Sigma^+$ $4s$ electron to the $4p\pi$ orbital results in the second $^2\Pi$ state,

which is the upper state observed in experiment. Donation from the $4p\pi$ orbital leads to a state that is more strongly bound than the ground state or the $^2\Pi(3d)$ state, but the $^2\Pi(4p)$ state has a bond length that is intermediate between the $^2\Sigma^+$ and $^2\Pi(3d)$ states. The more compact $3d$ orbital requires a shorter Ca-N bond length than the more diffuse $4p$ orbital. The smaller binding energy but the shorter r(Ca-N) for the $^2\Pi(3d)$ state probably arises from the increased Ca-N repulsion at the shorter distance required for good overlap of the Ca $3d$ and N_2 π^* orbitals. We are unable to treat the $^2\Pi(4p)$ state at the B3LYP level, since it is the second $^2\Pi$ state, so we use the CASSCF and ICMRCI+Q approaches. The computed results (Table III) show that the N-N stretching frequency has hardly changed from free N_2, shifting down 16 cm^{-1} at the CASSCF and down by 2 cm^{-1} at the ICMRCI+Q levels. It is somewhat distressing that experiment has been interpreted as showing a sizable (150 cm^{-1}) upward shift of the N-N stretch in the $(2)^2\Pi(4p)$ state. The small downward shift from theory or the sizable upward shift from experiment are different from the computed results for the $^2\Pi(3d)$ state, where the downward shift was 370 cm^{-1}. The computed Ca-N stretching frequency of 223 cm^{-1} at the CASSCF level and 267 cm^{-1} at the ICMRCI+Q level for the $(2)^2\Pi(4p)$ state are reasonably consistent with the experimental value of 278.7 cm^{-1}. The computed D_0 of 17.6 kcal/mol is smaller than the recommended value[5] of 18.6$\pm$1.4 kcal/mol. The computed r(Ca-N) and r(N-N) values of 2.470 and 1.086 Å, respectively, are in reasonable agreement with experiment, 2.484$\pm$0.067 and 1.165$\pm$0.1 Å. The ICMRCI+Q excitation energy agrees very well with experiment, see Table I, which must be somewhat fortuitous, as the error in the atomic $^2P - ^2S$ separation was about 500 cm^{-1}. Overall the agreement between theory and experiment is good, excluding the ω_e(N-N), where theory and experiment differ on the direction of the shift relative to free N_2.

As noted above, the charge-quadrupole term favors a linear structure. However if the Ca to N_2 donation becomes sufficiently large, the dative bonding can overcome

the electrostatic bonding and a nonlinear structure can result. We have therefore considered side-on bonding. All of the states, except $^2B_2(3d)$, are found to have an imaginary frequency—see Table II. In the other states, such at $^2A_1$, the Ca to N_2 donation is not possible, while for others, the overlap of the Ca orbitals with the N_2 π^* orbitals is very low. It is only for the $^2B_2(3d)$ state, where the occupied $3d$ orbital is in the plane of the molecule, that the donation to the in-plane N_2 π^* orbital is sufficiently large that this structure is a minimum. An inspection of Tables I and IV shows that the $^2B_2$ state is below the $^2\Pi(3d)$ state. A similar situation was found[7] for MgN_2^+.

The bonding in $Ca(N_2)_2^+$ is expected to be similar to that in CaN_2^+. It is therefore not surprising to find a $^2\Sigma_g^+$ ground state. The Ca $4s$ orbital undergoes $sd\sigma$ hybridization, which reduces the electron density on both sides of the Ca^+. Since the two N_2 molecules share the cost of the $sd\sigma$ hybridization, it might initially be assumed that the second N_2 would be more strongly bound than the first, but this is not the case, see Table IV. While the hybridization in $Ca(N_2)_2^+$ is only $sd\sigma$, as noted above, the hybridization in CaN_2^+ involved both $sd\sigma$ and sp. Apparently the sp hybridization is important in reducing the repulsion.

The optimal geometry for the $^2\Sigma_g^+$ state is very similar to that of the CaN_2^+ $^2\Sigma^+$ state—compare Tables II and V. At both the B3LYP and ICMRCI levels the Ca-N distance is slightly shorter for $Ca(N_2)_2^+$. The ICMRCI approach also predicts a small contraction of the N-N distance, but the contraction is probably too small to be meaningful. The vibrational frequencies, compare Table III and VI, show the N-N stretches are very similar for both systems. The average of the σ_u and σ_g Ca-N stretches for $Ca(N_2)_2^+$ is very similar to the Ca-N stretch in CaN_2^+. Thus all of the computed results support the view of similar bonding for the ground states of CaN_2^+ and $Ca(N_2)_2^+$.

