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First observation and electronic spectroscopy of chromium mononitride: The $A \,{}^{4}\Pi_{r} \leftarrow X \,{}^{4}\Sigma^{-}$ transition near 745 nm

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We report the first gas phase spectroscopic study of chromium mononitride. CrN molecules were generated in our laser vaporization molecular beam source and studied using laser induced fluorescence techniques. Twelve vibronic subbands of $Cr^{14}N$ have been rotationally analyzed in the 745–647 nm region. These bands are assigned to the $A \ {}^{4}\Pi_{r} \leftarrow X \ {}^{4}\Sigma^{-}$ transition. The assigned ground state electron configuration $1 \ {}^{2}9 \sigma^{1}$ and symmetry are identical to those of the isovalent VO, MoN, and WN molecules. The energy observed for the excited $\ {}^{4}\Pi_{r}$ state matches closely the first $\ {}^{4}\Pi$ state energy derived from a recent *ab initio* calculation [J. F. Harrison, J. Phys. Chem. **100**, 3513 (1996)]. In addition to the $A \ {}^{4}X$ transition, 11 other bands of $Cr^{14}N$ have been identified and vibrationally assigned to transitions involving two other excited states, presumably the $B^{4}\Sigma^{-}$, and a $\ {}^{2}\Pi$ state. Comparisons with the isovalent VO, MoN, and WN systems have provided more insights into the bonding and electronic structure of the CrN molecule. $\ {}^{0}$ *1997 American Institute of Physics.* [S0021-9606(97)01911-9]

INTRODUCTION

Gas phase spectroscopic studies of transition metal nitrides can provide crucial information about the bonding between a transition metal atom and a nitrogen atom and have attracted a significant amount of interest among experimentalists and theorists alike.¹⁻⁴⁰ In contrast to metal oxides and hydrides where many detailed studies exist,^{41,42} gas phase studies of metal nitrides are rather limited. To our knowledge, currently only 11 metal nitrides (ScN,¹ TiN,²⁻⁸ VN,⁹⁻¹¹ YN,¹² ZrN,^{13,14} NbN,¹⁵⁻²⁰ MoN,²¹⁻²⁵ WN,²⁶ ReN,²⁷ IrN,²⁸ and PtN^{29,30}) have published gas phase spectra. *Ab initio* calculations involving these molecules are also limited. Publications have appeared on ScN,³¹ TiN,^{32,33,35} VN,^{34,35} CrN,^{35,36} FeN,³⁶ YN,³⁷ NbN,³⁸ MoN,³⁹ and PtN⁴⁰ molecules.

In this paper, we detail the first spectroscopic characterization of the 3*d* metal nitride, chromium mononitride (CrN). LIF spectra of Cr¹⁴N and Cr¹⁵N have been recorded in the 370–745 nm region and rotational analyses have been carried out for 12 of the observed Cr¹⁴N vibronic subbands. Electron configurations for both the ground and the excited states have been assigned based on the *ab initio* calculations^{35,36} and by comparison with the isovalent VO,⁴¹ MoN,^{21–25} and WN²⁶ molecules. Experimental observations agree well with the *ab initio* results and point to the locations of several other excited states not included in the calculation.

EXPERIMENTAL METHOD

The experimental apparatus used to produce CrN has been described previously⁴³ and only a brief outline is given here. The setup consists of a typical laser vaporization molecular beam source, two pulsed laser systems, and the necessary hardware and software for LIF detection.

A homemade pulsed molecular beam valve (pulse width =200 μ s, 0.5 mm diameter) was used⁴⁴ with a rotating chromium rod (5 mm diameter and 3 cm long) mounted close to the opening of the nozzle. The carrier gas (2% ammonia in 1 atm helium) was then expanded through an attached 17 mm long (2 mm diameter) channel into a high vacuum chamber. The vacuum chamber, a 30 cm black anodized cubic aluminum one, was pumped by a 16 cm diffusion pump (Edwards diffstack 160). Ion gauge readings of 1×10^{-4} and 1×10^{-5} Torr are typical with the molecular beam switched on and off, respectively.

