Laser spectroscopy of CaNC and SrNC

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Low-resolution laser excitation and dispersed laser-induced fluorescence spectra of CaNC and SrNC were recorded. The laser excitation spectra of the $\tilde{B}\,^2\Sigma^+-\tilde{X}\,^2\Sigma^+$ and $\tilde{A}\,^2\Pi-\tilde{X}\,^2\Sigma^+$ transitions of SrNC are consistent with a linear, isocyanide structure. For both CaNC and SrNC, additional strong, non-resonant features occur to the red of the $\tilde{B}\,^2\Sigma^+-\tilde{X}\,^2\Sigma^+$ and $\tilde{A}\,^2\Pi-\tilde{X}\,^2\Sigma^+$ transitions in the dispersed fluorescence spectra. Although these features remain unassigned, they might be due to emission from the isomeric, linear cyanides, CaCN and SrCN. In this case, the excited state potential curves need to have a small barrier between the cyanide and the isocyanide forms.

1. Introduction

Pasternack and Dagdigian [1] first observed the alkaline earth monocyanide molecules. They noted that Ca, Sr and Ba vapors reacted with BrCN to make both the metal bromides and the metal monocyanides. More recently, Furio and Dagdigian [2] found a lower bound of 3.91 eV for the Ca–CN bond strength from chemiluminescence measurements. The ab initio calculations of Bauschlicher, Langhoff and Partridge [3] predict that the alkaline earth "monocyanides" are, in fact, monoisocyanides. They find linear M–NC structures for the entire family of molecules Be through Ba.

Gas-phase metal cyanides have long fascinated chemists because of the possibility of nearly free internal rotation of the CN group. Clementi, Kistenmacher and Popkie [4] called the ionic M–CN bond in LiCN polytopic because of the non-directional character of the bond. Experimentally, NaCN [5] and KCN [6,7] are found to be T-shaped, while LiNC [8,9] has a linear isocyanide structure. Clearly, the geometry of the M^+-CN^- molecules is deter-

mined by a balance between various subtle forces [10].

Very recently Whitham et al. [11] observed CaNC in a supersonic jet expansion source by pulsed laser excitation spectroscopy. They obtained a rotationally resolved spectrum of the 000–000 band of the $\tilde{A}\,^2\Pi-\tilde{X}\,^2\Sigma^+$ transition of linear CaNC near 615 nm. These results inspired us to re-examine some old, low-resolution CaNC and SrNC spectra [12].

2. Experimental methods

The CaNC and SrNC were made by the reaction of Ca and Sr vapors with CH_3CN in a Broida oven [13]. The experimental arrangement was similar to our previous work with monovalent derivatives of the alkaline earth metals [14–23]. The metals were resistively heated in an alumina crucible and the vapor entrained in a flow of Ar carrier gas. The total pressure in the oven was about 1.5 Torr with a few mTorr of CH_3CN.

No reaction occurs between acetonitrile (CH_3CN) and the Ca or Sr vapors without the help of a broadband (1 cm^{-1}) dye laser used to excite the $^3P_1-^1S_0$ transition of the metal atom. In a few experiments we used ICN as the oxidant. The reaction with ICN proceeds without laser excitation of the metal vapor but with a much reduced production of the metal

monoisocyanide. Even when a laser was used to promote the Ca or Sr reaction with ICN, the MNC signal was at least a factor of two less than with CH_3CN. Because CH_3CN is less toxic than ICN and the spectra were similar with both oxidants, we routinely used CH_3CN.

The CaCN and SrCN spectra are close to the corresponding CaOH [24,25] and SrOH [26,27] spectra. It was therefore helpful to dry the CH_3CN vapor by passing it through a $CaCl_2$ drying tube before it entered the oven.

A second broadband cw dye laser (Rhodamine 110, Rhodamine 6G, DCM or pyridine 2 dyes) was used to excite fluorescence from the CaNC or SrNC molecules. The first laser, which was resonant with the $^3P_1-^1S_0$ transition at 6573 Å for Ca and 6892 Å for Sr, was always operated with DCM dye. Laser excitation spectra of SrNC were recorded by scanning the second dye laser and detecting the total fluorescence through a red-pass filter which blocked the atomic transition at 6892 Å. No laser excitation spectra for CaNC were recorded because the CaNC transitions occur just to the blue of the Ca $^3P_1-^1S_0$ transition.

