THE JOURNAL OF PHYSICAL CHEMISTRY A LETTERS

2005, *109,* 3521−3526
Published on Web 03/29/2005

IR Spectroscopy and Density Functional Theory of Small $V^+(N_2)_n$ Complexes

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Received: January 17, 2005; In Final Form: March 16, 2005

$V^+(N_2)_n$ clusters are generated in a pulsed nozzle laser vaporization source. Clusters in the size range of $n = 3-7$ are mass selected and investigated via infrared photodissociation spectroscopy in the N−N stretch region. The IR forbidden N−N stretch of free nitrogen becomes strongly IR active when the molecule is bound to the metal ion. Photodissociation proceeds through the elimination of intact N_2 molecules for all cluster sizes, and the fragmentation patterns reveal the coordination number of V^+ to be six. The dissociation process is enhanced on vibrational resonances and the IR spectrum is obtained by monitoring the fragmentation yield as a function of wavelength. Vibrational bands are red-shifted with respect to the free nitrogen N−N stretch, in the same way seen for the C−O stretch in transition metal carbonyls. Comparisons between the measured IR spectra and the predictions of density functional theory provide new insight into the structure and bonding of these metal ion complexes.

Introduction

Studies of metal ion complexes in the gas phase provide simple models for solvent−solute interactions, metal−ligand bonding and molecular adsorption on metal surfaces.[1−3] Transition metal (TM)−nitrogen interactions are important in various biological and catalytic systems. For example, nitrogenases are naturally occurring enzymes that carry transition metal centers and catalyze the reduction of N_2 to ammonia.[4] The study of metal clusters has facilitated the understanding of the mechanism of these enzymes.[5,6] TM−nitrogen interactions also play an essential role in the industrial synthesis of ammonia on iron surfaces.[7] The reduction of N_2 in these situations entails the "activation" of the N−N triple bond, and the degree of activation is gauged by the change in the N−N bond distance and the N−N vibrational frequency.[7−9] In this study we investigate the TM−N_2 interaction with infrared spectroscopy of isolated gas-phase clusters, focusing on the $V^+(N_2)_n$ system.

Metal−nitrogen complexes have been investigated previously in the condensed phase and in gas-phase ion chemistry. In the latter area, ligand exchange studies and collision-induced dissociation have studied the bonding energetics of various TM cation−nitrogen complexes.[10] The binding of N_2 to a TM cation can occur in either the "side-on" or "end-on" configurations. Electronic spectroscopy studies carried out by Brucat and co-workers[11] on $Co^+(N_2)$ presented evidence for a side-on bonded ground state, but a combined experimental and theoretical study carried out by Schwarz[12] and co-workers questioned this conclusion. Detailed investigations of the structures, energies and vibrational frequencies of the neutral and ionic $Fe(N_2)$ cluster have been carried out by various groups[13−15] using ab initio and DFT methods, and these find that N_2 binds primarily end-on. Andrews and co-workers reported infrared spectra of *neutral* $V(N_2)_n$ for $n = 4$ and 6, as well as metal−nitride complexes in an argon matrix.[16] Other matrix isolation studies by Weltner and co-workers have obtained ESR spectra of $V(N_2)_6$ and proposed structures.[17] Ganteför and co-workers have studied the vibrations of N_2 adsorbed on larger metal atom clusters via photoelectron spectroscopy of mass-selected anions.[18] However, because of limitations in laser sources, there have been no studies of infrared spectroscopy of isolated $M^+-(N_2)_n$ complexes that probe the N−N stretch interaction or confirm the binding configuration.

