LASER SPECTROSCOPY OF CALCIUM AND STRONTIUM MONOCYANATES

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The Ca and Sr monocyanate species were observed by laser-induced fluorescence. The spectra are interpreted as arising from a molecule with a linear, ionic $M^+ - {}^-OCN$ structure.

1. Introduction

We have recently discovered that Ca, Sr and Ba vapors react with a wide variety of organic compounds [1] including alcohols, aldehydes and ketones [2], thioethers [3], and carboxylic acids [4]. The products are a variety of gas-phase, free radical organometallics containing one alkaline earth atom and a single ligand. The organometallics have visible electronic spectra and are detected by laser-induced fluorescence. In this paper we report the observation of calcium and strontium monocyanate from the reaction of the metal atoms with hydrogen isocyanate vapor.

There has been no previous work on gas-phase monocyanates except the mass spectrometric detection of BOCN [5] and AlOCN [6] by Gingerich. However, the most likely isomers for these molecules are O=B—CN and O=Al—CN [6] rather than the (iso)cyanate or (iso)fulminate structures [MOCN, cyanate; MCNO, fulminate; MONC, isofulminate].

The calcium and strontium monocyanate molecules have a linear, probably oxygen-bonded structure, MOCN. These cyanate observations are in contrast to work on the alkaline earth monocyanides. Calcium and strontium monocyanides are predicted to have linear isocyanide MNC structures [7]. We have made calcium monocyanide by reaction of $Ca({}^3P_1)$ with CH_3CN [3]. The laser-induced fluorescence spectrum of CaCN consisted of a relaxed, featureless blob near 6300 Å with no hint of vibrational structure or of resonant fluorescence. This suggests that CaCN may have very little barrier to the motion

of Ca^+ around CN^- although the equilibrium structure may be T-shaped like NaCN [8] and KCN [9] or linear like LiNC [10]. Our CaCN observations agree with the work of Pasternack and Dagdigian [11] who made calcium, strontium and barium cyanides by the beam—gas reactions of metal vapor with BrCN. More recently, Furio and Dagdigian [12] observed chemiluminescence attributable to CaCN (and CaBr) from the $Ca({}^1D)$ plus BrCN reaction.

2. Experimental methods

MOCN (M = Ca, Sr) molecules were produced in a Broida oven [13] by the reaction of the alkaline earth vapor with isocyanic acid, HNCO. The alkaline earth metal was resistively heated in an alumina crucible and entrained in Ar carrier gas; pressures were approximately 1.5 Torr argon and a few mTorr acid. The preparation of isocyanic acid has been described previously [14]. Briefly, concentrated aqueous KNCO was added slowly to chilled (0°C) concentrated phosphoric acid under vacuum. The reaction products were trapped at liquid nitrogen temperatures, and distilled once at −30°C. DNCO was similarly prepared by the reaction of D_3PO_4 (prepared from $P_2O_5 + D_2O$) with a deuterated aqueous solution of KNCO. The DNCO was used to demonstrate that the product molecule contained no hydrogen: the HNCO and DNCO oxidants gave identical spectra.

A broadband (1 cm^{-1}) dye laser was used to excite the ${}^3P_1 - {}^1S_0$ transition of the alkaline earth metal

atoms. This resulted in the production of a large con-
centration of MOCN. Without the excitation of the
atomic line essentially no product was formed. A sec-
ond broadband dye laser was tuned to the $\tilde{A}\,^2\Pi$–$\tilde{X}\,^2\Sigma^+$
MOCN transition. The resulting fluorescence was dis-
persed through a 0.64 m monochromator, and de-
tected with a cooled photomultiplier tube (RCA
C31034) with photon counting electronics.

3. Results and discussion

The alkaline earth monocyanate spectra closely re-
semble the alkaline earth hydroxide [15–20] and al-

