J. Phys. Chem. A **2003,** *107,* 4367−4372

Laser-Induced Fluorescence Spectroscopy of the BaNC Free Radical in a Supersonic Jet

Victor Mikhailov, Martyn D. Wheeler, and Andrew M. Ellis*

Department of Chemistry, University of Leicester, University Road, Leicester LE1 7RH, United Kingdom

Received: December 4, 2002; In Final Form: March 28, 2003

Laser-induced fluorescence spectra of the BaNC free radical in a supersonic jet have been recorded for the first time. A strong and rather complicated excitation spectrum was observed between 18 000 and 19 500 cm^{-1}. In the corresponding dispersed fluorescence (DF) spectra, long progressions in the bending mode have been identified. The low frequency of this mode, 70 cm^{-1}, for the fundamental demonstrates that BaNC is relatively floppy in the bending coordinate in its ground electronic state. The intensity profiles of the bending progressions suggest that BaNC undergoes a substantial change in its equilibrium bond angle on electronic excitation. This is most likely due to the formation of a bent structure in the excited electronic state. Ab initio calculations conducted in this work suggest that BaNC is linear in its ground electronic state. However, an apparent change in sign of the bending-mode anharmonicity, deduced from the DF spectra, is suggestive of a bent equilibrium structure with a small barrier to linearity.

I. Introduction

In recent years, there has been considerable interest in the alkaline-earth monocyanides and monoisocyanides (MCNs and MNCs, respectively, where M is an alkaline-earth element). The first spectroscopic observation of these molecules was reported by Pasternack and Dagdigian in the 1970s.[1] These molecules were formed by reacting alkaline-earth metal atoms with BrCN, and spectra were obtained using laser-induced fluorescence (LIF). The spectra were broad and largely featureless, presumably because of the high internal temperatures generated by the reaction. The symmetries of the electronic states were not specifically assigned, but it was assumed, by analogy with the alkaline-earth monohalides, that the $\tilde{C}-\tilde{X}$ transitions were being observed. Pasternack and Dagdigian proposed that MCN molecules were formed, but subsequent ab initio calculations have shown that the isocyanide isomer, MNC, is significantly more stable and is likely to be the spectral carrier.[2]

The more-recent experimental work has focused on the ground and lowest-lying excited electronic states. LIF spectra of the $\tilde{A}-\tilde{X}$ transitions of MgNC,[3] CaNC,[4−6] and SrNC[4] have been recorded. In both electronic states, the molecule is linear at equilibrium and the symmetries have been firmly established as $^2\Sigma^+$ and $^2\Pi$ for the $\tilde{X}$ and $\tilde{A}$ states, respectively. Both experimental and supporting theoretical studies have shown that the bonding in these states is strongly ionic and the unpaired electron resides primarily on the metal atom.[7−13] Pure rotational spectra for MgNC,[14−17] MgCN,[18] and CaNC[19,20] have also been recorded. One of the catalysts for the recent interest in the metal cyanides/isocyanides was the observation of both MgCN and MgNC free radicals in interstellar space.[21−24] Even more recently, metal cyanides and isocyanides, including MgNC, have been detected in planetary nebulae.[25,26]

The tendency for the alkaline-earth monoisocyanides to possess linear geometries is a consequence of the strongly ionic bonding in these molecules, because the coulombic attraction between M^+ and CN^- is a maximum for a linear structure. However, opposing this tendency is the exchange repulsion, which is a minimum for a T-shaped structure. In the alkali monoisocyanides, it is well-known that NaNC and KNC are bent at equilibrium,[27−31] suggesting that exchange repulsion dominates for the heavier alkali-metal atoms. In contrast, a linear structure is adopted for LiNC, because the small Li^+ ion can get close to the CN^- anion without generating excessive exchange repulsion.[32−36] Regardless of the structure adopted, all the alkali monoisocyanides are highly “floppy”, with respect to the bending coordinate, because of the influence of exchange repulsion. Similar behavior would be anticipated for the alkaline-earth isocyanides.

Prior to the present work, experimental evidence for the floppiness of alkaline-earth isocyanides was limited to MgNC. Kagi and co-workers have recorded the pure rotational spectrum of MgNC in vibrationally excited bending states.[16] From the *l*-type doubling constant, the bending frequency was found to be low, with an estimated value of 86 cm^{-1}. No corresponding rotationally resolved data are available for the heavier alkaline-earth isocyanides; however, ab initio calculations have been performed on CaNC, and these calculations have predicted a bending frequency of 27 cm^{-1} in the ground electronic state,[13] suggesting a highly floppy system.

In recent publications from our group, we have reported the first detailed studies of several higher-lying electronic transitions of CaNC[37] and SrNC,[37,38] including the “$\tilde{C}-\tilde{X}$” system for the latter molecule first reported by Pasternack and Dagdigian.[1] LIF spectra were recorded under supersonic jet conditions, yielding resolved vibrational structure. Analysis of the vibrational structure showed that the excited electronic states were bent at equilibrium, in contrast to lower-lying electronic states. This was attributed to the excitation of the unpaired electron on the metal into a more diffuse orbital, which increases the electrostatic attraction between the cation and the anion, draws them more closely together, and therefore amplifies the role of exchange repulsion.