Our group has recently employed new optical parametric oscillator/amplifier (OPO/OPA) infrared laser sources and photodissociation methods to study the vibrational spectroscopy of various metal cation−molecular complexes such as $M^+(CO_2)_n$,[19−22] $M^+(C_2H_2)_n$,[23,24] $M^+(H_2O)$[25,26] and $M^+(C_6H_6)_n$.[27,28] These studies made it possible to determine the structures of these complexes, their electronic ground state configuration, their coordination numbers and, in some cases, the occurrence of intracluster reactions. In the present work, we apply these methods to study the N−N stretch in $V^+(N_2)_n$ ions. Unlike previously studied ligands, the N_2 molecule has no IR activity in the gas phase. However, in our previous work with metal−acetylene complexes, the IR-forbidden symmetric C−H stretch of free acetylene became active because of the reduced symmetry in the metal complex.[23,24] Similar ideas apply for metal−N_2 complexes, but it is not clear that the IR *intensity* of these vibrations will be great enough to detect. As shown below, the N−N stretch becomes strongly IR active in $V^+(N_2)_n$ complexes, and we are able to measure the spectroscopy in this coordinate.

Experimental Section

$V^+(N_2)_n$ complexes are generated by laser ablation of a rotating metal rod in a pulsed nozzle source. A Spectra Physics Nd:YAG laser (Quanta Ray INDI 10) operating at 355 nm is employed for metal vaporization. The source and molecular

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10.1021/jp050294g CCC: $30.25

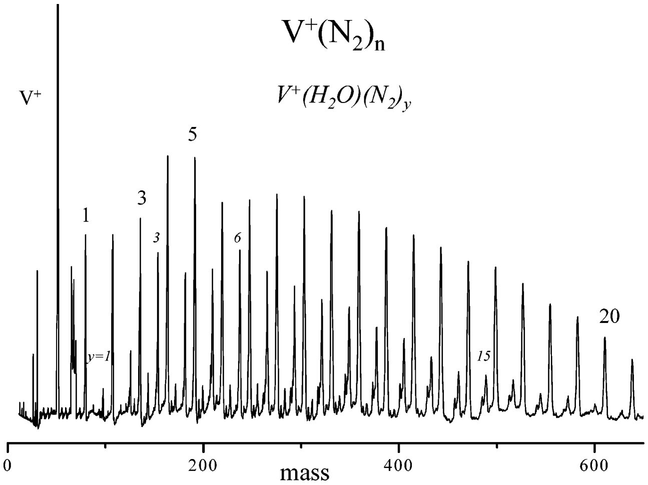

Figure 1. Mass distribution of $V^+(N_2)_n$ and $V^+(H_2O)(N_2)_y$ produced by laser vaporization in a pure N_2 gas expansion.

beam apparatus have been described elsewhere.[29,30] A General Valve (series 9) operating with a backing pressure of 70−80 psi of nitrogen produces a supersonic expansion where cluster growth occurs. The expansion is skimmed into a differentially pumped mass spectrometer chamber where cation complexes are extracted from the molecular beam with pulsed acceleration voltages. Ions are size selected in the first drift tube of the reflectron time-of-flight (RTOF) mass spectrometer using pulsed deflection plates, and excited with an infrared laser in the turning region of the reflectron. A Nd:YAG (Continuum 9010) pumped optical parametric oscillator/amplifier (OPO/OPA, LaserVision) is used for tunable IR excitation in the 2100−2500 cm^{-1} region. Parent and fragment ions are detected by an electron multiplier tube located at the end of the second drift tube whose output is recorded with a digital oscilloscope (LeCroy WaveRunner LT-342) connected to a PC via an IEEE-488 interface. Infrared spectra are acquired by monitoring the fragment ion yield as a function of the laser wavelength.

Theoretical Methods

The structures, energetics, vibrational frequencies and IR oscillators strengths for $V^+(N_2)_n$ with $n = 1-4$ were calculated using density functional theory (DFT). The B3LYP (Becke-3−Lee−Yang−Parr) functional available on the Gaussian 03W package[31] was utilized with an all-electron triple-ζ basis set employing diffuse and polarization functions (6-311+G*). The nitrogen molecules were presumed to bind via end-on or side-on configurations, but the calculations allowed for symmetry breaking from $C_{\infty v}$ and C_{2v} symmetry to obtain true minima. The primary interaction between the TM cation and nitrogen was believed to be electrostatic, and hence, the electronic states considered were those of the isolated vanadium cation. Vibrational frequencies were scaled using the difference between the calculated and experimental values for the N_2 vibration when N_2 was studied at the same level of theory.