The second harmonic (532 nm) output of a Nd:YAG laser (Continuum NY60) was used as the vaporization source whereas a Nd:YAG pumped tunable dye laser (Lumonics HY600 and HD300) was used to excite the jet-cooled CrN molecules. A 0.2 cm^{-1} resolution was typical in the 370–745 nm region and several dyes (e.g., DCM, LDS 698, and LDS 751) were used. The LIF detection system consists of a collection lens (50 mm diameter and f=75 mm), a Jobin Yvon H20 monochromator (used as a band pass filter) and a photomultiplier tube (PMT; Hamamatsu R106UH). The signal from the PMT was collected on a digital oscilloscope (Tektronix 2440) and transferred to a 386 computer. To record a LIF spectrum, the dye laser wavelength was scanned with a step size of 0.001 nm and for each wavelength setting, the signal was averaged for 10 laser shots.

To confirm the identity of the carrier and to establish vibrational assignments in the spectrum, ${}^{15}NH_3$ (99%, Cambridge Isotope) was used to obtain the LIF spectrum of Cr¹⁵N. The wavelength calibration was carried out using the observed Cr atomic LIF lines in this region.⁴⁵ The absolute wave numbers reported here are believed to be accurate within 2 cm⁻¹ and the relative positions should be precise

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(A)

within 0.1 cm^{-1} . To avoid power broadening and saturation, the amplifier of the dye laser was normally removed during our experiment. For several weak subbands (e.g., bands at 647.1, 650.3, 653.4, and 656.0 nm), however, the amplified dye laser output was used to obtain satisfactory signals.

RESULTS AND ANALYSES

A. The rovibrational analysis of the A-X system

Ab initio calculations³⁵ and comparison with the isovalent MoN²¹⁻²⁵ and WN²⁶ systems indicate with little doubt that the first optical transition should be the A ${}^{4}\Pi_{r} \leftarrow X {}^{4}\Sigma^{-}$ system. The observation of three groups of four subbands, each separated by about 910 cm⁻¹, and with an origin around 739 nm, immediately suggested the discovery of this expected transition. Isotope shifts of the Cr15N bands confirmed the carrier to be CrN and established the vibrational assignment. The three groups centered around 651.5, 692.5, and 739.2 nm are therefore confidently assigned to the (2-0), (1-0), and (0-0) bands of the A ${}^{4}\Pi_{*} \leftarrow X {}^{4}\Sigma^{-}$ system. Within each of the three bands, there are four subbands corresponding to transitions to the four Ω sublevels of the upper ${}^{4}\Pi_{r}$ manifold. The nearly equal spacing between the subbands suggests that we have a Hund's case (a)⁴⁶ [or case (ab)] ${}^{4}\Pi_{r}$ state with only small perturbations from another state (most likely, a ${}^{2}\Pi$ state, as in VO⁴¹).

Due to the complexity of the ${}^{4}\Pi_{r} \leftarrow {}^{4}\Sigma^{-}$ transition and our limited laser resolution, a simulation program written for RhO analysis was modified to fit the CrN system. In fact, two programs were created for each of the four subbands, one being used to simulate the spectrum, the other to perform the least squares analysis. These programs proved to be valuable since branch patterns are frequently unusual for CrN.

As displayed in Fig. 1, each of the 4 subbands consists of 12 branches with line spacing of about +5B' (one branch), +3B' (two branches), +B' (three branches), -B'(three branches), -3B' (two branches), and -5B' (one branch). The analyses were carried out in an iterative approach; the two branches with 5B' separation were first used in the least squares fit to obtain an initial fit. The output of the simulation program using the obtained fitting parameters then helped to identify other branches. Transitions from these branches were added to the least squares fit. Typically about 100 lines were used for each subband in the least squares fit with N'' up to 20. The root mean square deviation is about 0.07 cm^{-1} for a majority of the 12 subbands with the exceptions of 2 subbands involving the ${}^{4}\Pi_{3/2}$ v'=1 and v'=0 excited states. Careful examination of the deviations suggests that the high J levels of these particular excited states are perturbed in a way that cannot be described by the effective Hamiltonians used in our simulation and fitting programs.

The $\Omega = 5/2$ and 3/2 subbands of the (2-0) transition were first analyzed together using case (ab) formulas⁴⁷ for the upper state and the known Hamiltonian matrix elements for a ${}^{4}\Sigma^{-}$ state.⁴⁸ This analysis yielded the origin of the v'=2 state and the spin-orbit coupling constant. (These constants are included in Table II.) It is apparent that the centers



CrN $A^{4}\Pi_{5/2}$ (- $X^{4}\Sigma^{-}(2-0)$

FIG. 1. (A) and (B): sections of the LIF spectrum of the A ${}^{4}\Pi_{r} \leftarrow X {}^{4}\Sigma^{-1}$ (2-0) transition of Cr¹⁴N.