In this paper, we present the first vibrationally resolved LIF spectra of jet-cooled BaNC. This is expected to be the most strongly ionic of the alkaline-earth monoisocyanides. There have

---

Author to whom correspondence should be addressed. E-mail: andrew.ellis@le.ac.uk. Fax: 44 (0)116 2523789.

10.1021/jp027617i CCC: $25.00

been only two previous spectroscopic studies of this molecule: the low-resolution LIF study by Pasternack and Dagdigian discussed earlier and an IR spectroscopic investigation of BaNC in an argon matrix.[39] The matrix isolation work, which was conducted by Lanzisera and Andrews,[39] showed an IR absorption band that was due to excitation of the C≡N stretch, but no other vibrational structure was observed. In this work, we have reinvestigated the spectral region that was previously studied by Pasternack and Dagdigian.[1] The laser excitation spectrum shows a rather complicated vibrational structure, only part of which has been assigned. The dispersed fluorescence (DF) spectra consist of extensive vibrational structure in the bending mode. The low frequency of this vibration confirms the expected floppy nature of BaNC in its ground electronic state.

II. Experimental Section

A detailed description of the experimental apparatus and procedure can be found elsewhere.[37,40] Briefly, BaNC free radicals were generated in a pulsed supersonic jet by excimer laser ablation of barium in the presence of a gaseous mixture of acetonitrile (CH_3CN) and argon. The stagnation pressure of the gas behind the pulsed nozzle (General Valve) was 4 bar. A pulsed Sirah Cobra-Stretch dye laser pumped by a Nd:YAG laser was used to probe the radicals 20 mm downstream of the nozzle. LIF excitation spectra were obtained by scanning the laser wavelength and imaging the fluorescence onto a photomultiplier tube (PMT). Scattered laser light was removed using appropriate optical filters in front of the PMT.

DF spectra were obtained by exciting BaNC transitions, using the amplified output of the dye laser. The fluorescence was focused onto the entrance slits of a scanning monochromator (Acton SpectraPro 275) equipped with a PMT at the exit slit. The resolution attained in the DF experiments was ~ 15 cm^{-1}. Excitation and DF spectra presented in this work are typically averages of up to 50 laser shots per discrete wavelength point in a spectrum.

To obtain some information on the composition of the supersonic jet, time-of-flight (TOF) mass spectra were recorded using homemade Wiley−McLaren TOF mass spectrometry (TOFMS) equipment.[37] The mass spectrometer is located in a vacuum chamber separate from that containing the supersonic nozzle, and the two are linked by a skimmer with a 2-mm-diameter aperture. The base pressure in the TOFMS chamber is maintained at $<10^{-6}$ mbar, using an 800 L s^{-1} turbomolecular pump. The pulsed molecular beam enters the mass spectrometer between the first two plates of the TOFMS ion source, where photoionization takes place. The recording of resonance-enhanced multiphoton ionization spectra was impossible with the single tunable laser employed in this work. By analogy with BaCl,[41] which is isoelectronic with BaNC, the adiabatic ionization energy of BaNC is likely to be in the range of 5.0 ± 0.5 eV. Consequently, the two-photon energies employed in this work (4.45−4.84 eV) should fall below the ionization limit, ruling out 1+1 resonance-enhanced multiphoton ionization. However, mass spectra could be obtained by nonresonant multiphoton ionization with the dye laser. The photoionization of species with low ionization energies will be favored by this process; however, these are precisely the molecules of interest in this work.

Only two strong peaks were observed in the mass spectrum, which were identified as being from Ba^+ and $BaNC^+$ (or $BaCN^+$). This demonstrated that other barium-containing free radicals that might be formed in the laser ablation process when acetonitrile is the precursor, such as $BaCH_3$ or BaCCH, were minor products, if they were formed at all. No significant dependence of the mass spectra on the laser wavelength was found in the range of 18 000−19 500 cm^{-1}, confirming that the ions were formed by nonresonant photoionization.

III. Computational Details

As an aid in the assignment of the DF spectra, exploratory ab initio calculations were performed to examine the electronic ground-state Ba + CN potential energy surface (PES) and its associated vibrational levels.

The large degree of ionic character expected for BaNC/BaCN must be taken into consideration in electronic structure calculations, using sufficiently large and flexible basis sets on each of the atoms. Triple-zeta basis sets were employed with additional polarization and diffuse functions. Because of its large electron count, only the outermost 10 electrons of the Ba atom were treated explicitly. The inner 46 electrons in the Ba atom were taken into consideration by a 10-electron effective core potential (ECP), which included the dominant relativistic terms. This ECP and the corresponding valence basis set (8s9p6d)/[6s7p4d] have been described in detail by Bauschlicher et al.[2,42] For the basis sets on each of the atoms to be of a similar quality, the d-aug-cc-pVTZ correlation-consistent Gaussian basis sets (12s7p4d3f)/[6s5p4d3f] of Dunning and co-workers[43,44] were employed for the C and N atoms.