Results and Discussion

The mass spectrum of clusters produced by laser vaporization of a vanadium rod in a pure N_2 gas expansion is presented in Figure 1. As shown, clusters of the form $V^+(N_2)_n$ are produced out to beyond $n = 20$. A less intense series of peaks corresponding to $V^+(H_2O)(N_2)_y$ species is also present from water present in the gas lines. Water is added intentionally because its presence in the plasma improves the ion yield for weakly bound complexes such TM^+-Ar_n and $TM^+-(N_2)_n$.[29,30] In the size range of these clusters, it is unlikely that all the nitrogen molecules are bound directly to the metal ion. IR photodissociation spectroscopy is used to determine the perturbation that occurs for the N_2 molecule when it binds to the metal cation and when subsequent layers of N_2 molecules form, i.e., the coordination number for the vanadium cation.

We first attempted photodissociation experiments on the smallest complexes, $V^+(N_2)_n$ for $n = 1-3$. These species are present in high abundance, but their dissociation yield is extremely low. Bond energies have not been measured previously for these complexes, but we calculate them here using density functional theory. These results are presented in Table 1. Although the DFT/B3LYP method that we employ does not provide highly accurate dissociation energies, it is clear that elimination of N_2 from these complexes requires more than about 15 kcal/mol (∼5200 cm^{-1}). The inefficient photodissociation for the small clusters when IR excitation occurs near 2300 cm^{-1} is therefore understandable.

Beginning at the $V^+(N_2)_n$ cluster size of $n = 4$, infrared photodissociation is more efficient. Figure 2 shows examples of the photodissociation mass spectra for size-selected clusters at wavelengths near 2290 cm^{-1}, which is 69 cm^{-1} to the red of the free N−N stretch. As shown below, all of these clusters absorb at this frequency. The negative peaks correspond to the depletion of the mass-selected parent ions and the positive peaks represent the photofragments. The fragment masses show that the clusters dissociate by the elimination of whole N_2 molecules. There is no evidence for nitride fragments that might appear if the nitrogen molecules were dissociated due to metal bonding or by photochemistry.

The $n = 5$ complex dissociates to produce only the $n = 4$ fragment ion. In data not shown, the $n = 6$ complex produces both the $n = 4$ and 5 fragments. The $n = 7$ complex fragments by producing mainly the $n = 5$ fragment, whereas the $n = 8$ complex produces the $n = 5$ and 6 fragments. Throughout this region, no fragment ions smaller than $n = 4$ are produced with any strong intensity, but the species with $n = 4-6$ are all produced with comparable abundance from the complexes just above them in size. This suggests that these complexes have comparable binding energies for their outermost N_2 molecules. However, in the larger clusters, a new trend emerges. In each of the fragmentation spectra for $n = 9$ and 10 (and beyond) the fragmentation patterns indicate the elimination of multiple N_2 molecules, and these processes have a common termination point at $V^+(N_2)_6$. We have seen this same kind of behavior in other metal ion complex systems.[19−23] In each of these, a common termination point was observed, which distinguished the more strongly bound "core" ligands from the more weakly bound external ones. In the present case, the data suggest that the $n = 6$ and smaller complexes have nitrogen molecules attached directly to the metal ion, whereas those molecules beyond $n = 6$ are more weakly bound. In other words, the coordination number for V^+ in these complexes is six.

As noted above, the binding energies of nitrogen ligands to V^+ have not been measured. Our calculated values cover cluster sizes only up to $n = 4$. However, Armentrout and co-workers have measured the energetics for the isoelectronic species $V^+(CO)_n$ up to cluster sizes of seven ligands.[32] The binding energies for CO in these complexes range from about 6000 to 9500 cm^{-1}. This is comparable to or somewhat greater than the binding energies we calculate here for the $n = 1-4$ species. If we assume that the binding energies for N_2 ligands to V^+ are similar to or somewhat less than those of CO, then it is understandable