koxide spectra [2]. The observed band origins for the
calcium and strontium cyanate, MOCN, $\tilde{B}\,^2\Sigma^+$–$\tilde{X}\,^2\Sigma^+$
and $\tilde{A}\,^2\Pi$–$\tilde{X}\,^2\Sigma^+$ transitions are reported in table 1.
These data were obtained from monochromator scans
of the laser-induced fluorescence, for example figs. 1
and 2. The emission from these molecules was partly
resonant and partly relaxed. This is particularly clear
in the spectrum of SrOCN (fig. 2) since the sequence
band structure is more open for SrOCN than CaOCN.
In fig. 2 the laser is exciting a sequence band of SrOCN
and produces some resonance fluorescence but most
of the emission comes from vibrationally relaxed
levels. Although only the $\tilde{A}\,^2\Pi_{3/2}$ spin component is
excited there is relaxation to the other spin compo-
nent ($\tilde{A}\,^2\Pi_{1/2}$) as well as to the $\tilde{B}\,^2\Sigma^+$ state at our
pressure of $\approx$1.5 Torr. The 0–0 band appears to lie on
the red side of the $\tilde{A}$–$\tilde{X}$ features displayed in figs. 1
and 2 on the blue side of the $\tilde{B}$–$\tilde{X}$ feature (like the
corresponding CaOH and SrOH transitions [15–19]).
The calcium and strontium cyanate $\tilde{A}\,^2\Pi$–$\tilde{X}\,^2\Sigma^+$
spectra exhibit spin–orbit splittings of 68 ± 7 cm^{-1}
and 305 ± 40 cm^{-1}, respectively, for the $\tilde{A}$ state
(table 1). These spin–orbit coupling constants are
identical (within experimental error) with the corre-

Table 1
The band origins of Ca and Sr cyanate in cm^{-1}. The uncer-
tainties are approximately ± 5 cm^{-1} for the $\tilde{A}$–$\tilde{X}$ transitions
of CaOCN and ± 30 cm^{-1} for the other transitions

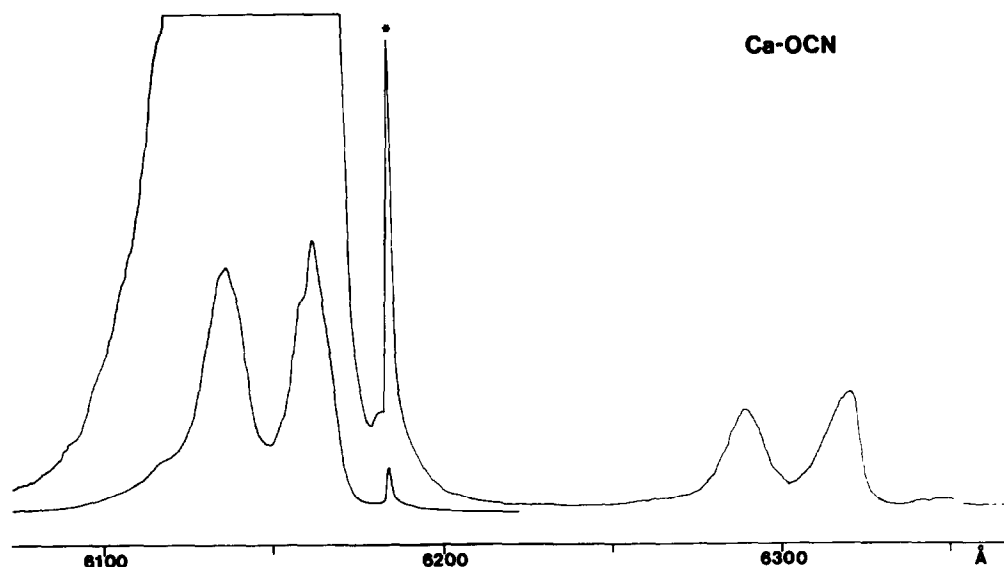| Molecule	$\tilde{A}_1\,^2\Pi_{1/2}$	$\tilde{A}_2\,^2\Pi_{3/2}$	$\tilde{B}\,^2\Sigma^+$
CaOCN	16230	16298	17180
SrOCN	14944	15249	16016