All the ab initio calculations were performed using the MOLPRO 2000[45] suite of programs operated on a desktop personal computer. The calculations were performed under C_s symmetry, to investigate the complete PES, including both linear and nonlinear geometries. In C_s point-group symmetry, the ground state of BaNC is a $^2A'$ state corresponding to a closed-shell occupation of the CN^- ion and a singly occupied 6s orbital for the Ba^+ ion. Electron correlation effects were taken into account, using the restricted coupled-cluster method including single, double, and a perturbative estimate of triple excitations (RCCSD(T)).[46,47] Overall, 19 electrons were correlated: the 10 electrons in the 3σ, 4σ, 5σ, $1\pi_x$, and $1\pi_y$ orbitals of the CN^- ion, and the 9 electrons in the 5s, 5p, and 6s orbitals of the Ba^+ ion. Initial calculations were run to determine the optimized geometries of the BaCN and BaNC isomers. The CN bond distance was then fixed at an average of the CN bond length in the two optimized geometries ($r_{CN} = 1.175$ Å) for subsequent calculation of the PES. This restriction was chosen because our interest is primarily in the Ba−ligand interaction. The CN stretching vibration is expected to possess the highest frequency, by far, of the vibrations in BaNC/BaCN and will therefore be effectively decoupled from the other modes.

To evaluate the vibrational eigenstates, the ab initio points first were fitted to a polynomial in the Jacobi coordinates R and θ, where R is the distance between the Ba atom and the CN center-of-mass and θ is the angle between R and the CN direction. The functional form chosen for the PES was

$$V(R,\theta) = \sum_{l=0}^{6} V_l(R) P_l(\cos\theta) \qquad (1)$$

where $P_l(\cos\theta)$ are Legendre polynomials and the radial functions, $V_l(R)$, are a modified version of those used by Essers and co-workers to represent the PES of LiCN:[33]

$$V_l(R) = A_l \exp(-\beta R) + \frac{E_l D_{l+1}(R,\beta)}{R^{l+1}} + \sum_{k=4}^{8} \frac{C_{lk} D_k(R,\beta)}{R^k} \qquad (2)$$

TABLE 1: Fitting Parameters (in Atomic Units) Determined for the Electronic Ground-State Potential Energy Surface of BaNC/BaCN[a]

	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$	$l = 5$	$l = 6$
A_l	118.2	6.945	100.8	−18.49	43.12	−5.489	5.182
E_l	−0.2476	0.2913	7.456	40.13	−768.5	−67.77	1052
C_{4l}	−736.8		−197.2				
C_{5l}		416.3		−410.8			
C_{6l}	44 985		6607		9864		
C_{7l}		25 050		8202		777.6	
C_{8l}	−1 161 000		−105 514		−279 900		−11 370

[a] The range parameter, β, was found to be 1.421 bohr^{-1}.

The first term in eq 2 represents the inner repulsive wall of the PES, whereas the second and third terms account for the damped long-range part of the potential resulting from electrostatic and induction interactions between the Ba$^+$ and CN$^-$ moieties. The damping terms, D_k, are given by the Tang−Toennies coefficients.[48] The summation in the final term runs over even values of k when l is even and odd values of k when l is odd. The form of the potential previously given contains terms up to the sixth order in the Legendre polynomial, giving a total of 29 adjustable parameters (A_l, β, E_l, C_{lk}) in the fit of the ab initio surface. Fitting the potential energy function to a total of 68 ab initio points yielded an overall standard deviation of 8.2 cm^{-1} (37.2 μhartree), compared with the dissociation energy of 37 850 cm^{-1}. All the fitting parameters are summarized in Table 1. The ab initio points and potential generating subroutines (Fortran 77) are available from the authors upon request.

Calculation of the vibrational energy levels supported by the PES was achieved using the TRIATOM suite of programs.[49] The minimum energy structure was that of the linear BaNC isomer; therefore, it was necessary to calculate levels with total angular momentum quantum numbers of both $J = 0$ and $J = 1$ to obtain all the bending levels supported by the PES. The calculations employed a radial basis set consisting of 40 Morse oscillator functions and an angular basis set of 40 Legendre polynomials. Off-diagonal Coriolis terms were neglected in all vibrational calculations.

IV. Results and Discussion

A. *Ab initio* Calculations. A contour plot of the calculated PES for the ground electronic state of BaNC/BaCN is shown in Figure 1. Two minima are observed: one corresponding to linear BaNC, and the other corresponding to linear BaCN. The BaNC isomer has the lowest energy, a finding in agreement with earlier (CISD) calculations on this system by Bauschlicher and co-workers.[2] The energy difference between the two minima is calculated to be 0.19 eV in this work, which is smaller than that reported by Bauschlicher et al. (0.32 eV). However, a good indication of the quality of the calculations comes from the dissociation energy (D_e) of BaNC, which was calculated to be 4.69 eV, in close agreement with the experimental value of 4.87 ± 0.26 eV.[50]

