

High-resolution laser spectroscopy of strontium isocyanate, SrNCO

L. C. O'Brien and P. F. Bernath^{a)}

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

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The 0-0 band of the $\tilde{A}^2\Pi-\tilde{X}^2\Sigma^+$ transition of the linear free radical strontium monoisocyanate, SrNCO, was recorded at high resolution. By comparing the molecular constants of SrNCO with related molecules, the NCO⁻ ligand was found to be nitrogen bonding to the strontium atom. The spectrum is extremely dense because of the small rotational constant, $B'' = 0.0426 \text{ cm}^{-1}$, and overlapping sequence structure. The Sr-N bond length was estimated to be 2.26 Å in the ground $\tilde{X}^2\Sigma^+$ state.

INTRODUCTION

We have previously published the low resolution (1 cm^{-1}) laser-induced fluorescence spectra of the gas-phase SrNCO and CaNCO molecules.¹ Estimated band origins for the $\tilde{B}^2\Sigma^+-\tilde{X}^2\Sigma^+$, $\tilde{A}^2\Pi-\tilde{X}^2\Sigma^+$ electronic transitions, and several vibrational frequencies were reported. The cyanate group is a well-known ligand in transition metal and main group chemistry,²⁻⁵ but little is known about gas-phase metal monocyanates. The cyanate free radical NCO has been studied by many authors⁶⁻¹⁴ in the ultraviolet/visible^{6,7} infrared^{8,9} and microwave¹⁰⁻¹⁴ regions of the spectrum. Quite recently, the vibration-rotation spectrum of the cyanate anion, NCO⁻ was observed by Gruebele, Polak, and Saykally.¹⁵

The infrared,¹⁶⁻²¹ Raman,^{22,23} and ultraviolet^{24,25} spectra of metal cyanate crystals and metal cyanates doped in alkali-halide crystals are well known. High-resolution spectra are available for many covalently-bonded molecules of the formula X-NCO [X = H, Cl, Br, CN, CH₃, SiH₃, etc. (Refs. 26-31, respectively)]. We report here the rotational analysis of the 0-0 band of the $\tilde{A}^2\Pi-\tilde{X}^2\Sigma^+$ transition of SrNCO. This work represents the first high-resolution analysis of an ionically-bonded metal monocyanate.

In our previous paper¹ we concluded that CaNCO and SrNCO were linear molecules, but we were unable to establish with certainty whether the NCO ligand was N-bonding or O-bonding. At that time we favored O-bonding, but we now believe that CaNCO and SrNCO are N-bonding. The CaNCO and SrNCO molecules are thus isocyanates rather than cyanates. The principal evidence for this conclusion is the strong similarity between the electronic spectra and vibrational frequencies of the SrNCO and SrNNN molecules. The laser spectroscopy of the CaN₃ and SrN₃ free radicals are described in the preceding paper.³² Our observations on SrNCO are part of a series of papers on polyatomic alkaline earth-containing free radicals.³³⁻⁴²

EXPERIMENTAL METHODS

The production of SrNCO in a Broida oven⁴³ has been described previously.¹ Briefly, Sr metal was vaporized from a resistively heated alumina crucible and entrained in a flow of Ar carrier gas ($\sim 1 \text{ Torr}$). Hydrogen isocyanate (~ 15

mTorr), HNCO, was introduced to react with the strontium atoms, producing strontium monoisocyanate, SrNCO. When excited strontium atoms ($^3P_1 \text{ Sr}$) are used for the reaction, a much larger concentration of SrNCO was produced. Excited strontium atoms were produced by using a broadband (1 cm^{-1}) dye laser tuned to the $^3P_1-^1S_0$ transition of strontium. This technique allows for concentration modulation by mechanically chopping the laser beam tuned to the atomic line.

A second laser system was used to record the high-resolution laser excitation spectrum of SrNCO. The 5145 Å output of a Coherent Innova 20 argon ion laser was used to pump a Coherent 699-29 computer controlled ring dye laser operated near 6560 and 6690 Å.