TABLE 1: Results of Theory for the Quintet Electronic States of $V^+(N_2)_n$ Complexes[a]

n	N_2 binding configuration (electronic state)	BE (kcal/mol)	D_e (kcal/mol)	IR freq (cm^{-1})	IR oscillator strength (km/mol)
1	linear ($^5\Sigma$)	33.8	33.8	2291	55
	T-shaped ($^5B_1$)	18.6	18.6	2160	169
2	linear ($^5\Sigma_g$)	53.1	19.7	2262	354
	mixed ($^5A_1$)	40.3	6.7[b]	2182, 2292	311, 67
	T-shaped (^5A)	27.0	8.5	2181	544
3	linear ($^5A_1$)	71.7	18.9	2267, 2275	129, 263
4	linear ($^5B_{2g}$)	88.3	33.8	2279	246

[a] Binding energies (relative to separated V^+ and nN_2), dissociation energies (D_e) for the process $V^+(N_2)_n \rightarrow V^+(N_2)_{n-1}$, predicted frequencies and IR oscillator strengths for calculated structures shown in Figure 4 (using B3LYP/6-311+G*). Frequencies were scaled by calculating isolated N_2 at the same level of theory and comparing to experimental values. [b] For removal of the more weakly bound T-configured ligand.

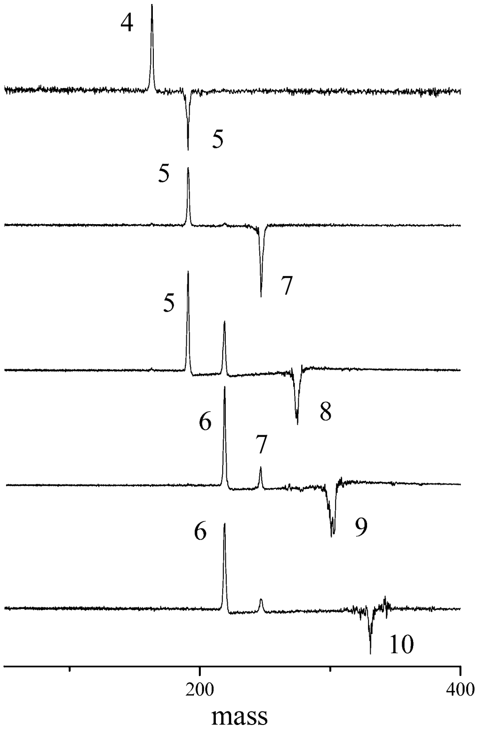

Figure 2. Fragmentation mass spectra for selected $V^+(N_2)_n$ clusters with $n = 5$ and 7−10. The complexes fragment by loss of N_2 and the loss process for the larger clusters terminates at $n = 6$.

that IR excitation near 2500 cm^{-1} would not be able to eliminate these efficiently. The fact that fragmentation is observed at all for the $n = 4-6$ complexes implies that our calculated binding energies are too high, that the clusters have residual internal energy or that some multiphoton absorption has occurred. Conversely, the $(N_2)_2$ dimer bond energy is predicted to be 50−100 cm^{-1}.[33,34] Outer ligands not attached to the metal would be bound primarily by van der Waals forces. Because of the low binding energies, elimination of multiple external ligands should be possible with IR excitation, consistent with the results in Figure 2. A coordination number of six for N_2 binding to V^+ is therefore understandable in light of the energetic information available.

A coordination number of six for the vanadium cation is not too surprising, because this coordination number is found in the condensed phase.[35] A similar result in the gas phase has been reported recently by Armentrout and co-workers for the $V^+(CO)_n$ system.[32] However, this is quite different from our previous results for $V^+(CO_2)_n$, where a coordination number of four was found.[21] Brucat and co-workers also found a coordination of four in their studies of $V^+(Ar)_n$ clusters.[36] Apparently, coordination numbers can be different depending on the ligand and the degree of its interaction with the metal ion. Argon and CO_2 bind largely through weaker electrostatic forces, whereas the greater binding energies suggest considerable covalent character for N_2 and CO bonding, perhaps explaining the different coordination trends. Our fragmentation experiments produced comparable amounts of $n = 4-6$ complexes, suggesting that there is not a great energetic difference in the binding energies for these species. It could be argued that $V^+(N_2)_7$ should be a stable complex because it has 18 electrons. However, the steric hindrance of seven ligands may offset any benefit from electronic stability. A similar argument has been put forth by Armentrout and co-workers[32] for the greater stability of $V^+(CO)_6$ compared to $V^+(CO)_7$.