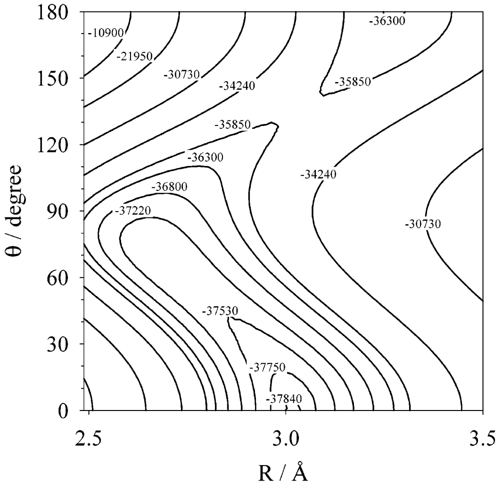

Figure 1. Contour plot of the ab initio potential energy surface (PES) for the ground electronic state of BaNC/BaCN. The coordinates refer to a Jacobi system in which R is the distance between the Ba atom and the CN center-of-mass and θ is the angle between R and the CN direction. The energy scale is given in cm^{-1}. The lowest-energy isomer is BaNC, for which $\theta = 0°$. For both isomers, the PES is highly "floppy" in the θ coordinate.

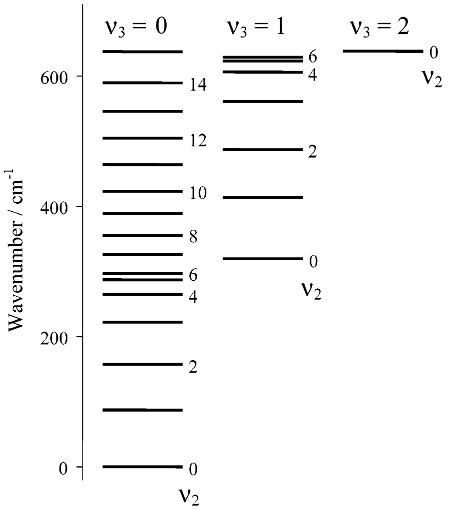

Figure 2. Ba−NC stretching and bending vibrational energy levels for BaNC. These levels were calculated using the TRIATOM program[49] and the ab initio potential energy surface shown in Figure 1. The assignment of levels to specific stretching and bending quantum numbers is approximate and becomes increasingly unreliable as the energy increases.

BaNC has three distinct vibrational modes: the C≡N stretch, the bending mode, and the Ba−(NC) stretch. We will label these modes v_1, v_2, and v_3, respectively. The C≡N bond length was fixed in the ab initio calculations; therefore, no information is obtained on the C≡N stretching mode. However, using the PES in Figure 1, all Ba−(NC) stretching and bending vibrational levels up to 1000 cm^{-1} above the BaNC minimum have been calculated. Attempts have been made to assign bending and stretching quantum numbers of each level by inspection of the nodal patterns of the corresponding vibrational wave functions obtained from TRIATOM.[49] Low-lying levels were relatively simple to assign; however, above 640 cm^{-1}, strong anharmonic coupling distorts the nodal patterns and quantum number assignments could not be made. The bending level manifolds for $v_3 = 0$, 1, and 2 are shown in Figure 2.

According to the calculations, the first excited stretching level is 320 cm^{-1} above the zero-point level. As expected, the bending

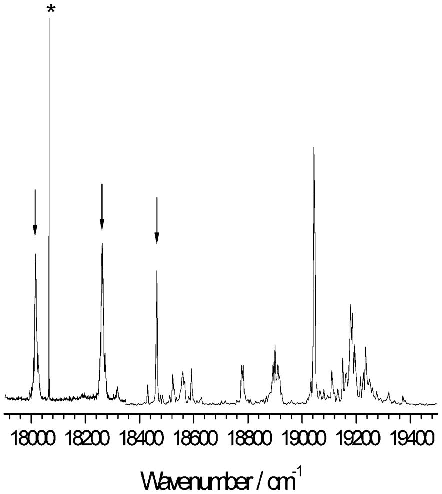

Figure 3. Laser excitation spectrum of BaNC from 17 900 to 19 500 cm^{-1}. The three transitions marked with arrows are those excited to obtain the dispersed fluorescence spectra shown in Figure 4. The sharp transition at 18 065.3 cm^{-1} is the Ba ^{1}P(6s^{1}6p^1)$-$^{1}S(6s^2) transition.

levels have a much lower frequency and the first and second bending levels ($v_2 = 1$ and 2) are calculated to be 87 and 159 cm^{-1} above the zero-point level, respectively. For $v_3 = 0$, the bending levels show normal anharmonic behavior up to energies close to the onset of the $v_3 = 1$ manifold, at which point the anharmonicity apparently changes sign and the bending levels diverge as the ladder is climbed. We attribute this changeover to the onset of Fermi resonance between bending levels in different stretching manifolds, in this particular case, between $v_3 = 0$ and $v_3 = 1$.

B. LIF Spectra: Identifying the Spectral Carrier. Excitation spectra were recorded between 17 500 and 20 400 cm^{-1}. A signal attributable to BaNC was observed over a narrower region, and a typical spectrum is shown in Figure 3. An asterisk marks the position of a strong narrow line of atomic barium (18 065.3 cm^{-1}, from Moore[51]), but all other features are attributed to a single molecule (BaNC). Support for this assignment comes from several sources.