For both CaNC and SrNC dispersed fluorescence were recorded by leaving fixed the wavelength of both lasers and scanning a 0.64 m monochromator. The monochromator was operated with a GaAs photomultipier tube (RCA 31034) and photon counting electronics. Unfortunately, the laser-induced fluorescence was nearly completely relaxed. Apart from some changes in the relative intensity of bands, all of the dispersed fluorescence spectra were very sim-

ilar, regardless of which band the laser was exciting. Both dc and ac detection (with a lock-in amplifier) were employed.

3. Results and discussion

The simplest spectrum to interpret is the laser excitation spectrum of SrNC (fig. 1). There are three strong peaks at 6478, 6577 and 6710 Å corresponding to $\tilde{B} \, ^2\Sigma^+ - \tilde{X} \, ^2\Sigma^+$, $\tilde{A} \, ^2\Pi_{3/2} - \tilde{X} \, ^2\Sigma^+$ and $\tilde{A} \, ^2\Pi_{1/2} - \tilde{X} \, ^2\Sigma^+$ transitions (fig. 1). The spin–orbit splitting in the $\tilde{A} \, ^2\Pi$ state is 301 cm^{-1}, very similar to the corresponding splitting in SrNCO (293 cm^{-1}) [21] and SrNNN (296 cm^{-1}) [20]. The value of the spin–orbit coupling constant is consistent with linear structure and the ab initio calculations of Bauschlicher, Langhoff and Partridge [3] suggest that SrNC is lower in energy than SrCN in the ground $\tilde{X} \, ^2\Sigma^+$ state. Unfortunately, these calculations [3] were for all of the alkaline earth monoisocyanides, BeNC through BaNC, except SrNC.

The dispersed fluorescence spectrum is much more difficult to interpret (fig. 2) because of the presence of additional red features at 6906, 7050 and 7224 Å. These features are present only very weakly in the laser excitation spectra (fig. 1) recorded with DCM and pyridine 2 dyes (not shown). It is initially tempting to assign these features to a vibrational progression in the Sr–NC stretching mode, but the ground state vibrational intervals would be 423, 295 and 342 cm^{-1}. These intervals are too erratic to be an unperturbed vibrational progression.
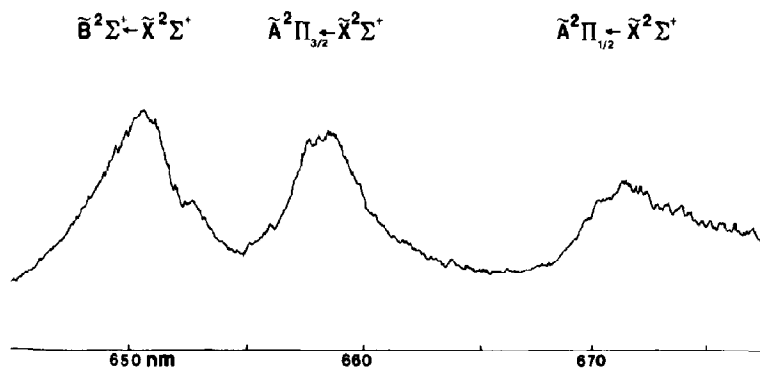

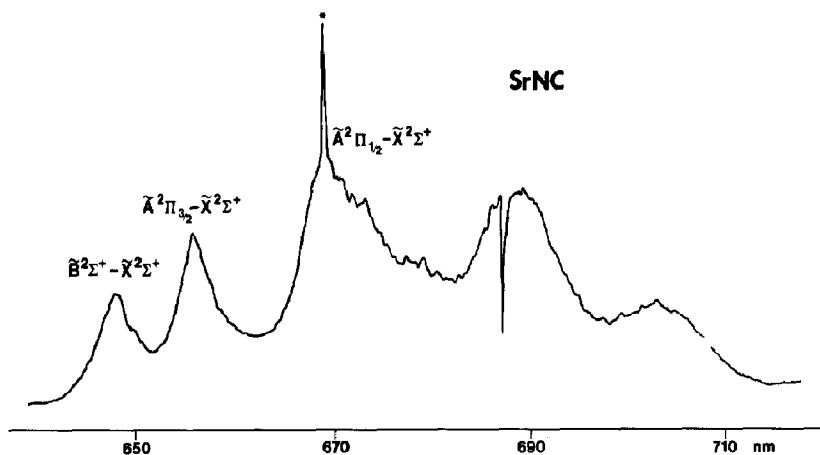Fig. 1. Laser excitation spectrum of SrNC.

