Rotational and Hyperfine Analysis of the $C^{4}\Sigma^{-}-X^{4}\Sigma^{-}$ (Blue) System of Niobium Oxide, NbO

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The $C^4\Sigma^- - X^4\Sigma^-(0, 0)$ band of NbO, whose *R* heads lie near 4690 Å, has been analyzed from high-resolution grating spectra. Both ${}^{4}\Sigma^-$ states have second-order spin-orbit splittings, $4\lambda = E({}^{4}\Sigma_{3/2}) - E({}^{4}\Sigma_{1/2})$, of about 60 cm⁻¹, so that they are in good case (a) coupling at low *J*, although the appearance of the band had been interpreted by previous workers as ${}^{4}\Sigma(b) - {}^{4}\Sigma(b)$. The ${}^{93}Nb$ nuclear hyperfine structure $(I = \frac{9}{2})$ is very impressive in the R_1 , P_1 , R_4 , and P_4 branches, with the 10 hyperfine components of a rotational line spread over more than 0.9 cm⁻¹ in the F_1 branches. The hyperfine linewidths vary considerably with *J*, in the manner expected for the rapid spin uncoupling from case (a_p) to (b_{gJ}) which occurs in a high-multiplicity state. The very great hyperfine linewidths arise because the sign of the Fermi contact parameter *b* (the coefficient of **I** · **S** in the magnetic hyperfine Hamiltonian) is different in the two ${}^{4}\Sigma$ states, so that the observed patterns are the sums of the splittings in the two electronic states. © 1988 Academic Press, Inc.

1. INTRODUCTION

The NbO spectrum has been known for over 35 years (1), but such is the complexity of its band systems in the visible that analysis progressed only slowly until laser studies by Féménias *et al.* (2) gave an unambiguous analysis of part of the $B^4\Pi - X^4\Sigma^-$ system near 6500 Å. The NbO molecule is now known to have a ${}^{4}\Sigma^-$ ground state (3) in case (a) coupling, where the second-order spin-orbit splitting between the $\Sigma = \frac{3}{2}$ and $\frac{1}{2}$ components is 62 cm⁻¹ (2, 4). Besides the ${}^{4}\Pi - {}^{4}\Sigma^-$ system in the red the other strong transition in the visible region is a ${}^{4}\Sigma^- {}^{4}\Sigma^-$ system in the blue, whose (0, 0) band is at 4690 Å (5-7); our analysis of this transition at Doppler-limited (grating) resolution is the subject of this paper. The upper ${}^{4}\Sigma^-$ state, denoted $C^{4}\Sigma^-$ by analogy with VO (8), is found to have almost exactly the same second-order spin-orbit splitting as the $X^{4}\Sigma^-$ state, so that the band structure, with its four close heads, appears to be ${}^{4}\Sigma(b)$ - ${}^{4}\Sigma(b)$, rather than ${}^{4}\Sigma(a) - {}^{4}\Sigma(a)$, a point which had led to some confusion in earlier work. More details of the history are given in Refs. (2, 9).

The hyperfine structure resulting from the $I = \frac{9}{2}$ nuclear spin of ⁹³Nb is particularly impressive in the C-X transition because the signs of the Fermi contact parameters in the two ${}^{4}\Sigma^{-}$ states are opposite. As a result the line splitting is the sum of the level splittings in the two electronic states, and in some of the branches the hyperfine widths are more than 0.9 cm⁻¹. In the uncrowded regions it is easy to resolve the 10 hyperfine components at grating resolution for these branches (7). The parallel polarization does not allow the upper state hyperfine parameters to be determined directly, but values can be obtained given the known ground state parameters from Refs. (2, 3), allowing for the spin uncoupling in the two ${}^{4}\Sigma^{-}(a)$ states.

2. EXPERIMENTAL DETAILS

The NbO radical was prepared in a 2450-MHz electrodeless discharge through a flowing mixture of NbCl₅ vapor, O_2 , and helium. The optimum conditions for NbO production were monitored by eye with a small spectroscope: the color of the discharge was bright pinkish-white, and the bands of the blue system of NbO were extremely prominent.

The emission spectrum of the (0, 0) band of the C-X system was photographed on Kodak II a-D plates in the 12th order of the 7-m Ebert-mounted spectrograph at the University of British Columbia; the slit width was 30 μ m, and the experimental resolution was about 450 000, corresponding to an effective temperature of about 1000°C in the discharge. Calibration was provided by an iron-neon hollow cathode lamp, for which the wavelengths have been tabulated by Crosswhite (10); a total of 44 iron lines were fitted to a four-term polynomial. For measurement the plates were digitized using the computer-controlled PDS microdensitometer at Nice Observatory, and the line positions were obtained by setting the cursor on the computer's graphics terminal. The estimated uncertainty in the hyperfine component positions is 0.003 cm⁻¹.