(1) The signal disappeared if the barium target was replaced with a different metal. Similarly, the signal disappeared if a non-CN containing volatile organic liquid was used in place of acetonitrile as a precursor.

(2) The photoionization mass spectrum spectrum indicates that BaNC (or BaCN) is the major barium-containing molecular product in the supersonic jet.

(3) The central part of our excitation spectrum coincides with a broad and rather featureless spectrum recorded by Pasternack and Dagdigian, which was attributed to BaCN (or BaNC).[1]

There are two additional observations worth mentioning. First, the fluorescence lifetimes of all excited states, except that corresponding to atomic barium in Figure 3, were the same, within experimental error (ca. 80 ns). Second, the spectrum in Figure 3 is in the same region as the $C^2\Pi - X^2\Sigma^+$ transition of BaCl.[52] BaCl is isoelectronic with BaNC, and the electronic states of the latter should resemble those of the former.[53] If the assignment to BaNC is correct, then it seems likely that at least some, if not all, of the features observed in Figure 3 arise from the analogue of the $C^2\Pi - X^2\Sigma^+$ transition of BaCl.

To summarize so far, there is good circumstantial evidence that the spectral carrier is BaNC or BaCN. Further evidence in support of this assignment comes from the analysis of the excitation and DF spectra, to which we now focus our attention.

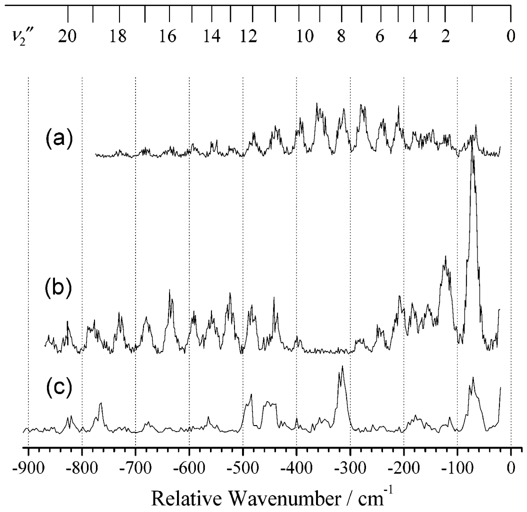

Figure 4. Dispersed fluorescence spectrum of BaNC obtained by laser excitation of transitions at (a) 18 016, (b) 18 261, and (c) 18 460 cm^{-1}. The wavenumber scale is relative to the wavenumber of the pump laser.

C. Excitation Spectrum. The excitation spectrum in Figure 3 is quite complex and we have been unable to identify a single, *regular* vibrational progression, although there is clearly considerable vibrational structure. We have recently observed similar behavior in the excitation spectra of CaNC[37] and SrNC,[37,38] as well as in the $\tilde{C}^2\Pi - \tilde{X}^2\Sigma^+$ spectrum of BaOH.[54]

Given that the spectrum in Figure 3 is in the same region as the $C^2\Pi - X^2\Sigma^+$ transitions of the barium monohalides and BaOH, it is tempting to propose the same assignment for BaNC. However, the complexity of the excitation spectrum argues against this assignment. It seems likely that some, if not all, of the BaNC bands in Figure 3 arise from an electronic transition correlating with $\tilde{C}^2\Pi - \tilde{X}^2\Sigma^+$. However, as discussed below, there is evidence to suggest that the excited electronic state is bent at equilibrium. This would remove the orbital degeneracy in the excited state and give rise to two transitions, $^2A' - ^2A'$ and $^2A'' - ^2A'$, both of which are optically allowed. Both of these transitions may contribute to the spectrum in Figure 3.

D. Dispersed Fluorescence Spectra. Figure 4 shows three different DF spectra of BaNC. These were obtained by laser excitation of the three transitions marked with arrows in Figure 3. Substantial structure is observed in each case, and the structure appears to be dominated by a single, low-frequency vibrational progression. The first member of this progression is seen ~70 cm^{-1} to the red of the pump laser position and is present in all three DF spectra, although the relative intensities differ markedly. Similarly, the next band is also seen in all three spectra, some 50 cm^{-1} further to the red. Thereafter, the vibrational structure becomes more difficult to interpret, although it is clear that most bands are common to two or all three spectra.

Given that BaNC is expected to be a strongly ionic molecule, the C≡N stretching frequency should be similar to that of the free CN$^-$ ion (2131.6 cm^{-1}, from Ha and Zumofen[55]). In fact, the C≡N stretching fundamental frequency of BaNC has been measured by Lanzisera and Andrews, using matrix isolation IR spectroscopy, yielding a value of 2048.9 cm^{-1}.[39] The high frequency of this mode clearly excludes any contribution to the DF spectra in Figure 4.