of the $\Omega = 1/2$ and -1/2 subbands are shifted to the blue by about 9 cm⁻¹ and 28 cm⁻¹, respectively, from values predicted using these constants. These shifts are most likely related to the perturbation caused by a $^{2}\Pi$ state located at higher energy. We proceeded by using the following case (a) effective Hamiltonian with individually adjustable T_{Ω} values:

$$F(J') = T_{\Omega} + BJ'(J'+1) - D[J'(J'+1)]^{2}$$

$$\pm q(J'+1/2)/2 \pm (-1/2)p_{j}(J'+1/2)^{3}.$$
(1)

This energy expression has been used by several groups^{21,26} in their analyses of ${}^{4}\Pi_{r} \leftarrow {}^{4}\Sigma^{-}$ transitions. The results of this analysis are listed in Table I and Table II. Several weak features cannot be assigned to ⁵²Cr¹⁴N: it is likely that they are due to the less abundant ⁵³Cr¹⁴N isotopomer.

B. Vibrational assignments of the other excited states

Two additional systems, with their (0-0) bands located near 488.0 and 488.5 nm [systems (II) and (III)], are also observed in this study. The strong transition (II) with its origin near 488 nm is assigned to the case (a) allowed $B {}^{4}\Sigma^{-} \leftarrow X {}^{4}\Sigma^{-}$ transition. Another much weaker system

TABLE I. Table of assigned lines of the CrN A-X (2,0) band (values in cm⁻¹).

=

$A^{4}\Pi$	$_{(5/2)} \leftarrow X^{4} \Sigma^{-}(2,$	0)								
N''	${}^{u}R_{41}$	${}^{t}R_{42}$	${}^{s}R_{43}$	${}^{r}R_{44}$	${}^{t}Q_{41}$	${}^{r}Q_{43}$	${}^{q}Q_{44}$	^r P ₄₂	${}^{q}P_{43}$	${}^{p}P_{44}$
0	15 460.72									
1	463.54	15 456.03			15 459.28					
2	466.39	456.89	15 449.58		460.86					
3	469.21	458.14	450.32		462.41	15 446.03				
4	472.06	459.52	450.94		464.14	445.45		15 447.29		
5	474.88	460.93	451.49		465.72	444.79	15 443.74	446.29	15 439.30	15 439.43
6	477.69	462.41	451.99	15 448.80	467.32	444.02	442.04	445.36	437.34	436.53
7	480.49	463.92	452.47	448.22	468.87	443.28	440.23	444.38	435.37	433.51
8	483.20	465.40		447.46	470.41	442.50	438.32	443.45	433.34	430.39
9	485.93	466.91		446.69	472.06	441.64	436.32	442.50	431.27	427.12
10	488.62	468.35		445.86	473.42	440.75	434.25	441.54	429.15	423.91
11	491.26	469.86		445.05		439.85	432.15	440.52	427.03	420.56
12		471.27		444.02		438.87	430.04	439.47	424.82	417.23
13				443.28			427.86	438.66	422.67	
14				442.40			425.65	437.75	420.46	
15				441.18			423.32		418.08	
16				440.23						
$A^{4}\Pi$	$_{(3/2)} \leftarrow X^{4}\Sigma^{-}(2,$	0)								
N″	${}^{t}R_{31}$	^s R ₃₂	${}^{r}R_{33}$	${}^{q}R_{34}$	${}^{s}Q_{31}$	${}^{q}Q_{33}$	${}^{p}Q_{34}$	${}^{q}P_{32}$	${}^{p}P_{33}$	°P ₃₄
0	15 381.03	15 375.85			15 378.03					
1	383.80	376.32			379.59					
2	386.59	377.20	15 369.92	15 368.90	381.17	15 366.89				
3	389.39	378.33	370.60	369.63	382.74	366.40	15 366.52	15 368.59		
4	392.11	379.59	371.15	369.73	384.25	365.69	365.48	367.46	15 361.46	
5	394.84	381.03	371.62	369.45	385.77	364.98	364.01	366.52	359.55	15 359.76
6	397.54	382.38	372.02	368.90	387.40	364.20	362.19	365.48	357.57	356.84
7	400.15	383.80	372.40	368.19	388.68	363.33	360.38	364.20	355.42	353.72
8	402.81	385.15		367.46	390.10	362.29	358.28	363.33	353.39	350.54
9	405.37	386.59		366.52	391.47	361.46	356.25	362.29		347.27
10	407.89	387.76		365.48	392.83	360.38	354.10	360.97		343.87
11	410.38	389.08		364.41	394.08		351.91	360.02		340.46
12	412.81	390.10		363.33	395.31		349.60	358.87		337.00
13	415.21	391.47		362.19	396.59		347.27	357.57		
14		392.83		360.97	397.54		344.93	356.25		
15				359.76	398.94		342.44	354.95		
16				358.35			339.85	353.72		
17				356.84			337.35			
18				355.54						
19				354.10						
20				352.66						
$A^{4}\Pi$	$(1/2) \leftarrow X^4 \Sigma^- (2,$	0) / D	<i>a</i> p	ⁿ D	ro	<i>p</i> ₀	00	¹ / ₁ D	⁰ D	<i>"</i> D
/N	<i>K</i> ₂₁	<i>K</i> ₂₂	¹ K ₂₃	^r K ₂₄	Q_{21}	$^{1}Q_{23}$	Q_{24}	$^{1}P_{22}$	P_{23}	P ₂₄
0										
1	15 311.12		15 296.36		15 306.62					
2	313.86		297.13	15 296.36	308.14	15 294.13		15 297.13		
3	316.54		297.79	296.80	309.52	293.46	15 293.95	295.75	15 290.65	
4	319.12	15 306.36	298.25	296.71	311.12	292.78	292.78	294.58	288.78	15 289.74
5	321.72	307.55	298.67	296.36	312.52	291.91	291.23	293.46	286.88	286.95
6	324.24	308.80	299.07	295.75	313.86	291.07	289.43	292.29	284.76	283.94
7	326.70	310.18		294.84	315.08	289.97	287.45	291.14	282.61	280.74
8	329.17	311.30		293.88	316.25	288.94	285.41	289.88	280.39	277.35
9	331.52		299.52	292.82	317.43	287.84	283.17	288.75	278.12	273.97
10	333.85		299.52	291.72	318.53	286.58	280.81	287.42		
11	336.08			290.49	319.56	285.37	278.50	285.97		
12	338.25				320.55					
13	340.44				321.25					
14	342.44									