The estimated uncertainties in the rotational line positions range up to 0.02 cm^{-1} in crowded portions of the spectrum.

3. ANALYSIS OF THE SPECTRUM

The general appearance of the C-X(0, 0) band in the spectrum of NbO was illustrated in our previous paper (2). It is red-degraded and has three R heads lying within 5 cm⁻¹, which are shown in more detail in Fig. 1. The outermost head is assigned as R_2 , the middle head as R_1 , and the inner head as a blend of R_3 and R_4 . The closeness of the R heads shows that the spin coupling is nearly identical in the two electronic states.

Eight branches can be picked out in this band, which are the four R and four P branches expected for a ${}^{4}\Sigma{}^{-4}\Sigma$ transition. The effect of the Nb nuclear hyperfine structure is that the high-J lines of the R_2 , R_3 , P_2 , and P_3 branches give fairly sharp and intense lines where the hyperfine structure is quite narrow, while the other four have very wide hyperfine structures where the same amount of intensity is spread out over a much larger frequency range, making them far less prominent. Uhler (6),

analyzing just the sharper branches, assigned the transition as ${}^{2}\Delta - {}^{2}\Delta$, but Dunn (7), using a lower temperature microwave discharge source, also found the weaker broad branches and gave the electronic assignment correctly as ${}^{4}\Sigma - {}^{4}\Sigma$.

The tail of the band is quite open and is where the assignment of the branches to their electron spin components can be made: for instance, the wider branches involving the F_1 and F_4 spin components are easily distinguished from the narrower F_2 and F_3 branches. Figure 2 shows the general appearance, although the specific region has been chosen to illustrate the single upper state rotational perturbation that has so far been detected (6), at F'_2 (67.5). This perturbation is useful because the ground state constants from our laser work (2) give the rotational and spin assignments unambiguously, confirming Uhler's numbering and carrying the assignments into the crowded *R*-branch region. The R_3 and P_3 branches are then easily numbered. See also Fig. 1 of our previous article (2).

The branches involving the F_1 and F_4 spin components were more difficult. These branches have most impressive hyperfine structures at high N; the R_1 and P_1 branches, for example, have the 10 hyperfine components of each line spread over more than 0.9 cm^{-1} . The R_4 and P_4 branches have slightly smaller widths, because of the details of the spin uncoupling. The very great hyperfine linewidths, beautiful though the patterns may be, are a severe hindrance anywhere except in the tail of the band because they cause extensive blending which makes the process of picking out the branches most laborious. The one great advantage of the hyperfine structure is that the F(F+ 1) dependence of the hyperfine component positions is in the opposite sense in the R_1 and P_1 branches compared to the R_4 and P_4 branches at high J values and also the overall width is different: as a result it is possible to associate the R branches immediately with their corresponding P branches. In our experience, this is the usual consequence of hyperfine effects in a molecular spectrum: the hyperfine patterns frequently carry very useful information about the branch assignments and numbering but this is more than offset by the severe blending that results.

Our procedure has been to reduce what information is available for each rotational line to the "midpoint" of the hyperfine structure as far as possible. In this way, we can mainly decouple the rotational problem from the hyperfine problem. However, it is not straightforward to do this, even where the 10 hyperfine components are mostly resolved. If most of the components can be measured the line frequencies can be fitted to the approximate expression

$$\nu_{\rm hfs}(F, I, J) \cong \nu_{\rm rot} + k[I(I+1) + J(J+1) - F(F+1)] \tag{1}$$

which follows from the form of the magnetic hyperfine Hamiltonian and the coupling scheme J + I = F. Equation (1) holds in both (a_β) and $(b_{\beta J})$ coupling and is exact for Q branches, where the upper and lower state J values are the same, but is an approximation when $J' \neq J''$, as in the present spectrum where only R and P branches are seen; nevertheless the approximation improves with increasing J because the hyperfine spacings in the upper and lower states become more nearly in the same ratio. The equation becomes exact for all branches if the hyperfine spacings are near zero in one of the states, but this is only roughly so in the present case.