We have found a $^2A_1(4s)$ state, where the N_2 molecules still bond end-on to the

Ca, but the angle between the two N_2 molecules is 73.5°. In this case sp and sd hybridization polarizes the Ca $4s$ away from the two N_2. While bringing the two N_2 molecules close together increases the ligand-ligand repulsion, it allows the sp hybridization to mix with the $sd\sigma$ hybridization, as found for the $^2\Sigma^+$ state of CaN_2^+. This structure is about 1 kcal/mol above $^2\Sigma_g^+$ at both the B3LYP and CCSD(T) levels of theory. At the B3LYP level, the barrier connecting the linear and bent structures is 2.3 kcal/mol above the bent structure. The barrier is only 0.5 kcal/mol at the CCSD(T) level, using the B3LYP geometries. With such a small barrier it would be difficult to observe the bent structure. We have also found a bent minima for the $^2B_1$ state derived from the $^2\Pi_g$ state; the $^2B_1$ is about 2 kcal/mol above the $^2\Pi_g$ state. Since these bent structures are above the linear structures and the barrier for the ground state potential is so small, we do not consider the bent structures further.

Exciting the $4s$-like electron into the $3d\pi$ and $3d\delta$ orbitals produces the $^2\Pi_g(3d)$ and $^2\Delta_g(3d)$ states, respectively. The $^2\Pi_g(3d)$ state has a longer Ca-N distance, smaller Ca-N_2 bond energy, and smaller shift in the N-N frequency (relative to free N_2) in comparison with the $^2\Pi(3d)$ state of CaN_2^+. The B3LYP shows 0.38 electrons donated to the N_2 π^* orbital for CaN_2^+, but only 0.21 electrons per N_2 for $Ca(N_2)_2^+$. The populations therefore suggest that the changes between the $^2\Pi(3d)$ state of CaN_2^+ and the $^2\Pi_g(3d)$ state of $Ca(N_2)_2^+$ are due to a reduced dative bonding component. The $^2\Pi_g(3d)$ state is still more strongly bound than the $^2\Sigma_g^+$ state, so the $^2\Pi_g - ^2\Sigma_g^+$ excitation is smaller than the $^2\Pi - ^2\Sigma^+$ excitation energy in CaN_2^+.

At the CCSD(T) level, the $^2\Delta_g$ state shows a small reduction in the Ca-N_2 bond energy compared with the CaN_2^+ $^2\Delta$ state. This is similar to differences between the $^2\Sigma^+$ state of CaN_2^+ and the $^2\Sigma_g^+$ state of $Ca(N_2)_2^+$. That is, in states with little dative bonding, the addition of the second ligand makes only small differences.

The $^2\Pi_u(4p)$ state of $Ca(N_2)_2^+$ is analogous to the $(2)^2\Pi(4p)$ state of CaN_2^+. Since the $^2\Pi_u(4p)$ is the lowest state of this symmetry, it can be treated using the B3LYP

approach; this is different from the $^2\Pi(4p)$ state of CaN_2^+. However, in order to directly compare the two states, the UHF approach is also applied to the $^2\Pi_u(4p)$ state. To our surprise, both approaches yield imaginary frequencies, but for different modes. Previously[28] we have observed observed nonphysical symmetry breaking for the B3LYP approach, but this problem was avoided by using the BP86 functional. However, for this state the BP86 functional also gives an imaginary frequency—see Table VI. The UHF Mulliken populations are very reasonable, showing 0.91 $4p\pi$ electrons on Ca, with 0.09 electrons donated to the N_2 molecules. The B3LYP approach shows only 0.33 $4p\pi$ electrons on Ca and a large donation from the N_2 molecules to the Ca $3d$ orbitals. The basis set is improved from set A to set B, and the B3LYP and UHF calculations repeated. Using the larger basis set, does not eliminate the imaginary frequency at the B3LYP level, but does at the UHF level. In light of the strange populations at the B3LYP level, we suspect that the UHF approach is correct and that the $^2\Pi_u(4p)$ state of $Ca(N_2)_2^+$ is a linear molecule.