The outputs of the two dye lasers were spatially overlapped and focused into the Broida oven. High-resolution laser excitation spectra were recorded through a 0.64 m monochromator to reduce the background fluorescence. The presence of a very low-frequency bending vibration produces strongly overlapped sequence structure. The monochromator acts as a narrow bandpass filter to select rotational lines of interest. For example, to record the R_2 branch the monochromator bandpass wavelength was tuned to the P_2 branch because these two branches have common upper rotational states. An iodine cell was used to calibrate the wave meter of the computer controlled dye laser. The absolute accuracy of our line positions is approximately 0.005 cm^{-1} .

RESULTS AND DISCUSSION

The electronic and vibrational structure of SrNCO was described previously.¹ Briefly, the bonding in SrNCO is very ionic, Sr⁺-NCO⁻, and there is one nonbonding valence electron centered on the strontium atom in the 5s orbital. The electronic transitions involve the promotion of this valence electron to the 4d-5p metal centered hybrids.

The 0-0 band of the $\tilde{A}^2\Pi-\tilde{X}^2\Sigma^+$ electronic transition was recorded at high resolution and analyzed. The $\tilde{A}^2\Pi$ state has a relatively large spin-orbit splitting ($A_{SO} = 292 \text{ cm}^{-1}$) and thus follows Hund's case (a) coupling. There are 12 branches for each vibronic transition, six branches for each spin-orbit component, as described in detail by Herzberg.⁴⁴ These branches are spaced at approximately $-3B$, $-1B$, $+1B$, and $+3B$ at low J and the $-1B$ and $+1B$

^{a)} Alfred P. Sloan Fellow.

branches are doubled due to the spin-rotation interaction in the ground state.

A sample spectrum of individual rotational lines in the $+3B$ (R_{21}) branch is shown in Fig. 1. In our experiment, the spin-rotation doubling was resolved in the $+B$ ($Q_{21} + R_2$) branch of the $\tilde{A}^2\Pi_{3/2}-\tilde{X}^2\Sigma^+$ electronic transition for $J > 44.5$ (Fig. 2). Individual rotational lines were not observed for the $-B$ (P_{21} , Q_2 , P_1 , and Q_{12}) branches because of the formation of bandheads.

The observed SrNCO transition wavenumbers are listed in Table I (see PAPS, Ref. 56). Three hundred and fifty lines were fit to 12 parameters with a standard deviation of 0.003 cm^{-1} . The molecular Hamiltonian and matrix elements used are the same as in the SrNNN analysis.³² The molecular constants determined from the nonlinear least squares fit are given in Table II.

The high-resolution analysis confirms the linear geometry but does not, without consideration of additional information, determine whether the structure is SrNCO or SrOCN. The *ab initio* quantum chemical calculations of Poppinger *et al.*⁴⁵ on RNCO derivatives provides some guidance. A geometry optimization of the ionic molecule LiNCO results in a linear nitrogen bonding structure.

There are three structural parameter for the linear SrNCO molecule to be determined from only one rotational constant. We, therefore, assumed the C-N bond length to be 1.19 \AA and the C-O bond length was set to 1.23 \AA .²¹ These values are the estimates of Smith *et al.*²¹ from a force field analysis of dilute NCO^- in ionic single crystals of KCl and KBr. The gas-phase rotational constant of Gruebele, Polak, and Saykally¹⁵ is in agreement with these bond lengths. There are no suitable crystal structures available for ionic cyanates such as NaNCO or $\text{Ca}(\text{NCO})_2$, and the available quantum chemical calculations of the geometric structure of NCO^- (Refs. 46 and 47) utilized only modest-sized basis sets with no configuration interaction.