It is also an approximation to take the rotational frequency as the mean of the two outermost hyperfine component frequencies, although this is the obvious way of coping



with lines where the hyperfine structure is too narrow to be resolved, or where a weaker line lies under a stronger one and its extent can only be estimated from the discontinuity that its edge causes in the intensity of the overlying hyperfine pattern. Fortunately the approximation is not unduly severe: for example, it is easy to show that, for $J = 45\frac{1}{2}$ and a total hyperfine width (F = 41-50) of 0.9 cm⁻¹, the mean of the two outer components differs from the true rotational frequency by only 0.005 cm⁻¹. A rather more severe approximation, which was occasionally used as a last resort, was to take the rotational frequency as the average of the two central hyperfine components; this approximation is poorer by a factor of four. In summary, therefore, there is no simple way of extracting the rotational frequencies from the measured hyperfine frequencies without considerable effort, and we recognize that the overall rms error in our rotational fit has been worsened by these approximations.

After some difficulty caused by the blending at low J, the rotational frequencies given in Table I were obtained. These were then fitted to the eigenvalues of the 4Σ Hamiltonian in two steps. The first step was to determine the ground state rotational constants from the rotational line frequencies measured in the sub-Doppler laser work on the red system (2), plus some higher J data from the present work, using Aslund's modified term value approach (11, 12); this produced a set of ground state constants and two sets of upper state energy levels, one for the $B^4\Pi_{-1/2}$ upper state of the red system and one for the $C^{4}\Sigma^{-}$ state. The second step was to fit the term values for the $C^{4}\Sigma^{-}$ state to the same Hamiltonian (which is given in Table II). This method has the advantage of transferring some of the accuracy of the laser measurements of the red system to the $C^{4}\Sigma^{-}$ state. The same problem of deducing the rotational frequencies from the measured hyperfine frequencies naturally occurs in the laser data for the red system, but its effects are less severe because of the higher resolution which eliminates much of the blending. No attempt has been made to refine the constants for the $B^{4}\Pi$ state because a full rotational and hyperfine analysis of the more than 10 000 lines of the B-X(0,0) band is presently in progress.

The results for the $X^{4}\Sigma^{-}$ and $C^{4}\Sigma^{-}$ states are given in Table III. The most interesting values are the two second-order spin-orbit parameters, λ ; these are even more similar than the 5 cm⁻¹ spread of the *R* heads would indicate. The parameter γ_{s} , which represents the spin-orbit distortion of the spin-rotation interaction (13), is very definitely required for the present data, as it was for the corresponding transition of VO (14).

4. HYPERFINE LINEWIDTHS

Spin uncoupling causes much more dramatic effects in high-multiplicity states than it does in doublets (15). One of its effects is to limit quite severely the validity of the pure case (a) expressions for the linestrengths. Another of its effects is to cause an unexpectedly rapid variation of the hyperfine linewidths with increasing rotation (16), which we now document for the C-X transition of NbO.

The magnification of the effects of spin uncoupling in high-multiplicity states arises because the operator $-2BJ \cdot S$ has matrix elements in a case (a) basis that include



the factor $[S(S + 1) - \Sigma(\Sigma \pm 1)]^{1/2}$, which is roughly proportional to S. The effect in the two ⁴ Σ states of NbO is that they are already in good case (b) coupling at the highest J value we observe even though their spin-orbit splittings are about 60 cm⁻¹. The hyperfine coupling case changes quickly from (a_{β}) to $(b_{\beta J})$ with increasing rotation, and the hyperfine structure can be explained quantitatively using exact rotational wavefunctions for the intermediate coupling case.

The four electron spin sublevels of the ${}^{4}\Sigma$ states in intermediate coupling can each be described as

$$|F_{i}(J)\rangle = \alpha |\Omega, J, x\rangle + \beta |\Omega', J, x\rangle, \qquad (2)$$

where α and β are coefficients given by the eigenvectors from the diagonalization of the rotational part of the case (a) Hamiltonian matrix (Table II), Ω and Ω' are $\frac{1}{2}$ and $\frac{3}{2}$, and x is e or f. Since we do not observe quadrupole effects in the present work, the hyperfine structure can be taken as purely magnetic in origin (2, 7), and the hyperfine Hamiltonian of Frosch and Foley (17) applies:

$$H_{\rm hfs} = aI_z L_z + b\mathbf{I} \cdot \mathbf{S} + cI_z S_z. \tag{3}$$

Since $\langle L_z \rangle = 0$ for Σ states, a suitable case (a) expansion is

$$H_{\rm hfs} = (b+c)I_z\Sigma + (b/2)(I_+S_- + I_-S_+) \tag{4}$$

from which we obtain the general formula for the hyperfine width of a rotational level of a ${}^{4}\Sigma$ state in the intermediate coupling case,

$$E(J, F = J + I) - E(J, F = J - I) = \Delta E(J)$$

= $\frac{2I(J + \frac{1}{2})}{J(J + 1)} \left[\frac{1}{4}(b + c)(8\alpha^2 + 1) + b\beta\{\alpha(3X)^{1/2} \pm \beta(J + \frac{1}{2})\}\right].$ (5)