At the ICMRCI level of theory, the geometries of the $^2\Pi_u$ and $(2)^2\Pi$ states are very similar, as are the Ca–N_2 bond energies. As observed for the $X^2\Sigma_g^+$ state, the average of the σ_u and σ_g Ca-N stretching frequencies for the $^2\Pi_u(4p)$ state of $Ca(N_2)_2^+$ is very similar to the value for $(2)^2\Pi(4p)$ state of CaN_2^+. As observed for many of the other states, the N-N stretching frequency is at a lower frequency than found in N_2. The π_u bending frequency is very low, as found for the other states of $Ca(N_2)_2^+$. The $^2\Pi_u(4p) \leftarrow X^2\Sigma_g^+$ excitation energy is lower than found for CaN_2^+, but it is still in a region that should be accessible to experiment.

As discussed above, a strong dative interaction can lead to side-on bonding. We have therefore considered this structure for $Ca(N_2)_2^+$. We considered both planar and nonplanar structures. The only minima at the B3LYP level that we found was for the $^2B_{3g}$ state of the planar system, where the in-plane $3d$ orbital is occupied; this state is analogous to the $^2B_2$ state of CaN_2^+. While the $3d$ to N_2 π^* donation makes

this a minima, as noted above for the $^2\Pi_g$ state, the donation per N_2 is reduced when the second N_2 is added; in this case from 0.58 electrons for CaN_2^+ to 0.28 electrons per N_2 in $Ca(N_2)_2^+$. This means that the side-on bonding is less favorable than for CaN_2^+. While it is still bound at the B3LYP level, at the CCSD(T) level, it is above CaN_2^+ $^2B_2+N_2$—see Table IV.

A mixed complex of one end-on and one side-on N_2 is also possible. The B3LYP geometries for this orientation are summarized in Table VII. The states arising from the open-shell in either the Ca $4s$ or out-of-plane $3d$ orbitals are not minima, as expected from the results for CaN_2^+ with a side-on N_2 and $Ca(N_2)_2^+$ with two side-on N_2 molecules. The $^2B_2$ state, with the in-plane Ca $3dyz$ open-shell orbital, is a minimum. The geometries of the mixed structure states are consistent with those found for CaN_2^+ and for Ca^+ with two end-on or two side-on N_2 molecules. It is interesting that the mixed $^2B_2$ state is 7.5 kcal/mol below the $^2\Pi_g(3d)$ state. This is very similar to the 7.9 kcal/mol difference between the $^2B_2(3d)$ and $^2\Pi(3d)$ states of CaN_2^+. The Ca donation to the side-on N_2 is 0.51 electrons for the $^2B_2(3d)$ state of the mixed system; this is very similar to the 0.58 electrons found for the $^2B_2(3d)$ state of side-on CaN_2^+. Therefore unlike the $^2B_{3g}$ state of the planar D_{2h} $Ca(N_2)_2^+$, where the donation per N_2 is dramatically reduced relative to CaN_2^+, adding the end-on N_2 does not significantly reduce the donation to the side-on N_2. Even though the $^2B_2(3d)$ state is below the $^2\Pi_g(3d)$ state, it will probably be very difficult to observe this state in the absorption experiments because of the very small Frank-Condon factors, as is also true for CaN_2^+.

IV. CONCLUSIONS

The results for the $X^2\Sigma^+(4s)$ and $(2)^2\Pi(4p)$ states of CaN_2^+ are in good agreement with experiment. The only significant difference is the N-N stretching frequency in

the $(2)^2\Pi(4p)$ state, where theory predicts a small downward shift relative to free N_2, while experiment shows a 150 cm^{-1} shift to higher frequency. The computed results show that $Ca(N_2)_2^+$ is very similar to CaN_2^+ in many ways; for example, the geometries of the analogous states of $Ca(N_2)_2^+$ and CaN_2^+ are very similar, as are the N_2Ca^+–N_2 and Ca^+–N_2 bond energies. We predict that the Ca^+ $4s$-like to $4p\pi$-like excitation in $Ca(N_2)_2^+$ will be at 16,000 cm^{-1}.

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TABLE I. Computed excitation energies, in cm^{-1}.