TABLE I. (C	ontinued.)
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$A^{4}\Pi_{(-1/2)} \leftarrow X^{4}\Sigma^{-}(2,0)$										
N''	$r_{R_{11}}$	${}^{q}R_{12}$	${}^{o}R_{14}$	${}^{q}Q_{11}$	${}^{o}Q_{13}$	${}^{n}Q_{14}$	${}^{p}P_{11}$	°P ₁₂	${}^{n}P_{13}$	${}^{m}P_{14}$
0	15 242.90									
1	245.53			15 241.55						
2	248.09			243.00						
3	250.53	15 239.95	15 231.64	244.37	15 228.37			15 230.64		
4	252.95	241.07	231.59	245.72	227.51	15 227.30		229.34	15 223.24	
5	255.39	242.18	231.11	246.97	226.70	225.65		228.21	221.37	15 221.83
6	257.70	243.27	230.41	248.09	225.65	223.71		226.95	219.09	218.70
7	259.93	244.27	229.41	249.16	224.52	221.60			216.73	215.43
8	262.08	245.20	228.37	250.23	223.36	219.35		224.29	214.32	212.01
9	264.01	246.09	227.07	251.13	221.97	216.87		222.83	211.85	208.44
10	266.06	246.97	225.75	252.00	220.65	214.32			209.25	
11	267.95		224.38			211.66				
12			222.83				15 237.28			
13			221.25				236.68			
14			219.44				235.96			

(III), very close to system (II), seems to be related to system (II). The appearance of the vibronic bands within each system (i.e., II and III) changes substantially with the vibrational quanta suggesting that these two systems share a common (ground) state and that their excited states are strongly interacting.

Very weak (0-1) bands have been observed for these two systems and suggest that all share a common ground state. The vibrational assignments are obtained solely from the observed $^{14}N^{-15}N$ isotope shifts. Due to the weak intensities of some bands and perturbations appearing in the stronger bands, rotational analyses are not completed for these systems and will be the subject of a future study.⁴⁹

TABLE II. Spectroscopic constants for the A ${}^{4}\Pi_{r}$ and X ${}^{4}\Sigma^{-}$ states (cm⁻¹).