In Eq. (5) $X = (J - \frac{1}{2})(J + \frac{3}{2})$ and the upper and lower signs refer to the *e* and *f* levels, respectively. It is interesting to note the forms of the eigenvector elements: for the F_1 and F_2 levels we have

$$\alpha \propto \left\langle \frac{1}{2} | H | \frac{3}{2} \right\rangle, \qquad \beta \propto E(J) - \left\langle \frac{1}{2} | H | \frac{1}{2} \right\rangle, \tag{6}$$

while, for the F_3 and F_4 levels,

$$\alpha \propto E(J) - \left\langle \frac{3}{2} |H| \frac{3}{2} \right\rangle, \qquad \beta \propto \left\langle \frac{1}{2} |H| \frac{3}{2} \right\rangle, \tag{7}$$

where E(J) is the eigenvalue energy. The hyperfine linewidth is, of course, the difference between the level widths of the upper and lower states given by Eq. (5), remembering that these are signed quantities.

For the C-X system of NbO it was fairly straightforward to combine the ground state level widths, which are given by our laser work on the red system (2), and the observed linewidths to obtain the upper state level widths. In the resolved F_1 and F_4 branches, for example, we know the electron spin assignment from the rotational combination differences and we can see from the Landé patterns of the lines whether

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TABLE I

5	ď	R,	P2	R2	P ₃	R ₃	P4	R 4
0.5	21315, 7148		21314.7051			21316.2578		
10 H	21314.8477		21313.75754		21310.8789	21317,5137		
7 IA	21312.9238		21311.7930		21309.7832	21318.0449		
2.2	0E47.11E12		21310.6641		21309.5840	21318.4922		
5.9	21310.6289		21309.5781		21307.3691	2124.91512		
5.2	21309.4980		21308.4062		21306.0352	21319.2520		
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	1204.00212		21304.0781		21301.7520	21319.8867	21301.8711	
	21303.9277		21302.5410		21300.2129	21319.9727	21300.4375	
12.5	21302.3809		21300.8398		21298.6152	21319.9922	21298.7012	
13.5	21300.6875		21299.1934		21296.9258	21319.8906	21297.0508	
14.5	21299.0059		21297.4141	_	14/1°64717	774/*/TCT7	21221212212	
15.5	21297.2988		21295.6895		1995.5712	7440.710171C	21201.4445	
	1110-04212		21291.9316		21289.5625	21319.0078	21289.6934	
	21291.2148		21289.9453		21207.5312	21318.5781	21287.6816	
10.01	21289.6934		21287.9727		21285.4707	21318.1348	21285.5840	
20.5	21287.6152		21285.8164		21203,3516	21317.6152	21283.4570	
21.5	21285.4570		21283.7031		21281.1348	2090./1512	0707-19717	
22.52	21283.2695		21281.4668		212/0.4720	21315.2012	17/4 8/712	2040.41510
	0040.00717		1058 74C1C	21317.5273	21274.1816	21314.9609	21274.1211	21315.5410
	21276.0781		21274.4004	21316.7285	21271.7012	21314.1152	21271.6777	21314.7344
24.5	21273.5820		21271.9297	21315.7793	21269.1641	21313,1855	21269.0879	21313.8281
27.5	21271.0312		21269.3867	21314.7930	21266.5937	21312.2246	21266.4805	21312.8711
28.5	21268.4004		21266.7578	21313.7109	21263.9863	21311.1772	21263.8535	21311.8711
29.5	21265.7344		18/0.40717	0402.11217	2062110212	1110 0111	C111110212	1050.01512
5.0 M	21263.0020		2475,10212 2475,10212	10471 VILIC	21255.4719	21307.7266	21255.4002	21308.4805
	21257.2949		21255.6328	21308.8398	21252.7891	21306.4160	21252.5645	21307.1816
	21254, 3086		21252.7109	21307.4434	21249.8320	21305.0625	21249.5957	21305.7832
19.40	21251,3164	21304.5566	21249.7148	21306.0352	21246.7148	21303.6465	21246.5020	21304.3320
33.5	21248.2754	21303.2578	21246.6230	21304.5039	21243.6113	21302.1455	21243.4004	21302.8413
29.5	21245.1836	21301.8711	21243.4785	CAFA 70F12	8/0C'06717	1000 00017	7012.07212	84.94 00010
37.5	21241.9395	21300.4330	2210 22010	21200.5077	9449.15415	BB92,79212	71717.7187	71208.1441
	21230./127	ATEL 10010	21233.6758	21297.8340	21230.6230	21295.5762	21230.3594	21296,3887
		21295.5117	21230.2734	21296.0078	21227.2012	21293.7754	21226.9687	21294.6133
2	21228.4961	21293.6973	21226.8145	21294.1230	21223.7012	21291.8555	21223.4570	21292.7500
	21224 9824	21291.7832	21223.2910	21292.1543	21220.1734	21289.9375	21219.9121	21290.8164