Assuming a N-bonding structure, $r_{\text{CN}} = 1.19 \text{ \AA}$ and $r_{\text{CO}} = 1.23 \text{ \AA}$ (Ref. 21) provides a Sr-N bond length of 2.26 \AA for the $\tilde{X}^2\Sigma^+$ state of SrNCO from the B_0'' value in Table

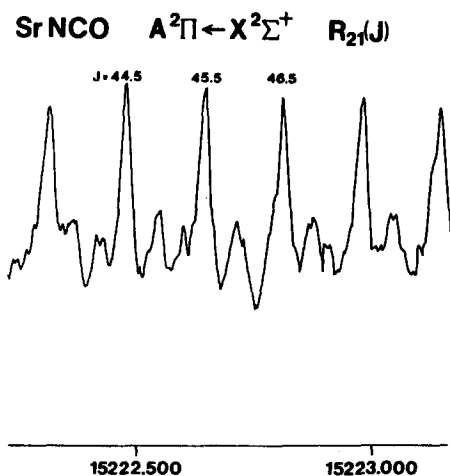


FIG. 1. Laser excitation spectrum of the $R_{21}(J)$ branch of the 0-0 band of the $\tilde{A}^2\Pi_{3/2}-\tilde{X}^2\Sigma^+$ transition of SrNCO. The fluorescence was simplified by recording through a monochromator filter set to pass the connecting 0-0 band $P_{21} + Q_{22}$ branches.

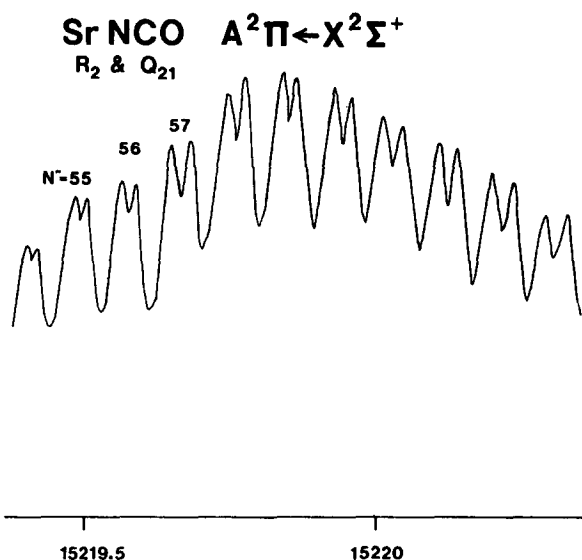


FIG. 2. Laser excitation spectrum with filtered fluorescence detection of the R_2 and Q_{21} branches of the 0-0 band of the $\tilde{A}^2\Pi_{3/2}-\tilde{X}^2\Sigma^+$ transition of SrNCO. The R_2 and Q_{21} branches connect to the same upper level but are separated by the ground state spin-rotation splitting in the $\tilde{X}^2\Sigma^+$ state. For each pair of lines labeled by the same N'' quantum number, the R_2 line lies to the blue (higher frequency) of the Q_{21} line.

II. The corresponding value for the Sr-N bond length in the $\tilde{A}^2\Pi$ state is 2.24 \AA .

The assumption of Sr-N bonding is confirmed by an examination of Table III, a comparison between selected spectroscopic properties of SrNCO, SrN_3 , and $\text{SrOCH}_2\text{CH}_3$. The NCO^- and N_3^- ligands have identical masses (42 amu), while $\text{CH}_3\text{CH}_2\text{O}^-$ has a mass of 45 amu . The N_3^- ligand is chosen as an example of an N-bonding ligand while the $\text{CH}_3\text{CH}_2\text{O}^-$ serves to represent O-bonding ligands.

The SrN vibrational frequencies are similar for SrNCO and SrN_3 ,³² while the Sr-O frequency³⁷ is higher even though the $\text{CH}_3\text{CH}_2\text{O}^-$ ligand is heavier. The spin-orbit coupling constant in the $\tilde{A}^2\Pi$ states of SrNCO and SrN_3 (Ref. 32) are close to 295 cm^{-1} rather than the 260 cm^{-1} typical for Sr-O bonding³⁷ species. The band origins for the $\tilde{A}^2\Pi-\tilde{X}^2\Sigma^+$ transitions of SrNCO and SrN_3 are very simi-

TABLE II. Molecular constants for the 0-0 band of the $\tilde{A}^2\Pi-\tilde{X}^2\Sigma^+$ transition of SrNCO (cm^{-1}).