Fig. 1. Laser-induced fluorescence from the $\tilde{A}$–$\tilde{X}$ transition of CaOCN. The splitting between the two strong features is due to the
spin–orbit coupling in the $\tilde{A}\,^2\Pi$ state. The asterisk marks scattered light from the dye laser exciting the $\tilde{A}\,^2\Pi$ state from an excited
vibrational level in the ground state (i.e. the laser is not resonant with the 0–0 band). The lower trace has the sensitivity reduced
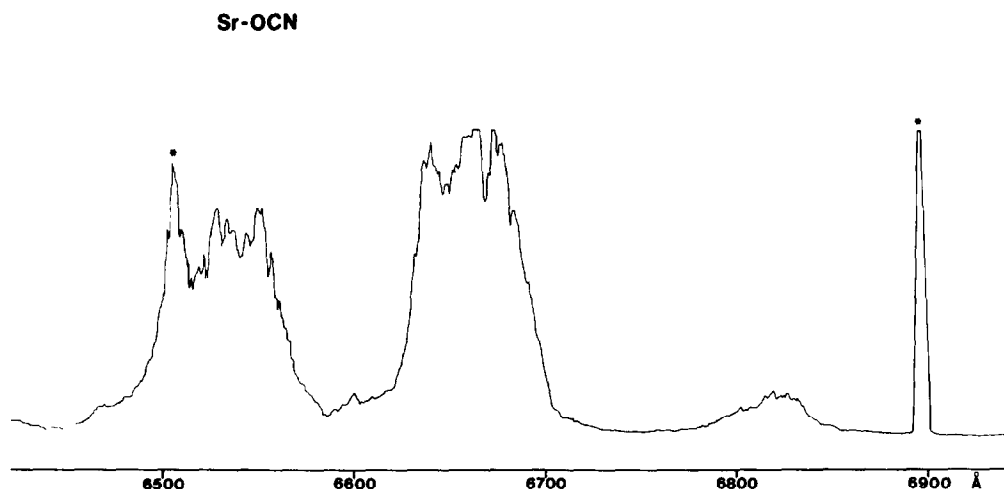by 10 in order to put the 0–0 band on scale.

Sr-OCN

Fig. 2. Laser-induced fluorescence from the $\tilde{A}$–$\tilde{X}$ transition of SrOCN. The splitting between the two strong features is due to the spin–orbit splitting in the $\tilde{A}\,^2\Pi$ state. The asterisks mark the scattered light from the two dye lasers exciting the atomic $^3P_1$–$^1S_0$ transition (6892 Å) and the $\tilde{A}_2\,^2\Pi_{3/2}$–$\tilde{X}\,^2\Sigma^+$ transition. Note that the emission is partly resonant and partly relaxed.

sponding values for the linear CaOH (67 cm^{-1} [18]) and SrOH (264 cm^{-1} [19]) molecules as well as the corresponding Ca and Sr alkoxide values [2]. This constitutes strong evidence for a linear oxygen-bonded structure. If MOCN were bent then the symmetry would be lowered from $C_{\infty v}$ to C_s and no spin–orbit interaction could exist for the $\tilde{A}$ state. Instead the $\tilde{A}\,^2\Pi$ state would correlate with two electronic states of A$'$ and A$''$ symmetry [20]. The bent CaSH and SrSH molecules [3] have C_s symmetry and completely different (more complicated) spectra than the corresponding linear CaOH and SrOH molecules.

The size of the spin–orbit coupling constant of the $\tilde{A}$ state suggests M–O bonding rather than M–N bonding for the cyanate group. The electronic structure of the alkaline earth monohalides and monoalkoxides is well described by an ionic M$^+$–X$^-$ structure. The remaining valence electron on the Ca$^+$, Sr$^+$ and Ba$^+$ is perturbed by the X$^-$ ligand. Hence, the spin–orbit coupling constant of the $\tilde{A}$ state is determined by properties of M$^+$ but modulated by the nearest neighbor, X$^-$, atom or group. For example, Ca$^+$ perturbed by $^-$OR (R = alkyl) has A = 70 cm^{-1} [2] while A = 72.5, 70.5, 64.3 and 45.7 cm^{-1} for CaF [21], CaCl [22], CaBr [23] and CaI [24], respectively. The observed spin–orbit coupling constants are consistent with the expected M$^+$–$^-$OR (M = Sr, Ca;

R = CN) values rather than the probably different M$^+$–$^-$NR (M = Sr, Ca; R = CO) values.

The known affinity of the alkali and alkaline earth metals for oxygen also favors the M–O bonding structure. This is in contrast to the transition metal isocyanate complexes which are almost always N-bonded [25]. However, the early transition elements such as Ti, Zr and Hf, which also have a strong affinity for oxygen, can form O-bonded cyanate complexes [26]. Many main group elements such as Si, Ge, Sn and Ga have N-bonded structures (Si(NCO)$_4$, Ge(NCO)$_4$, (CH$_3$)$_3$SnNCO, (CH$_3$)$_3$GaNCO [27,28]). The NCO$^-$ ligand also probably bonds through the N atom to surface Si atoms of silica [29].

The laser-induced fluorescence spectra of Ca$^+$–$^-$OCN electronic transitions contain vibrational information. Since the electronic transitions involve a non-bonding, unpaired, metal-centered electron all of the electronic states have similar geometries and vibrational frequencies. The Franck–Condon factors for non-diagonal transitions are small and only the vibrational modes associated with the metal center (such as the M–O stretch) are expected to occur strongly.