10.12	21221.3848	21289.8730	21219.7129	21290.1484	21216.5820	21287.9727	21216.2559	21288.8223
14.55	7E97.71212	21287.8457	21216.0391	21288.0742	21212,9023	51285.400 F	21212.6289	21286.7969
	21214.0645	21285.4582	21212.3242	21285.9160	21209.1/17	21283.7902	21208.8015	21284./070
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21275.4668	21272.9785	21270.5039	21267.8926	21265.2598	21262.562.5	A01/ A0217	21253.9590	21250.9590	21247.9609	21244.8242	21241.5781	21238.3477		21228.1777	21224.6406	21221.0781	21217.4648	21213.7383	1714.40212	21202.1641	21198.1562	21194.1406	21190.0430	21185.8359	21181.280	21172.8477	21168.4219	21163.8574	21159.2891	21154.6680	21145.1543	21140.4102	21135.5723	21130.5977	21120.4238	21115.3418	21110.0840	21104.8711	21094.1738	21088.7168	21083.1699								_
21193,1680	21189.1230	21184.9785	21180.7910	21176.5918	8/02/2/112	2116/ BUB. 20112	1158.9941	21154.3437	21149,7383	21144.9785	21140.2656	21135.4043	0/10/00117	21120.4238	21115.3750	21110.1484	21104.9414	21099.6523	21000 0K12	21083.4395	21077.8906	21072.2285	21066.5430	21060.8164	21034.9746	1748 1 248	21037.1895	21031.1152	21024.9414	21018.6582	21004.1211	20999.7207	20993.2871	20986.7773	402273.7324	20966.9922	20960.2676												-
21274.4609	21271.9766	21269.4453	21266.8105	21264.2187	21261.4687	1002 33414	21222 B452	21249.9141	21246.7988	21243.6895	21240.4844	21237.2109	7170.00717 1917 010717	21220.94277	21223.4980	21219.9121	21216.2559	21212.5527	21208.7930	71200-0941	21197.0059	21192.9824	21108.8457	21184.7227	21180.3848	21176.0469	5/89.1/11Z	21162.6756	21158.1289	21153.4746	21148.6836	21143.9414	21134.1600	21128.9590	21124.0840	21118.9922	21108.5410	21103.2207	21097,7754	21084.8044	21081.1855	21075.5254	21069.8164	21058-1270	21052.1445	21046.2227	21033,9434		
21193.5605	21189.5000	21185.3906	21181.1914	21176.9316	21172.5977	7912.99112		21154.6680	21150.0703	21145.3437	21140.5723	21135.7402	21130.0242	CFCB.CZ112	21115.7031	21110.5449	21105.2930	21100.0039	21094.6641	21087.7441	21078.1816	21072.5781	21066.8984	21061.1660	21055,3457	21049.4570	21045.42.012	21031.4062	21025.2773	21019.0566	21012.7891	21006,4375	20993.5586	20987.0445	20980.4629	CI 10.74905	20460.2773	20953.4766											~
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21196.8223	21192.7793	21188.6699	21184.5020	21160.2852	21175.9707	2/12/1/1/2/22	0501./0112	21158.1289	21153,5312	21148.8105	21144.0488	21139.2402	11/5.65117	21129.42112	10EE.91112	21114.2031	perturbation	21103.7090	21098.3413	21082.5312	21081.9707	21076.3926	21070.7812	21065.0430	21059.2383	21053.3809	21047.4121	21035.3867	21029.3242	21023.1523	21016.8770	21010.5859	20997.8340	20991.1836	20984.6797	20978-0449	20964.6270								_				-
21276.4551	21274.0918	21271,5879	21268.9336	21266.3926	21263.6465	21260.9023		21252.1738	21249.0742	21245.9922	21242,8848	21239,6465	CO10.00212	21232,9648	21226.0449	21222.5605	21218.8926	21215.1875	21211.4336	20279 /0717	21199. BOBA	21195,7559	21191.7051	21187.5898	21183.3184	21179.0527	21174.6445	21145.7891	21141.2480	21156.5742	21151.8613	21147.0547	21137.4336	21132.5273	21127.4883	21122.3379	21112.1270	21104.7812	21101.4434	1000 5714	21084,9707	21079.3789	21073.7051						-
21198.5527	21194.5488	21190.4355	21186.2754	21181,9883	21177.7383	211/3.3867	0/10/10117	21159.9141	21155.3613	21150.6758	21145.9590	21141.1465	8407 90117	21131.28/1	21121.2207	21116.1152	21110.9043	21105.6270	21100.3359	21084.9902	21083-9824	21078.4102	21072.7539	21067.0391	21061.2793	21055.4687	21049.5703	21037.5312	21031.4102	21025.2383	21018.9805	21012,7031	21000.0195	20993.5684	20987.0547	20980.4238	20967.2363	20960.5312	20953.8437	•									
49.5	50.5	51.5	52.5	21.5		0 W 1			26.22	60.5	51.5	10 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1			566.5	67.5	68.5	69.5	5.02	2012	23.55	24.5	75.5	74.5	77.5	78.5	C	81.5	82.5	03.5	84.5	82.3	87.5	88.5	89.5	100	92.5	93.5	64 6 6 6 7 6 7 6 7 6	1 1 0	57,5	98.5	99.5	10010	102.5	103.5	105.5	106.5	