To explore the energy dependence of these processes, we monitor the fragment ions produced from each mass-selected parent cluster as we scan the IR wavelength. In each system, we record the various fragment mass channels separately to investigate the possibility of different spectra in different channels. However, we find no such dependence and therefore present the spectrum for each cluster in the fragment channel that carries the greatest signal.

Consistent with the difficulty in fragmenting the smaller clusters, the $n \leq 3$ species gave featureless spectra with a continuous weak signal level. We have found such weak, broad spectra for other strongly bound complexes. When IR excitation is not energetic enough to cause dissociation, it might be expected that no dissociation signal should be detected. However, a small subset of clusters are apparently produced that do not cool completely in the supersonic expansion, and their unquenched internal energy can assist in the photodissociation process. In the small sizes, warm clusters therefore have an advantage over cold ones in the dissociation process and are essentially the only species contributing to the spectrum. Warm clusters may adopt several isomeric structures, and this plus the internal energy leads to broad spectra. When more weakly bound ligands are present, IR excitation probes the most abundant population of cold clusters, and the broad spectra from warm clusters become insignificant by comparison.

Figure 3 shows the IR spectra acquired for $V^+(N_2)_n$ ($n = 3-7$). The dashed line indicates the frequency of free nitrogen at 2359 cm^{-1}. The $n = 3$ complex has only a hint of a resonance near 2280 cm^{-1}. However, all the larger complexes have clearly identified resonances in the 2250−2300 cm^{-1} region. It is clear that the IR forbidden N−N vibration of free nitrogen is activated by binding to the vanadium cation. The small clusters have one main peak that is red-shifted from free nitrogen by about 70 cm^{-1}. The $n = 5-7$ species also have a secondary peak that is red-shifted more than the main one and much smaller in intensity. All of these bands appear significantly shifted to lower frequency from the 2359 cm^{-1} position of the resonance in the free nitrogen molecule. Such red shifts can be understood qualitatively using the so-called Dewar−Chatt−Duncanson

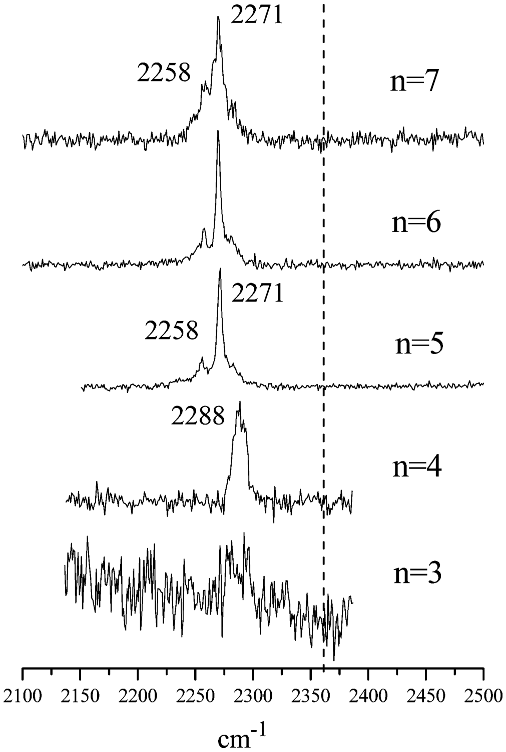

Figure 3. IR photodissociation spectra for $V^+(N_2)_n$ with $n = 3-7$ obtained by monitoring the loss of N_2 as a function of wavelength. The vertical dashed line indicates the N−N vibrational frequency of free N_2.

complexation model (DCD),[37,38] which is often applied to TM−carbonyl complexes.[39,40] In this picture, the bonding includes σ-type donation of π electron density from the ligand into the d-orbitals of the metal and π-type back-donation of metal electron density into the π^* orbitals of the ligand. Both factors weaken the N−N bond and drive the vibrational frequency to lower values. A stronger version of this kind of interaction forms the basis for activation of nitrogen in more reactive systems.