System	State[a]	B3LYP	CCSD(T)[b]	ICMRCI	ICMRCI+Q	Expt
Ca^+						
	^2S	0	0	0	0	0
	^2D	10249	13617	13964	13718	13687[c]
	^2P	23545	24956	24571	24853	25340[c]
CaN_2^+						
End-on	$^2\Sigma^+(s)$	0	0	0	0	0
Side-on	$^2B_2(dyz)$	3249	7299	10178	8366	
End-on	$^2\Pi(dyz)$	4617	10058	11751	10902	
End-on	$^2\Delta(dxy)$	9611	12524			
End-on	$^2\Pi(py)$			20425	20463	20510[d]
$Ca(N_2)_2^+$						
Linear	$^2\Sigma_g^+(s)$	0	0	0	0	
Linear	$^2\Pi_g(dyz)$	1827	8286	9856	9269	
Linear	$^2\Delta_g(dxy)$	9282	11493			
Linear	$^2\Pi_u(py)$	9804	15330	16250	16134	
Mixed	$^2B_2(dyz)$	1676	5677			

[a] The character of the open-shell orbital is given in parentheses.

[b] The CCSD(T) calculations are performed at the B3LYP geometries.

[c] Moore[27].

[d] Pullins et $al.$[5], average of the ν_{00} for $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$.

TABLE II. CaN_2^+ optimized geometries, in Å.

Orientation	State[a]	B3LYP		ICMRCI	
		r(Ca-N)	r(N-N)[b]	r(Ca-N)	r(N-N)
End-on[c]	$^2\Sigma^+$(s,0)	2.638	1.104	2.716	1.083
	$^2\Pi$(dyz,0)	2.215	1.134	2.243	1.098
	$^2\Delta$(dxy,0)	2.654	1.104		
	$^2\Pi$(py,0)			2.470	1.086
Side-on[d]	$^2A_1$(s,1)	3.532	1.106		
	$^2B_1$(dxz,1)	3.097	1.106		
	$^2B_2$(dyz,0)	2.294	1.161	2.246	1.143
	$^2A_2$(dxy,1)	2.501	1.134		
	$^2B_2$(py,1)			2.732	1.095

[a] The character of the open-shell orbital and number of imaginary frequencies are given in parentheses. For those systems where the B3LYP results are not given, the CASSCF results are used to count the imaginary frequencies.

[b] For comparison the B3LYP and ICMRCI values for free N_2 are 1.105 and 1.089 Å, respectively.

[c] The molecule is along the z axis.

[d] The molecule is in the yz plane, with the Ca and N_2 bond midpoint on the z axis.

TABLE III. CaN_2^+ vibrational frequencies, cm^{-1}.

System	Level	ω_e(N-N)	ω_e(Ca-N)	ω_e(bend)[a]
N_2	B3LYP	2457		
	UHF	2761		
	ICMRCI+Q	2396		
CaN_2^+				
$^2\Sigma^+$(s)	B3LYP	2467	164	136
	UHF	2756	235	177
	ICMRCI+Q	2445	135	
$^2\Pi$(dyx)	B3LYP	2087	324	212
$^2\Delta$	B3LYP	2470	174	148
$^2\Pi$(py)	CASSCF	2745	223	204
	ICMRCI+Q	2394	267	
System	Level	ω_e(N-N)	ω_e(Ca-N)	ω_e(wag)
$^2B_2$(dyz)	B3LYP	1968	369	307

[a] The average of the two bending frequencies.

TABLE IV. Computed dissociation energies, in kcal/mol.

System	State[a]	B3LYP	CCSD(T)	ICMRCI	ICMRCI+Q
Ca^+-N_2					
End-on	$^2\Sigma^+(s)$	9.29	6.87	5.51	5.97
Side-on	$^2B_2(dyz)$	29.30	24.93	16.34	21.39
End-on	$^2\Pi(dyz)$	25.40	17.04	11.84	14.13
End-on	$^2\Delta(dxy)$	11.12	9.99		
End-on	$^2\Pi(py)$			17.36	18.52
$CaN_2^+-N_2$					
Linear	$^2\Sigma_g^+(s)$	9.68	6.67	4.97	5.37
Bent(C_{2v})	$^2A_1(s)$	8.80	5.65		
Linear	$^2\Pi_g(dyz)$	17.66	11.73	11.40	10.63
Linear	$^2\Delta_g(dxy)$	10.62	9.61		
Linear	$^2\Pi_u(py)$			16.88	17.71
Side-on(D_{2h})	$^2B_{3g}(dyz)$	8.82	−0.17		
Mixed[b](C_{2v})	$^2B_2(dyz)$	14.18	11.30		

[a] The character of the open-shell orbital is given in parentheses.