In view of both the single-bond character and the much-larger reduced mass, the Ba$-$NC stretch will occur at a much lower frequency than the C≡N stretch. An estimate of the frequency of the former can be obtained by comparison with the barium monohalides. For example, the harmonic vibrational frequency of BaCl in its $X^2\Sigma^+$ state is 279 cm^{-1}.[52] CN is lighter than the Cl atom, which will raise the vibrational frequency. Furthermore, CN has a higher electron affinity than the Cl atom (3.82 versus 3.615 eV[56,57]), which is likely to strengthen the ionic bonding in BaNC, compared with BaCl. These two factors taken together suggest that the Ba−Cl stretching frequency will be a *lower* limit for that of Ba−NC. This conclusion is consistent with the calculated value of 320 cm^{-1} obtained from the ab initio PES described previously. Consequently, although the Ba−NC stretch may contribute to the spectra in Figure 4, it is clear that a lower-frequency mode must be responsible for much of the structure; that mode is the bending vibration of BaNC.

Extensive Franck−Condon activity in the bending mode would not be expected if BaNC were linear in both the ground and excited electronic states. Clearly, BaNC must be nonlinear at equilibrium in at least one of the electronic states. The alkaline-earth monoisocyanides MgNC, CaNC, and SrNC are all known to be linear at equilibrium in their ground electronic states.[3−6] Consequently, it is likely that BaNC is also linear in its electronic ground state. Assuming this to be the case, then BaNC must be nonlinear in the excited electronic state(s) observed in this work. Nonlinear excited electronic states were also proposed for CaNC[37] and SrNC[37,38] in previous work from our laboratory to account for the complex vibrational structure seen in their LIF spectra.

The bands at −70 and −120 cm^{-1} in the DF spectra are assigned to the fundamental and first overtone bending transitions in the ground electronic state. The ab initio calculations predict a bending fundamental at 87 cm^{-1}, which is higher than the observed value but not too dissimilar. Given the floppiness of the PES along the bending coordinate, higher-level calculations employing, in particular, a larger and more-flexible basis set than that used here would be essential to model the bending motion precisely. Our calculated value is satisfactory, considering the more-limited basis set employed in the present work.

Using the ratio of the observed and predicted bending fundamental frequencies as a scaling factor for the ab initio calculations, the separation of the $v_2 = 2$ and $v_2 = 1$ levels is predicted to be 58 cm^{-1}. The second member of the bending progression is actually observed 50 cm^{-1} to the red of the bending fundamental, which is in reasonable agreement with the prediction.

There are clearly many bending levels accessed in the DF spectra. Intriguingly, there is an apparent change in sign of the anharmonicity early in the bending progression. The bending vibrational levels initially converge above the zero-point level. However, a change of sign of the anharmonicity occurs at ∼150−200 cm^{-1} above the zero-point level, i.e., between the second and third bending overtones (seen most clearly in Figure 4b). All bands to the red of this “crossover” point form a divergent series.

The reason for the change in sign of the anharmonicity is unclear. Fermi resonance is unlikely to be responsible, because the first excited Ba−N stretching level is expected to be more than 100 cm^{-1} above the crossover point. An alternative explanation is that BaNC is nonlinear in the ground electronic state. Acccording to Dixon,[58] bending vibrational levels below the barrier to linearity in a nonlinear triatomic molecule will converge, whereas those above diverge. If applicable to BaNC, this would imply a barrier to linearity of 150−200 cm^{-1}. However, the ab initio calculations reported here do not support the suggestion that BaNC is bent at equilibrium in its ground electronic state. Therefore, the source of the change in anharmonicity in the bending progression remains an open question.

E. Franck−Condon Intensity Profile. Differences in the relative intensity profiles in the DF spectra in Figure 4 are quite striking. These spectra originate from the first three strong bands in the excitation spectrum and, given their comparable intensities, it seems plausible that these bands might form part of the same vibrational progression. In the DF spectrum in Figure 4a, the intensity profile rises smoothly from the laser position to reach a maximum at approximately −300 cm^{-1}, before falling smoothly away again further to the red. In contrast, in Figure 4b, the first member of the bending progression is far stronger than any other band. Furthermore, in this DF spectrum, there is a clear intensity minimum in the middle of the spectrum.

For emission from a single vibrational level in the excited electronic state, the occurrence of intensity minima will reflect the nodal structure of the vibrational wave function in the excited state. Consequently, the band at 18 016 cm^{-1} corresponds to emission from the $v_2' = 0$ level, whereas that at 18 261 cm^{-1} is from the $v_2' = 1$ level. Although much more sparse in structure, the observed bands in Figure 4c seem to cluster into three groups, between which there are intensity minima. This suggests that the band at 18 460 cm^{-1} might be the next member in the excited-state bending progression, despite the substantial anharmonicity that is required for this assignment to be correct (see Figure 3). We have observed no bands attributable to BaNC to the red of the region shown in the excitation spectrum in Figure 1, so there is no evidence for any significant hot bands. Thus, we tentatively assign the bands at 18 016, 18 261, and 18 460 cm^{-1} in the excitation spectrum to the 0_0^0, 2_0^1, and 2_0^2 transitions, respectively.

This assignment implies a much-higher frequency (245 cm^{-1} for the fundamental) for the bending vibration in the excited electronic state, compared to the ground state, and therefore a much-stiffer bending potential for the former. It appears that BaNC is quite strongly bent in this excited state.