Fig. 2. Dispersed fluorescence spectrum of SrNC. The laser wavelength, marked with an asterisk, is exciting the $\tilde{A}\,^2\Pi_{1/2}$-$\tilde{X}\,^2\Sigma^+$ transition. A definitive assignment is unavailable for the strong red emission at 6906 and 7050 Å. The negative-going feature at 6892 Å is the Sr $^3P_1$-$^1S_0$ atomic transition. At 6892 Å both the SrNC molecule and the Sr atom are emitting light, so the lock-in amplifier was overloaded.

Moreover, by assuming the CN ligand is a point mass, a pseudodiatomic reduced mass can be computed. Since CN^- is often treated as a pseudohalide with properties intermediate between F^- and Cl^-, one can empirically estimate a vibrational frequency of 393 cm^{-1} for SrNC and 464 cm^{-1} for CaNC from the vibrational frequencies of SrF (502 cm^{-1}), SrCl (302 cm^{-1}), CaF (581 cm^{-1}) and CaCl (367 cm^{-1}) [27]. A similar calculation using SrNNN (316 cm^{-1}) as the parent molecule predicts 377 cm^{-1} for SrNC and 449 cm^{-1} for CaNC from the vibrational frequency of CaNNN (396 cm^{-1}). The predicted SrNC ground state vibrational frequency of 377-393 cm^{-1} is not consistent with the observed intervals.

The corresponding dispersed fluorescence spectrum for CaNC (fig. 3) shows structure to the red of the $\tilde{A}\,^2\Pi$-$\tilde{X}\,^2\Sigma^+$ and $\tilde{B}\,^2\Sigma^+$-$\tilde{X}\,^2\Sigma^+$ transitions. In this case, the $\tilde{A}$-$\tilde{X}$ and $\tilde{B}$-$\tilde{X}$ transitions are completely overlapped at 6173 Å in our spectra. The laser excitation spectra of the cold CaNC recorded by Whitham et al. [11] showed the $\tilde{A}\,\Pi_{3/2}$-$\tilde{X}\,^2\Sigma^+$ and $\tilde{A}\,^2\Pi_{1/2}$-$\tilde{X}\,^2\Sigma^+$ transitions at 16268 cm^{-1} (6145 Å) and 16191 cm^{-1} (6175 Å), respectively. They did not assign the $\tilde{B}\,^2\Sigma^+$-$\tilde{X}\,^2\Sigma^+$ transition although it is probably just to the blue.

For CaNC the red emission occurs at 6326 and 6478 Å (fig. 3) and the intervals between the three peaks are 392 and 370 cm^{-1}. These intervals are too small to be unperturbed ground state Ca–NC

stretching frequencies, expected to be 449-464 cm^{-1}. Unfortunately, we were unable to record a good laser excitation spectrum (see section 2), but like the SrNC, these red features would probably be relatively weak in the excitation spectrum.

Another possible explanation for these unassigned red features is that they belong to another molecule. One possible molecule is, for example, $CaNCCH_2$, and Whitham et al. [11] found some evidence for a heavier molecule in their spectrum. However, Whitham et al.'s [11] impurity spectrum lies to blue of the CaNC features. Molecules other than CaNC and SrNC are probably minor contributors to the observed spectra because we find the spectra essentially unchanged when ICN is used as an oxidant rather than CH_3CN.

The rapid relaxation which occurs in the excited electronic states of CaNC and SrNC is an important clue. In our extensive experience with monovalent alkaline earth derivatives [14-23], the observation of completely non-resonant emission for a small triatomic molecule is unique. Most of the laser-induced emission from the tetra-atomic SrNNN [20] was resonant under our experimental conditions and this allowed a rotational analysis to be carried out. We observed mainly non-resonant emission for the larger members of the monoalkoxide [14], monothiolate [28] and monoalkylamide [17] families (MOR, MSR and MNHR), but not for small molecules such
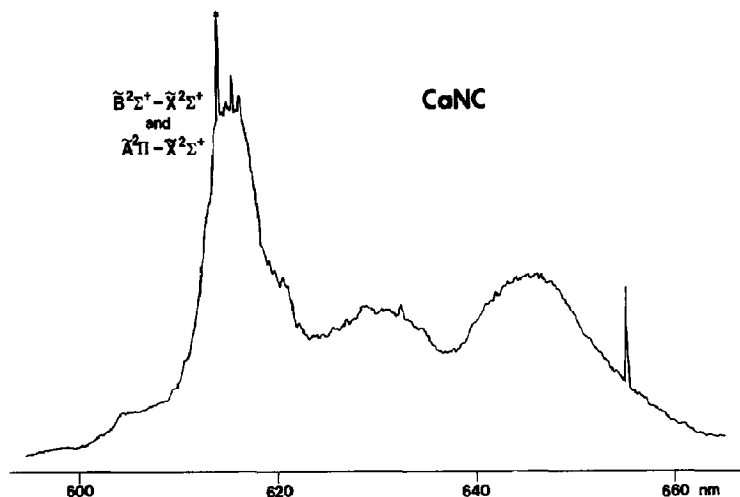
Fig. 3. Dispersed fluorescence spectrum of CaNC. The laser wavelength, marked with an asterisk, is exciting both the $\tilde{A}$ $^2\Pi$–$\tilde{X}$ $^2\Sigma^+$ and $\tilde{B}$ $^2\Sigma^+$–$\tilde{X}$ $^2\Sigma^+$ transitions. The sharp feature at 6573 Å is the Ca $^3P_1$–$^1S_0$ atomic transition. A definitive assignment for the strong red emission features at 6326 and 6478 Å is not available.