[b] For the loss of the more weakly bound end-on N_2 molecule.

TABLE V. $Ca(N_2)_2^+$ optimized geometries, in Å.

Orientation	State[a]	B3LYP			ICMRCI	
		r(Ca-N)	r(N-N)[b]	$\angle$(NCaN)[c]	r(Ca-N)	r(N-N)
End-on	$^2\Sigma_g^+(s,0)$	2.628	1.104	180.	2.685	1.079
Linear	$^2\Pi_g(dyz,0)$	2.345	1.121	180.	2.453	1.084
	$^2\Delta_g(dxy,0)$	2.670	1.104	180.		
	$^2\Pi_u(py,1)$	2.332	1.131	180.	2.453	1.084
End-on	$^2A_1(s,0)$	2.541	1.108	73.5[d]		
Bent C_{2v}	$^2B_1(dxz,0)$	2.340	1.121	79.3[e]		
Side-on	$^2A_g(s,2)$	3.480	1.106	18.3		
Planar	$^2B_{3g}(dyz,0)$	2.486	1.132	26.3		
D_{2h}	$^2B_{2g}(dxz,2)$	3.105	1.106	20.5		
	$^2B_{1g}(dxy,2)$	2.635	1.122	24.6		
	$^2B_{3u}(px,1)$	2.977	1.107	21.4		
	$^2B_{2u}(py,1)$	2.509	1.145	26.4		

[a] The character of the open-shell orbital and number of imaginary frequencies at the B3LYP level are given in parentheses.

[b] For comparison the B3LYP and ICMRCI values for free N_2 are 1.105 and 1.089 Å, respectively.

[c] For the end-on bonding structures, the nitrogen atoms used to compute the angle are those bonded to the Ca. For the side-on structure, the two N atoms are from one of the N_2 subunits.

[d] The CaNN angle is 170.5°; the terminal N atoms have bent away from each other.

[e] The CaNN angle is 180.7°.

TABLE VI. $Ca(N_2)_2^+$ vibrational frequencies, cm^{-1}.

System	Level	π_u	π_u	σ_g	π_g	π_g	π_u	π_u	σ_u	σ_u	σ_g
N_2	B3LYP										2457
	B3LYP(B)										2445
	UHF										2761
	UHF(B)										2728
linear											
$^2\Sigma_g^+(s)$	B3LYP	40	40	131	133	133	162	162	200	2469	2469
$^2\Pi_g(dyz)$	B3LYP	43	57	231	176	205	190	338	256	2151	2258
$^2\Delta_g(dxy)$	B3LYP	49	49	132	138	138	155	155	199	2470	2471
$^2\Pi_u(py)$	B3LYP	235i	52	258	184	246	75	206	553	2188	2144
	B3LYP(B)	216i	59	258	183	251	82	221	574	2184	2122
	BP86	258i	44	266	175	229	66	190	493	2005	2051
	UHF	24	47	134	163	200	169	260	86i	2558	2638
	UHF(B)	35	32	166	186	231	209	223	306	2724	2654
		a_1	a_1	b_2	a_2	b_2	b_2	a_1	a_1	b_2	
bent											
$^2A_1(s)$	B3LYP	65	141	147	162	177	188	233	2359	2347	
$^2B_1(dxz)$	B3LYP	65	297	294	216	145	190	220	2080	2253	

[a] The average of the two bending frequencies.

TABLE VII. $Ca(N_2)_2^+$, side-on plus end-on[a], B3LYP optimized geometries, in Å.

State[b]	End-on		Side-on	
	r(Ca-N)	r(N-N)[c]	r(Ca-N)	r(N-N)
^2A_g(s,1)	2.625	1.104	3.396	1.107
$^2B_2$(dyz,0)	2.215	1.135	3.072	1.107
$^2B_1$(dxz,2)	2.512	1.109	2.345	1.154

[a] The system is planar (in the yz plane) with C_{2v} symmetry.

[b] The character of the open-shell orbital and number of imaginary frequencies at the B3LYP level are given in parentheses.

[c] For comparison the B3LYP value for free N_2 is 1.105 Å.