$V^+(N_2)_4$ is the smallest cluster for which an IR spectrum with a reasonable signal can be acquired. Its spectrum has a single peak centered at 2288 cm^{-1} that is 71 cm^{-1} red-shifted from the free N_2 vibration. The signal level in this spectrum is low because it is difficult to dissociate this cluster. Consistent with our earlier discussion, this difficulty in dissociation results in a relatively broad line width. The spectrum of $V^+(N_2)_5$ has a higher signal, with the principal peak now appearing at 2271 cm^{-1}. This represents an *additional* red shift of 17 cm^{-1} from the peak in the $n = 4$ spectrum, and an 88 cm^{-1} shift from free nitrogen. A minor peak is also evident in the spectrum at 2258 cm^{-1}, and a similar feature is also present for $n = 6$ and 7. The spectra of $V^+(N_2)_5$ and $V^+(N_2)_6$ are virtually identical with no apparent change in the band positions or the signal level, and both spectra have sharper lines. $V^+(N_2)_7$ has a spectrum similar in appearance, but its signal level is worse and its lines are somewhat broader.

On the basis of the results above, only the first six N_2 molecules are believed to be bound to the metal ion. Thus, the $n = 7$ complex should have one external nitrogen molecule. Because this is not attached to the metal ion, its vibrational frequency should be closer to that of free nitrogen. The free nitrogen van der Waals dimer, $(N_2)_2$, has a T-shaped geometry with an IR mode at 2329 cm^{-1}.[41] Thus, we might expect a band near this frequency in the $n = 7$ spectrum, signaling the presence of external N_2, but we do not detect such a feature. However, the N−N vibration would not be strongly IR active for external N_2 species. This may limit the detection of such a band for $n = 7$, where only one external molecule is expected. In preliminary scans of larger clusters, we do detect a weak band near 2330 cm^{-1} in the position expected for external N_2 species.

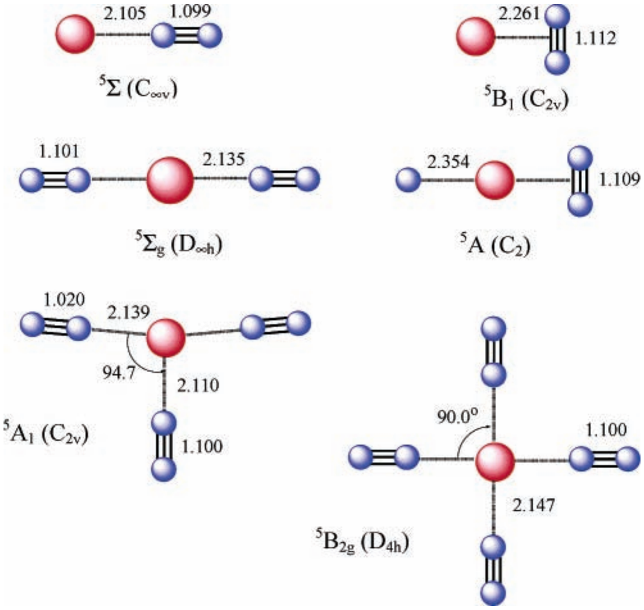

Figure 4. Calculated structures for the lowest energy quintet states of $V^+(N_2)_n$ ($n = 1-4$) using B3LYP/6-311+G*.