DISCUSSION

A. Molecular orbitals and electronic configurations

Recently, Harrison³⁵ has carried out a detailed *ab initio* calculation which established the symmetries, bond lengths, and energies of the ground and first excited quartet state of CrN. Here we discuss the molecular orbital (MO) scheme to provide a coherent picture both about the *X* and *A* states, and other excited states not included in the *ab initio* calculation. The MO scheme is also convenient for the comparison with isovalent VO, MoN, and WN systems. An MO diagram believed to be appropriate for CrN is presented in Fig. 2. This diagram is similar to the MO diagram used by Merer for

A state ^a Ω'	Т	В	$(10^6) D$	р	$(10^4) p_j$	Deviation ^b
			v' = 0			
5/2	13 639.98 (9)	0.6216 (6)	_	_	_	0.07
3/2	13 559.61 (15)	0.6123 (10)	_	0.005 (30)	_	0.15
1/2	13 485.37 (5)	0.6040 (4)	_	0.042 (10)	—	0.05
-1/2	13 419.52 (9)	0.5924 (11)	2.0 (60)	-0.035 (25)	_	0.11
			v'=1			
5/2	14 553.48 (7)	0.6158 (8)	_	_	_	0.07
3/2	14 471.86 (15)	0.6051 (8)	12.0 (30)	-0.001 (14)	_	0.13
1/2	14 397.44 (5)	0.5980 (5)	_	0.042 (13)	_	0.05
-1/2	14 332.46 (8)	0.5891 (9)	12.0 (60)	-0.032 (20)	1.4 (8)	0.08
			v'=2			
5/2	15 454.56 (6)	0.6109 (6)	_	_	_	0.06
3/2	15 371.32 (8)	0.6031 (6)	_	-0.001 (20)	_	0.08
1/2	15 297.45 (6)	0.5937 (6)	_	0.042 (15)	_	0.06
-1/2	15 233.43 (7)	0.5821 (8)	_	-0.038 (16)	_	0.06
	X	state: $v''=0; \lambda=2.628(82)$), $\gamma = 0.005(8)$, $B'' = 0.6$	259(8), $r_0'' = 0.1563$ nm.		

 ${}^{a}A = 83.067(85)$, $T_{v'=2} = 15$ 329.99(9) and $B'_{v'=2} = 0.5986(8)$ were obtained from a global fit of (v'=2). $\Omega' = 5/2$ and 3/2 subbands, see text for detail. ^bThe deviation indicates two standard deviation.

TABLE III. Vibronic band assignments of CrN.

$B^{4}\Sigma^{-}$	$-X^{4}\Sigma^{-}$ (sys	tem II)	System III				
υ'	λ (nm)	$T_{v'} (cm^{-1})$	υ'	λ (nm)	$T_{v'} ({\rm cm}^{-1})$		
0 ^a	488.0	20 486	0	488.5	20 465		
1	473.0	21 136	0	482.0	20 741		
2	459.2	21 773	1	466.3	21 439		
3 ^a	446.1	22 410	1				
4	433.7	23 051	2	447.0	22 365		
5 ^a	422.2	23 682	2	441.3	22 654		
6	411.2	24 313					

^aBands seem to be perturbed.

metal oxides.⁴¹ We have added the metal p orbitals since several *ab initio* calculations have shown they are somewhat relevant to the nonbonding π orbitals.

The comparison with the isovalent VO molecule is very helpful. However, the number of CrN excited states within the same energy range should be significantly reduced over that in VO where a small energy gap between the nonbonding 9σ and 1δ orbitals results in a particular complicated electronic structure.⁴¹ This difference between the two molecules can be understood by comparing the atomic spectroscopy of vanadium and chromium. The gap between the Cr 4s and 3d orbitals must be quite large such that the ground state of Cr has a d^5s^1 configuration with the d^4s^2 configuration much higher in energy.⁴⁵ Similarly, in CrN, the nonbonding 9σ orbital should be significantly higher in energy than the nonbonding 1δ orbitals. As a result, the low-lying states of CrN are derived only from $1\delta^2 9\sigma^1$, $1\delta^2 9\sigma^0 10\sigma^1$, and $1\delta^2 9\sigma^0 4\pi^1$ configurations. A molecular energy level diagram can then be adapted (Fig. 3) from that of VO⁴¹ by keeping only these three configurations.

The *ab initio* calculation³⁵ has yielded the first excited state with a $1\delta^2 9\sigma^0 4\pi^1$ configuration which is consistent with our MO diagram and can be used to assign the 745 nm transition. The corresponding excited state for VO, however, is the *second* ⁴ Π state.⁴¹ There are many similarities between the first ⁴ Π state of CrN and the second ⁴ Π state of VO.