DF spectra have been recorded that correspond to all of the bands in the excitation spectrum in Figure 3. In each case, the only assignable structure is due to the low-frequency bending mode of BaNC. However, the intensity profiles are generally far more complicated than the previously mentioned three examples and do not readily aid in the assignment of the excitation spectrum. As a result, a full understanding of the excitation spectrum is not yet available. Contributions from both the $^2A'$ and $^2A''$ states, which correlate with the $\tilde{C}^2\Pi$ state in the linear molecule limit, are plausible. Perturbations between the vibrational manifolds of these states may be the source of the irregular vibrational structure seen in the excitation spectrum.

V. Conclusions

The first laser-induced fluorescence spectra of BaNC in a supersonic jet have been reported. A relatively complex excitation spectrum has been obtained between 513 and 556 nm (19 500−18 000 cm^{-1}). Some of the stronger features in this spectrum have been tentatively assigned to a progression in the bending vibration. The occurrence of a prominent progression in the bending mode indicates a substantial change in structure between the ground and excited electronic state. We have recently discovered similar behavior for the lighter alkaline-earth monoisocyanides CaNC and SrNC,[37,38] and, by comparison with those molecules, we propose that BaNC is nonlinear at equilibrium in the excited electronic state.

The observation of a low-frequency bending progression in the dispersed fluorescence spectra demonstrates that BaNC is a floppy molecule. The apparent switch in the sign of the anharmonicity observed early in the bending progression is unusual and merits further investigation. A possible explanation, which is contradicted by the ab initio calculations that have been performed in this work, is that BaNC is also nonlinear in its ground electronic state, with a small barrier to linearity (150−200 cm^{-1}).

Acknowledgment. The authors are grateful to the UK Engineering and Physical Sciences Research Council for a research grant in support of this work. M.D.W. also acknowledges the EPSRC for the award of an Advanced Research Fellowship. The authors would like to thank Professor J. Tennyson for assistance with the TRIATOM program.

References and Notes

(1) Pasternack, L.; Dagdigian, P. J. *J. Chem. Phys.* **1976**, *65*, 1320.

(2) Bauschlicher, C. W., Jr.; Langhoff, S. R.; Partridge, H. *Chem. Phys. Lett.* **1985**, *115*, 124.

(3) Wright, R. R.; Miller, T. A. *J. Mol. Spectrosc.* **1999**, *194*, 219.

(4) Douay, M.; Bernath, P. F. *Chem. Phys. Lett*. **1990**, *174*, 230.

(5) Steimle, T. C.; Fletcher, D. A.; Jung, K. Y.; Scurlock, C. T. *J. Chem. Phys*. **1992**, *97*, 2909.

(6) Scurlock, C. T.; Fletcher, D. A.; Steimle, T. C. *J. Chem. Phys*. **1994**, *101*, 7255.

(7) Ishi, K.; Hirano, T.; Nagashima, U.; Weis, B.; Yamashita, K. *Astrophys. J*. **1993**, *410*, L43.

(8) Ishi, K.; Hirano, T.; Nagashima, U.; Weis, B.; Yamashita, K. *THEOCHEM* **1994**, *111*, 117.

(9) Kieninger, M.; Irving, K.; Rivas-Silva, F.; Palma, A.; Ventura, O. N. *THEOCHEM* **1998**, *422*, 133.

(10) Taketsugu, T.; Carter, S. *Chem. Phys. Lett.* **2001**, *340*, 385.

(11) Odaka, T. E.; Taketsugu, T.; Hirano, T.; Nagashima, U. *J. Chem. Phys.* **2001**, *115*, 1349.

(12) Odaka, T. E.; Hirano, T.; Jensen, P. *J. Mol. Spectrosc*. **2002**, *211*, 147.

(13) Nanbu, S.; Minamino, S.; Aoyagi, M. *J. Chem. Phys.* **1997**, *106*, 8073.

(14) Kawaguchi, K.; Kagi, E.; Hirano, T.; Takano, S.; Saito, S. *Astrophys. J*. **1993**, *406*, L39.

(15) Anderson, M. A.; Ziurys, L. M. *Chem. Phys. Lett*. **1994**, *231*, 164.

(16) Kagi, E.; Kawaguchi, K.; Takano, S.; Hirano, T. *J. Chem. Phys.* **1996**, *104*, 1263.

(17) Walker, K. A.; Gerry, M. C. L. *J. Mol. Spectrosc*. **1998**, *189*, 40.

(18) Ziurys, L. M.; Apponi, A. J.; Guelin, M.; Cernicharo, J. *Astrophys. J*. **1995**, *445*, L47.

(19) Steimle, T. C.; Saito, S.; Takano, S. *Astrophys. J.* **1993**, *410*, L49.

(20) Scurlock, C. T.; Steimle, T. C.; Suenram, R. D.; Lovas, F. J. *J. Chem. Phys*. **1994**, *100*, 3497.

(21) Kawaguchi, K.; Kagi, E.; Hirano, T.; Takano, S.; Saito, S. *Astrophys. J.* **1993**, *406*, L39.