To further investigate these spectra, we performed comprehensive DFT calculations on the $n = 1-4$ cluster sizes. Calculations on larger complexes did not converge because of the many geometric isomers lying close in energy, and so we focus here on what we can learn from the smaller systems. Figure 4 shows the optimized geometries for the $n = 1-4$ clusters. The predicted IR active frequencies along with the oscillator strengths and dissociation energies (D_e) for the addition of the last ligand are listed in Table 1. In each complex, we explored both the quintet and triplet spins states on the core V^+ ion and found that the quintet is significantly more stable (15-30 kcal/mol). We therefore present only the data for quintet complexes in the table. For the $n = 1$ cluster, two minima were found corresponding to the end-on and side-on binding configurations, with the end-on structure more strongly bound by about 15 kcal/mol. For both structures, the N−N frequency is predicted to be significantly red-shifted compared to free nitrogen. For the linear complex ("L-complex"), this shift is about 68 cm^{-1}, whereas for the T-shaped complex, it is approximately 200 cm^{-1}. A greater red shift is understandable for the T-complexes, given that the metal is bound directly to the π framework and hence can perturb the N−N bond more effectively. For the $n = 2$ species, minimum energy structures were found for ligands in "both-L", "both-T" and one L, one T ("L−T") configurations. The both-L structure has a greater binding energy than the both-T, whereas the L−T complex has an intermediate value. The both-T complex has a structure with staggered nitrogen (one molecule perpendicular to the plane defined by V^+ and the other molecule). Again red shifts are predicted for all of these that are greater for the T-configuration than for the linear one. The both-L-complex is calculated to have a frequency near 2262 cm^{-1} with a dissociation energy (D_e) of 20.0 kcal/mol, whereas the both-T-complex has a frequency of 2181 cm^{-1} with a D_e of 8.5 kcal/mol. The L−T complex has two vibrations near the frequencies of the L and T species. For clusters larger than $n = 2$, there are many possible

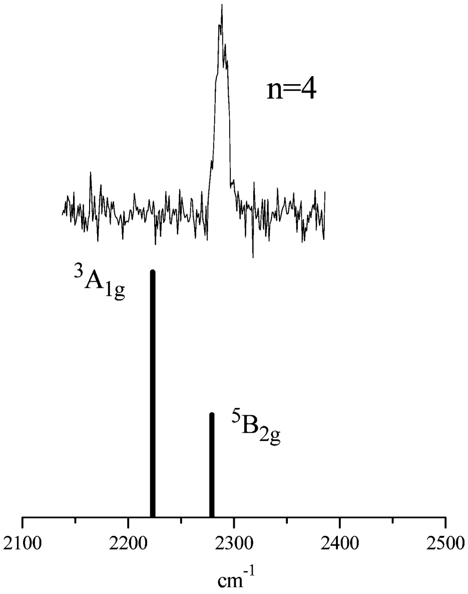

Figure 5. Calculated spectra for $V^+(N_2)_4$, with the V^+ correlating to the ^5D or ^3F atomic states, compared to the experimental spectrum. Predicted intensities have been normalized for direct comparison.

L_xT_y isomers, and the number is expanded by the rotational configuration of each T-ligand. A full investigation of all of these isomers is beyond the scope of the present study. However, as demonstrated by the $n = 2$ system, such clusters would have at least two distinct IR bands corresponding to the two ligand binding types. In the spectra for the small clusters we observe either no spectrum ($n = 1-3$) or only a single main band ($n = 4-7$). Hence the available spectra suggest that all the N_2 molecules bind in equivalent orientations. All of the small complexes have relatively large infrared oscillator strengths for vibrations corresponding to both L- and T-bonded molecules.

For the $n = 1$ and 2 systems, the linear complexes appear to bind more strongly. This trend continues for the $n = 3$ cluster, where no minimum could be found for all three N_2 molecules binding in the side-on orientation. For end-on bonding, a minimum energy structure is found that is distorted from trigonal planar. Attempts to constrain the molecule to a trigonal planar arrangement did not lead to a stationary point. The stable structure has a D_e of 18.9 kcal/mol with two IR active modes, one at 2267 cm^{-1} and the other at 2275 cm^{-1} (with the latter twice as intense as the former). Changing the orientation of the axial N_2 to side-on bonded results in a second-order saddle point with a D_e of 3.80 kcal/mol. Unfortunately, the $n = 3$ spectrum with its low signal level does not lend itself to any detailed analysis. However, the spectrum appears to have a structure in the 2270−2300 cm^{-1} region that could be consistent with the predicted bands.