TABLE II

Matrix of the Rotational Hamiltonian for a ${}^{4}\Sigma^{-}$ Electronic State in a Case (a) Parity Basis

	3/2 >	1/2 >
< 3/2	$2\lambda + BX - 3\gamma/2 + 2\lambda_D - DX(X+3) - 3\gamma_D X$	$\frac{-\sqrt{3X}\{(B-\gamma/2)-2D[X+2\mp(J+\frac{1}{2})]}{-\frac{1}{2}\gamma_D[X+7\mp(2J+1)]-\gamma_S\}}$
< 1/2	symmetric	$\begin{array}{l} -2\lambda + B(X+4) - 7\gamma/2 - 2\lambda_D(X+4) \\ -D[(X+4)^2 + 7X+4] - \gamma_D(7X+16) \\ \mp 2[(B-\gamma/2) - 2\lambda_D - 2D(X+4) \\ -\frac{1}{2}\gamma_D(X+11) + \frac{3}{2}\gamma_S](J+\frac{1}{2}) \end{array}$

 $X = (J - \frac{1}{2})(J + \frac{3}{2})$. Upper and lower signs give the e (F_1 and F_3) and f (F_2 and F_4) levels respectively. The basis functions $|J\Sigma >$ have been written $|\Sigma >$.

the high-F hyperfine components lie on the high-frequency side or the low-frequency side; it turns out that the energy order of the hyperfine components in the upper state is opposite to that in the ground state, or in other words, that the very great observed hyperfine linewidth is the difference of two oppositely signed contributions from the two states. The F_2 and F_3 electron spin components posed some problems because their hyperfine structures are never resolved. In order to obtain consistent linewidth data, we measured their widths at half-maximum and then subtracted a Doppler profile correction of 0.13 cm⁻¹, obtained from the well-resolved F_1 and F_4 lines (being the difference between their widths at half-maximum and the separations of their outermost hyperfine components—see Fig. 3). At certain J values the widths of the F_2 and F_3 lines pass through a minimum: since the widths at half-maximum are found to be ~ 0.13 cm⁻¹ at these places it is evident that the hyperfine linewidth passes through zero and that the frequency order of the hyperfine F components reverses. This con-

TABLE III

	$X^4\Sigma^-$		$C^4\Sigma^-$	
To	31.1650	(4)	21346.002	(5)
B	0.434981	(5)	0.402854	(4)
$10^7 D$	3.35	(1)	3.551	(7)
λ	15.5825	(2)	14.915	(2)
γ	0.03411	(1)	-0.01570	(6)
10 ⁶ λ _D	5.5	(2)	-8	(1)
$10^3 \gamma_s$	0.099	(3)	3.47	(2)
b	0.0549 ^ª		-0.0136	(9)

The Rotational Parameters of the Ground $X^{4}\Sigma^{-}$ and the Excited $C^{4}\Sigma^{-}$ States of NbO

The r.m.s.errors are 0.003 cm^{-1} for the ground state (from the laser data) and 0.03 cm^{-1} for the upper state (from the grating data). Numbers in parentheses are ONE standard deviation, in units of the last significant digit quoted.