The MOCN molecules have five vibrational modes ν_1 (C–N stretch), ν_2 (C–O stretch), ν_3 (M–O stretch), ν_4 (O–C–N bend) and ν_5 (M–O–C bend). The ν_1, ν_2 and ν_3 modes have Σ symmetry while ν_4 and ν_5 have

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Table 2

Vibrational frequencies of Ca and Sr monoxcyanates in cm^{-1}. The uncertainties are ± 5 cm^{-1} for CaOCN and ± 30 cm^{-1} for SrOCN

Mode	$\tilde{X}\,^2\Sigma^+$	$\tilde{A}_1\,^2\Pi_{1/2}$	$\tilde{A}_2\,^2\Pi_{3/2}$
CaOCN			
ν_3	390	395	393
$2\nu_3$	778	779	774
ν_1	2200	–	–
SrOCN [a]			
ν_3	297	–	320

[a] $\nu_3 = 314$ cm^{-1} for $\tilde{B}\,^2\Sigma^+$ state.

Π symmetry. ν_1 and ν_2 are often described as pseudo-asymmetric stretch and pseudosymmetric stretch, respectively, because of the similarities between the isoelectronic NCO^- and CO_2 molecules.

The observed MOCN vibrational frequencies are listed in table 2. The M–O stretch (ν_3) occurs most strongly in the spectrum. For example both spin components of the 00000–00100 $\tilde{A}\,^2\Pi$–$\tilde{X}\,^2\Sigma^+$ transition of CaOCN occur near 6300 Å in fig. 1. $2\nu_3$ and ν_1 (C–N stretch) modes were found for CaOCN but not for SrOCN. The very compact CaOCN sequence structure allowed very weak modes such as ν_1 to be located by enhancing the effective signal-to-noise ratio for CaOCN.

In addition to the stretching modes in table 1, there are very weak features in the CaOCN spectra which suggest that ν_4 (OCN bend) ≈ 640 cm^{-1} (650 cm^{-1} in the $\tilde{A}$ state) and ν_5 (Ca–O–C bend) ≈ 50 cm^{-1} may occur. The observation of $\tilde{A}$–$\tilde{X}$ 00000–00010 and 00000–00001 transitions are formally forbidden because ν_4 and ν_5 have Π symmetry [20] (transitions involving the allowed modes $2\nu_4$ and $2\nu_5$ have very small Franck–Condon factors). However, spin–orbit vibronic coupling caused by a breakdown of the Born–Oppenheimer approximation can allow these modes to occur [19]. For SrOH [19] and BaOH [30] (but not CaOH) we have observed the analogous forbidden 000–010 vibronic transitions. The ν_5 assignment is not very secure. For instance, it is possible that $2\nu_5$ rather than ν_5 occurs in the spectrum which would imply a ν_5 of 25 cm^{-1}. These very low frequency bends are unusual but the

ionic structure provides a very flat bending potential. The corresponding Ca–O–R bend is 90 cm^{-1} for the alkoxides [2] and 20 cm^{-1} for the quasisymmetric top SiH_3NCO [31].

The expected OCN^- vibrational frequencies are 631 cm^{-1} for the bend, 2182 cm^{-1} for the pseudo-asymmetric stretch and 1211 cm^{-1} for the pseudo-symmetric stretch, based on solid state spectra of KOCN in a KCl matrix [32]. The 1211 cm^{-1} mode was not found but modes at 2200 cm^{-1} and a very weak overlapped mode ≈ 640 cm^{-1} (ν_4'') were found. The M–O stretch, 390 cm^{-1} for CaOCN and 297 cm^{-1} for SrOCN, are just the frequencies expected by comparison with the Ca and Sr monoalkoxides. For the alkoxides the M–O stretch was found to correlate linearly with $\mu^{-1/2}$, where μ is a pseudodiatomic reduced mass computed by assuming that all of the ligand mass is concentrated at a single point. This sort of an empirical correlation suggests that all of the M–O force constants are similar. The M–O frequency for MOCN agrees with the observed trend in the corresponding MOH, $MOCH_3$, MOC_2H_5, MOC_3H_7 and MOC_4H_9 molecules (M = Ca, Sr). Thus, the value of the M–O stretching frequency is also suggestive of M–O rather than M–N bonding.

4. Summary

Ca and Sr vapors react with HNCO to form the linear and probably O-bonded CaOCN and SrOCN molecules. The laser-induced fluorescence spectra closely resemble the corresponding vibronic spectra of the alkaline earth monoalkoxides. The CaOCN and SrOCN free radicals are the first gas phase, metal monocyanates to be detected.

Acknowledgement

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