as CaOH, CaOCH$_3$, CaSH, CaNH$_2$, etc. What is even more remarkable is that this non-resonant red emission in CaNC also occurred at the low pressures of the free jet expansion experiments of Whitham et al. [11]. Presumably some sort of non-radiative process is occurring.

One possibility is that for CaNC and SrNC the red emission is due to emission from the $\tilde{A}'$ $^2\Delta$ state. For BaF [29] and BaCl [30], the $\tilde{A}'$ $^2\Delta$ state occurs below the $\tilde{A}$ $^2\Pi$. In this case, the excitation spectra could be relatively weak but perturbation-enhanced population of the $\tilde{A}'$ $^2\Delta$ state would result in relatively strong emission. $\tilde{A}'$ $^2\Delta$–$\tilde{X}$ $^2\Sigma^+$ emission is possible because the $\tilde{B}$ $^2\Sigma^+$, $\tilde{A}$ $^2\Pi$ and $\tilde{A}'$ $^2\Delta$ states form an interacting d-complex [31]. This possibility seems unlikely because for all of the other known monovalent derivatives of Ca and Sr, there is no sign of this $\tilde{A}'$ $^2\Delta$ state. The recent calculations of Ortiz [32] for CaF, CaOH, CaNH$_2$ and CaCH$_3$ all predict that this $^2\Delta$ state lies considerably above both the $\tilde{A}$ $^2\Pi$ and $\tilde{B}$ $^2\Sigma^+$ states. An ab initio calculation of the excited states of CaNC would be very helpful.

A more likely possibility is that the red emission is due to a different isomeric form of CaNC and SrNC. For example, it is possible that the T-shaped forms or the linear cyanide (CaCN and SrCN) forms are more stable than the isocyanide forms in the ex-

cited $\tilde{A}$ and $\tilde{B}$ states. The problem with this explanation is that, by the Franck–Condon principle, a change in geometry in the excited state should result in a long progression in the bending mode. The HCN molecule is the classic case of a bent–linear transition and a long progression in the excited state bending mode is seen in the $\tilde{A}$ $^1A''$–$\tilde{X}$ $^1\Sigma^+$ absorption spectrum [33].

However, if there is a small barrier in the excited state between the linear isocyanide and a lower energy linear cyanide form, then a long progression would not be expected. In this case, the $\tilde{A}$ and/or $\tilde{B}$ states would have double minima in their potential curves. Note that in the ground $\tilde{X}$ $^2\Sigma^+$ state there is no ab initio evidence [3] for a barrier between the cyanide and the isocyanide forms of CaCN and BaCN, while for BeCN and MgCN small barriers are predicted. Note also that MgOH [34] is linear in the $\tilde{X}$ $^2\Sigma^+$ state but bent in the $\tilde{A}$ $^2\Pi$ state.

Additional high resolution spectroscopic experiments on jet-cooled CaNC an SrNC are clearly necessary to obtain more information about the excited state potential curves. Ab initio calculations on the excited states of CaNC and SrNC would also be very useful. However, there may be some complications in these calculations because of the Renner–Teller effect [33] in the $\tilde{A}$ $^2\Pi$ state. In addition, the spin–

orbit coupling will be quenched in the $\tilde{A}\,^2\Pi$ state as the linear isocyanide structure bends. These "complications" should be viewed as a unique opportunity to study the dynamics of molecular motion in the excited electronic states of CaCN and SrCN. Indeed, the ground state potential surfaces of LiNC, NaCN an KCN are often studied theoretically as examples of systems which display "chaos" (for example, see refs. [35–39]).

Acknowledgement

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