(22) Guellin, M.; Lucas, R.; Cernicharo, J. *Astron. Astrophys.* **1993**, *280*, L19.

(23) Guelin, M.; Foestini, M.; Valiron, P.; Ziurys, L. M.; Anderson, M. A.; Cernicharo, J.; Kahane, C. *Astron. Astrophys*. **1995**, *297*, 183.

(24) Ziurys, L. M.; Apponi, A. J.; Guellin, M.; Cernicharo, J. *Astrophys. J.* **1995**, *445*, L47.

(25) Highberger, J. L.; Savage, C.; Bieging, J. H.; Ziurys, L. M. *Astrophys. J.* **2001**, *562*, 790.

(26) Highberger, J. L.; Savage, C.; Bieging, J. H.; Ziurys, L. M. *Astrophys. J.* **2002**, *571*, 1022.

(27) Klein, M. L.; Goddard, J. D.; Bounds, D. G. *J. Chem. Phys*. **1981**, *75*, 3309.

(28) van Vaals, J. J.; Meerts, W. L.; Dynamus, A. *J. Chem. Phys*. **1982**, *77*, 5245.

(29) van Vaals, J. J.; Meerts, W. L.; Dynamus, A. *Chem. Phys*. **1984**, *86*, 147.

(30) Wormer, P. E. S.; Tennyson, J. *J. Chem. Phys*. **1981**, *75*, 1245.

(31) Törring, T.; Bekooy, J. P.; Meerts, W. L.; Hoeft, J.; Tiemann, E.; Dynamus, A. *J. Chem. Phys.* **1980**, *73*, 4875.

(32) Clementi, E.; Kistenmacher, H.; Popkie, H. *J. Chem. Phys.* **1973**, *58*, 2460.

(33) Essers, R.; Tennyson, J.; Wormer, P. E. S. *Chem. Phys. Lett***.** **1982**, *89*, 223.

(34) Brocks, G.; Tennyson, J. *J. Mol. Spectrosc*. **1983**, *99*, 263.

(35) van Vaals, J. J.; Meerts, W. L.; Dynamus, A. *Chem. Phys*. **1983**, *82*, 385.

(36) Makarewicz, J.; Ha, T.-K. *Chem. Phys. Lett*. **1995**, *232*, 497.

(37) Greetham, G. M.; Ellis, A. M. *J. Chem. Phys*. **2000**, *113*, 8945.

(38) Greetham, G. M.; Ellis, A. M. *Chem. Phys. Lett*. **2000**, *332*, 303.

(39) Lanzisera, D. V.; Andrews, L. *J. Phys. Chem. A* **1997**, *101*, 9666.

(40) Beardah, M. S.; Ellis, A. M. *J. Chem. Phys*. **1999**, *110*, 11244.

(41) Hildenbrand, D. L. *J. Chem. Phys*. **1970**, *52*, 5751.

(42) Bauschlicher, C. W., Jr.; Jaffe, R. L.; Langhoff, S. R.; Mascarello, F. G.; Partridge, H. *J. Phys. B* **1985**, *18*, 2147.

(43) Dunning, T. H., Jr. *J. Chem. Phys*. **1989**, *90*, 1007.

(44) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys*. **1992**, *96*, 6796.

(45) MOLPRO, a package of ab initio programs designed by H.-J. Werner, P. J. Knowles (version 2002.1, R. D. Amos, A. Bernhardsson, A. Berning, P. Celani, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, P. J. Knowles, T. Korona, R. Lindh, A. W. Lloyd, S. J. McNicholas, F. R. Manby, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, G. Rauhut, M. Schütz, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, and H.-J. Werner).

(46) Knowles, P. J.; Hampel, C.; Werner, H. J. *J. Chem. Phys*. **1993**, *99*, 5219.

(47) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys*. **2000**, *112*, 3106.

(48) Tang, K. T.; Toennies, J. P. *J. Chem. Phys*. **1984**, *80*, 3726.

(49) Tennyson, J.; Miller, S.; Le Sueur, C. R. *Comput. Phys. Commun.* **1993**, *75*, 339.

(50) L'vov, B. V.; Pelieva, L. A. *Prog. Anal. At. Spectrosc*. **1980**, *3*, 65.

(51) Moore, C. E. *Atomic Energy Levels*; National Bureau of Standards, Circ. 467, U.S. Department of Commerce: Washington, DC, 1949.

(52) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

(53) Ellis, A. M. *Int. Rev. Phys. Chem*. **2001**, *20*, 551.

(54) Pooley, S. J.; Beardah, M. S.; Ellis, A. M. *J. Electron Spectrosc. Relat. Phenom*. **1998**, *97*, 77.

(55) Ha, T.-F.; Zumofen, G. *Mol. Phys*. **1980**, *40*, 445.

(56) Klein, R.; McGinnis, R. P.; Leone, S. R. *Chem. Phys. Lett.* **1983**, *100*, 475.

(57) Trainham, R.; Fletcher, G. D.; Larson, D. J. *J. Phys. B: At. Mol. Phys*. **1987**, *20*, L777.

(58) Dixon, R. N. *Trans. Faraday Soc*. **1964**, *60*, 1363.