^aFixed at the e.s.r. value (ref. <u>3</u>). Bond lengths:- $X^{4}\Sigma^{-1}$: $r_{0} = 1.6853$ Å, $C^{4}\Sigma^{-1}$: $r_{0} = 1.7512$ Å.

-0.0020^a

с



FIG. 3. Determination of the Doppler profile correction for the hyperfine linewidths. The difference between the width at half-maximum (WHM) and the separation of the outermost hyperfine components (OHC) in the well-resolved $P_1(41\frac{1}{2})$ line (partially blended by the $R_4(65\frac{1}{2})$ line) gives the Doppler profile correction for the F_2 and F_3 linewidths.

clusion is supported by our calculations of the linewidths, which cannot be made to agree with experiment unless these reversals are assumed to occur.

The observed linewidths, defined as the separations of the outermost hyperfine components for the F_1 and F_4 lines, or the corrected widths at half-maximum for the F_2 and F_3 lines, are shown plotted against $J + \frac{1}{2}$ in Fig. 4. In this figure, the full lines are widths obtained from a crude fitting procedure based on Eq. (5). For this, we first calculated the ground state hyperfine widths from the α and β coefficients given by the rotational constants of Table III, together with the b'' and c'' parameters given by the esr spectrum (3), and subtracted them from the linewidths; we then fitted the resulting upper state widths to Eq. (5). It was found that the upper state b parameter was quite well determined,

$$b(C^{4}\Sigma^{-}) = -0.0136 \pm 0.0009 \text{ cm}^{-1}$$
 (8)

but that $c(C^{4}\Sigma^{-})$ was not determinable. The fact that c could not be determined is not surprising; its contribution to the linewidth goes as 1/J in case (a_{β}) , and as 1/Nor $1/N^{2}$ in case $(b_{\beta J})$ coupling (depending on the electron spin component, so that it



FIG. 4. Hyperfine widths in the rotational lines of the (0, 0) band of the $C^4\Sigma^- - X^4\Sigma^-$ system of NbO plotted against $J + \frac{1}{2}$. The solid lines represent calculated values. The widths of the R and P lines with the same lower state are not distinguishable at our resolution; a positive sign indicates that the F = J + I component lies at the high-frequency side.

will be negligibly small at the high J values of our spectra. The value given in Eq. (8) was determined using data only from the well-resolved F_1 and F_4 lines: if data from the F_2 and F_3 lines are included the value is essentially the same but its uncertainty is greater, and the rms error of the fit rises from 0.02 to 0.03 cm⁻¹.

5. DISCUSSION

The $C^{4}\Sigma^{-}-X^{4}\Sigma^{-}$ system of NbO at 4675 Å is clearly the equivalent of the $C^{4}\Sigma^{-}-X^{4}\Sigma^{-}$ system of VO at 5740 Å because the bond length change is virtually identical and the ratio of the Fermi contact parameters, $b(C^{4}\Sigma^{-})/b(X^{4}\Sigma^{-})$ is also very similar. By analogy with the electron configurations of the known states of VO, which have been discussed by Merer *et al.* (18), we can write those of the ${}^{4}\Sigma^{-}$ states of NbO as

$$X^4\Sigma^- \sigma\delta^2 \qquad C^4\Sigma^- \delta^2\sigma^*,$$

where the σ and δ orbitals are mainly $5s\sigma(Nb)$ and $4d\delta(Nb)$ and the σ^* orbital is an antibonding combination of $4d\sigma(Nb)$ and $2p\sigma(O)$. The principal difference between VO and NbO is the much larger size of the second-order spin-orbit parameter $\lambda(C^4\Sigma^-)$ in NbO, which by chance is nearly equal to $\lambda(X^4\Sigma^-)$. Unfortunately not enough is known about the other states of NbO to rationalize this in detail. So far the only other

definitely characterized state of NbO is $B^4\Pi$ at 6500 Å, which seems to be the equivalent of $\delta^2 \pi B^4\Pi$ in VO, though the upper state of an absorption system of NbO near 7100 Å appears to correspond to $\sigma \delta \pi A^4\Pi$ in VO (9, 19). The simplest rationalization for the λ values in NbO is that they result from the spin-orbit interaction elements $\langle 2\Sigma^+ | H_{SO} | 4\Sigma^- \rangle$ in the two configurations $\sigma \delta^2$ and $\delta^2 \sigma^*$; then, if the Coulomb splitting between the two Σ states is roughly the same in the two configurations the λ values should also be roughly equal. This simple model does, in fact, account for the λ value of the ground state of NbO. For instance, if we take the spin-orbit parameter a_{δ} for the δ electrons as the value found for VO (18) scaled by the ratio of the spin-orbit splittings of the $nd^4(n + 1)s^6D$ states of Nb and V we find

$$a_{\delta}(\text{NbO}) = a_{\delta}(\text{VO}) \times (1050.3/312.6) = 143.5 \times 3.36 = 482.2 \text{ cm}^{-1}.$$
 (9)