For $V^+(N_2)_4$, the IR spectrum has only one band at 2288 cm^{-1}, suggesting that all nitrogens are equivalent in its structure. The only structure with equivalent nitrogens resulting in a stationary point has square planar symmetry, as shown in Figure 4. Such a structure is understandable because the vanadium ion is known to form octahedral and square pyramidal structures in condensed phase inorganic chemistry,[35] and a square planar structure is a precursor to such geometries. This structure is predicted to have a doubly degenerate vibration resulting in a single IR band. Figure 5 shows a comparison between theory and experiment for the $n = 4$ complex. As shown, the band predicted for the square planar structure in the quintet state is only 9 cm^{-1} off from the peak measured in the experimental spectrum. Side-on bonding would have vibrations much further to the red than the band observed. Likewise, the corresponding higher energy triplet state species would also have more red-shifted vibrations. To illustrate this, the figure also shows the resonance predicted for the triplet state species, which has a similar square planar structure. We therefore conclude that the $n = 4$ complex has the all-L bonding configuration in a square planar structure, with a quintet electronic ground state.

The primary band in the $n = 5$ and 6 spectra falls at 2271 cm^{-1}, which is 17 cm^{-1} further to the red from the band in the $n = 4$ spectrum. Such a shift in the principal peak between the $n = 4$ and the $n = 5$ and 6 clusters is also seen in our recent work with $Nb^+(N_2)_x$.[42] The additional shift seen for the $n = 5$ and 6 clusters is great enough to suggest that these complexes might have an electronic structure different from that of the $n = 4$ species, but not great enough to suggest a radically different bonding configuration. Therefore, a square pyramid structure for $V^+(N_2)_5$ and an octahedral structure for $V^+(N_2)_6$ seem likely for these systems, as V^+ favors these symmetries in the condensed phase.[35] The $n = 5$ and 6 spectra have an additional peak at 2258 cm^{-1} with much lower intensity. It is possible that these clusters are slightly distorted from square pyramidal and octahedral geometries. Weltner and co-workers[17] interpreted the ESR spectrum of *neutral* vanadium hexanitrogen as evidence for tetragonal axial elongation of the octahedral crystal field due to Jahn−Teller effects, thus reducing the symmetry to D_{4h}. If our cations have a structure similar to that of Weltner's neutrals, one N_2 (for $n = 5$) and two (for $n = 6$) molecules are in slightly different positions and hence will have slightly different IR absorptions. This might explain the secondary peaks in the spectra.

The $n = 7$ complex has essentially the same spectrum as those for $n = 5$ and 6. On the basis of our fragmentation data, this complex has a core of six N_2 molecules, and one additional external N_2. External N_2 molecules should have weak IR activity, if any, and therefore this should not perturb the spectrum seen for the $n = 6$ core ion, consistent with the spectrum measured.

Conclusion

This work reports the first gas-phase infrared spectra of $V^+(N_2)_n$ complexes, which apparently represents the first IR data for metal ion−nitrogen complexes in the N−N stretching region. Photodissociation for all cluster sizes occurs exclusively by the loss of whole N_2 molecules. The fragmentation mass spectra terminate at $n = 6$ for the elimination of N_2 from the larger clusters, signifying that six N_2 molecules comprise the first coordination sphere for V^+. The IR spectra of the small complexes show a single main peak that is red-shifted with respect to free nitrogen and is consistent with the qualitative predictions of the DCD model. Coupled with DFT calculations, the IR spectra present strong evidence for structures that have N_2 molecules bound end-on to a quintet V^+. The structure of the $n = 4$ complex is concluded to be square planar, and the structures of the $n = 5$ and 6 complexes are suggested to be slightly distorted from square pyramid and octahedral.

In preliminary calculations that we have performed on other transition metal ion complexes with nitrogen, we find similar behavior to that shown here. End-on binding is usually preferred, strong IR activity is found for the N−N stretch and N−N vibrational bands are predicted to be red-shifted from the free N_2 frequency. IR spectroscopy on various $TM^+(N_2)_n$ complexes should therefore provide a convenient way to examine the trends in the metal-nitrogen interaction.

Acknowledgment. We gratefully acknowledge support from the U.S. Department of Energy through grant no. DE-FG02-96ER14658.

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