The observed CrN spin-orbit constant *A* can be compared with an estimation based on atomic spin-orbit constants. The ${}^{4}\Pi_{5/2}$ state can be expressed by a Slater determinant $|\delta^{+}\alpha\delta^{-}\alpha\pi^{+}\alpha\rangle$. The molecular spin-orbit constant is



B. Equilibrium constants and the bonding in the *X* and *A* states

With our CrN analysis, the A-X transitions for three group VI A nitrides are now characterized.^{21–26} The A state energy increases systematically as one moves down the group, Cr, Mo, W. This can be viewed as evidence for the changing nd-(n+1)p hybridization in the π nonbonding orbitals. As was demonstrated sometime ago for MoN, the π nonbonding orbital has a significant 5p contribution.³⁹ The present observation seems to indicate that this d-p hybridization is even more important for CrN.

Another interesting observation is that the ground state bond length (r_0) of 0.1563 nm for CrN is the shortest among the 3*d* nitrides reported to date. This seems to suggest that the three nonbonding electrons play only minor roles in weakening the Cr=N triple bond. The excited state bond length (r_0) of 0.1585 nm is very close to that of the ground state, implying that the excited 4π orbital is mainly nonbonding.

C. Perturbations and other excited states

There are two signatures of perturbation in the ${}^{4}\Pi$ excited state: (i) the spacing among different sublevels is not even and (ii) several sublevels seem to be perturbed such that the deviation with a case (a) effective Hamiltonian fit is noticeable. Since the electronic structure of the CrN *A* state is quite similar to that of the *B* state of VO, the pattern of perturbing states may also be compared (Fig. 3). In the case of VO, two other states perturb the *B* state, the ${}^{2}\Pi$ from above and ${}^{2}\Sigma^{+}$ on the side. Merer and co-workers have studied the VO *B* state extensively and carried out a deperturbation analysis of the interacting $B {}^{4}\Pi - a {}^{2}\Sigma^{+}$ states.⁵¹ The



FIG. 2. The qualitative CrN molecular orbital diagram and the ${}^{4}\Sigma^{-}$ ground state electron configuration.



FIG. 3. Energy level diagram of the electronic states of CrN. Solid lines indicate the observed electronic states whereas the dashed line points to the $^{2}\Sigma$ state inferred from perturbation.

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observed CrN *A* state energy pattern mirrors that of the deperturbed VO *B* state. The uneven pattern can be associated with off-diagonal matrix elements with the higher ${}^{2}\Pi$ state, as in the case of VO *B* state. The deviation from a case (a) Hamiltonian may be due to weak perturbations from the ${}^{2}\Sigma^{+}$ state. Another possible perturber is the ${}^{2}\Delta$ state from the $1\delta^{3}$ configuration not included in Fig. 3. A sensible deperturbation analysis must await the availability of a high resolution spectrum.

The magnitude of the observed Λ -doubling parameters is somewhat smaller than that in MoN. This is consistent with the smaller spin-orbit interaction in CrN. A direct comparison with VO is not meaningful since we did not use the full matrix employed in the VO analysis in our least squares fit.

In the present study we have concentrated on the detailed analysis of the $A^{4}\Pi_{r} \leftarrow X^{4}\Sigma^{-}$ transition. Evidence for two other electronic transitions has been noted. Although rotational analyses have not yet been carried out for these systems, the nature of the transitions involved can be inferred. It is reasonable to assume that all observed bands with the jet-cooled source have $X^{4}\Sigma^{-}$ as the lower state. Two low-lying doublet states arise from the $1\delta^2 9\sigma^1$ configuration (see Fig. 3) but they are expected to be several thousands of cm⁻¹ above the ground state and should be depopulated in the supersonic cooling. The (0-1) bands, with lower state about 1000 cm⁻¹ above the ground state, have very weak signals in our experiments. Case (a) allowed upper states are then the $B^{4}\Sigma^{-1}$ and $A^{4}\Pi_{r}$, as indicated in Fig. 3. Several other excited doublet states can mix with these two bright states through spin-orbit coupling and transitions to them can become weakly allowed. The most plausible assignment for the observed systems is that the two transitions involve $B^{4}\Sigma^{-}$, and ${}^{2}\Pi(1\delta^{2}4\pi)$ upper states. This conjecture is currently being explored.

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