B''	$0.042\,580\,7(51)^a$
D''	$0.589(72) \times 10^{-8}$
γ''	$0.447(13) \times 10^{-3}$
γ_D''	0.116×10^{-8b}
T_0	$15\,069.620\,6(4)$
A'	$292.566\,32(66)$
A_D'	$-0.311(31) \times 10^{-5}$
B'	$0.042\,972\,4(50)$
D'	$0.573(71) \times 10^{-8}$
q'	-0.651×10^{-6b}
p'	$-0.048\,025(41)$
p_D'	$-0.50(15) \times 10^{-7}$

^a One standard deviation uncertainty.

^b Fixed to the value from SrN_3 (Ref. 32).

TABLE III. A comparison of molecular constants (in cm^{-1}).

Property	SrNCO	SrN ₃	SrOCH ₂ CH ₃
$\nu^*(\text{Sr}-\text{X})$	297	316	345
$A_{\text{so}}(\text{Å})$	293	296	260
$T_0(\text{Å})$	15 070	15 058	14 637
$T_0(\text{B})$	16 016	15 872	16 090
$r_0(\text{Sr}-\text{X})$	2.26 Å	2.26 Å	2.11 Å*

*From SrOCH₃ (Ref. 49).

lar. Finally, and most convincingly, the Sr–N bond length is found to be 2.26 Å for SrNCO, identical to the corresponding SrN₃ value. The known Sr–O bond lengths are 2.11 Å for SrOH (Ref. 48) and 2.12 Å for SrOCH₃.⁴⁹ The Sr–N bond length in SrNH₂ is 2.25 Å,⁵⁰ the typical Sr–N value.

The similarities between SrNCO and SrN₃, contrasted with the SrNCO and SrOCH₂CH₃ differences, strongly suggest that SrNCO is N-bonding. By implication, other gas-phase ionic “cyanates” such as NaNCO should be linear N-bonding species (i.e., linear isocyanates). The quantum chemical calculations of Poppinger and Radom⁴⁵ on LiNCO are consistent with this conclusion. Additional calculations with larger basis sets and configuration interaction would help confirm these linear isocyanate structures.

The Λ -doubling constant, $p = -0.048 \text{ cm}^{-1}$, of SrNCO in the $\tilde{A}^2\Pi$ state supports the simple picture of the $\tilde{B}^2\Sigma^+$ and $\tilde{A}^2\Pi$ states as $p\sigma - d\sigma$ and $p\pi - d\pi$ hybrid orbitals centered on Sr⁺. The electronic structure is analogous to the alkaline earth monohalides.^{51–53} The pure precession value⁵⁴ of p is

$$p = \frac{2ABl(l+1)}{\Delta E(\tilde{A} - \tilde{B})} = -0.053 \text{ cm}^{-1}$$

for $l = 1$. The corresponding value of p for SrN₃ is -0.059 cm^{-1} . The pure precession⁵⁴ or unique perturber⁵⁵ models are much too simple, but they provide some qualitative indication of the atomic character of molecular orbitals.

CONCLUSIONS

The rotational analysis of the 0–0 band of the $\tilde{A}^2\Pi - \tilde{X}^2\Sigma^+$ transition of SrNCO was carried out by laser excitation spectroscopy with narrow band fluorescence detection. A comparison of the molecular constants of SrNCO with SrN₃ strongly suggests a linear isocyanate structure. The Sr–N bond length was found to be 2.26 Å in the $\tilde{X}^2\Sigma^+$ state. This work is the first high resolution analysis of a metal isocyanate molecule.

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⁵⁶See AIP document no. PAPS JCPSA-88-2117-4 for 4 pages of Table I (Observed Line Positions of the $\tilde{A}^2\Pi-\tilde{X}^2\Sigma^+$ Transition of SrNCO). Or-

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