Then since

$$\left\langle \sigma \delta^{2} {}^{2} \Sigma^{+} | \sum_{i} a_{i} \boldsymbol{l}_{i} \cdot \boldsymbol{s}_{i} | \sigma \delta^{2} {}^{4} \Sigma^{-}_{1/2} \right\rangle = \frac{4}{\sqrt{6}} a_{b}, \qquad (10)$$

we obtain the second-order spin-orbit splitting as

$$4\lambda(\text{NbO}, X^{4}\Sigma^{-}) = \frac{8a_{\delta}^{2}}{3\Delta E(2\Sigma^{+}, 4\Sigma^{-})}.$$
 (11)

Taking the experimental value $\lambda = 62.3 \text{ cm}^{-1}$ from Table III, Eq. (11) leads to $\Delta E(^{2}\Sigma^{+}, ^{4}\Sigma^{-}) \simeq 10\ 000 \text{ cm}^{-1}$. The corresponding $\sigma\delta^{2} \,^{2}\Sigma^{+}$ state of VO lies near 12 430 cm⁻¹, which is consistent with this result. However, a similar calculation for VO, given the known position of $\sigma\delta^{2} \,^{2}\Sigma^{+}$, leads to $\lambda(\text{VO}, X^{4}\Sigma^{-}) = 1.10 \text{ cm}^{-1}$, compared to the experimental value 2.03 cm⁻¹ (14).

In view of the fact that the only upper state hyperfine parameter determined in this work is $b(C^{4}\Sigma^{-})$, it does not seem worthwhile to discuss the hyperfine structure in more detail at present. There are no internal hyperfine perturbations between the F_{2} and the F_{3} levels of the ${}^{4}\Sigma$ states, of the type first found by Richards and Barrow (20, 21) in VO, expected in the range up to J = 100.

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REFERENCES

- 1. V. R. RAO, Indian J. Phys. 24, 35-49 (1950).
- 2. J. L. FEMENIAS, G. CHEVAL, A. J. MERER, AND U. SASSENBERG, J. Mol. Spectrosc. 124, 348-368 (1987).
- 3. J. M. BROM, C. H. DURHAM, AND W. WELTNER, J. Chem. Phys. 61, 970-981 (1974).

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- 4. A. J. MERER, U. SASSENBERG, J. L. FEMENIAS, AND G. CHEVAL, J. Chem. Phys. 86, 1219-1224 (1987).
- 5. K. S. RAO, Nature (London) 170, 670 (1952); 173, 1240 (1954).
- 6. U. UHLER, Ark. Fys. 8, 265-279 (1954).
- 7. T. M. DUNN, in "Molecular Spectroscopy: Modern Research" K. Narahari Rao and C. W. Mathews, Eds.), pp. 231-257, Academic Press, New York, 1972.
- 8. K. P. HUBER AND G. HERZBERG, "Constants of Diatomic Molecules," Van Nostrand-Reinhold, New York, 1979.
- 9. M. VALA, R. D. BRITTAIN, AND D. POWELL, Chem. Phys. 93, 147-155 (1985).
- 10. H. M. CROSSWHITE, J. Res. Natl. Bur. Stand., Sect A 79, 17-69 (1975).
- 11. N. ÅSLUND, J. Mol. Spectrosc. 50, 424-434 (1974).
- 12. N. ÅSLUND, Ark. Fysik 30, 377-396 (1965).
- 13. J. M. BROWN AND D. J. MILTON, Mol. Phys. 31, 409-422 (1976).
- 14. A. S.-C. CHEUNG, R. C. HANSEN, AND A. J. MERER, J. Mol. Spectrosc. 91, 165-208 (1982).
- 15. U. SASSENBERG, A. S.-C. CHEUNG, AND A. J. MERER, Canad. J. Phys. 62, 1610-1615 (1984).
- 16. A. S.-C. CHEUNG, A. W. TAYLOR, AND A. J. MERER, J. Mol. Spectrosc. 92, 391-409 (1982).
- 17. R. A. FROSCH AND H. M. FOLEY, Phys. Rev. 88, 1337-1349 (1952).
- 18. A. J. MERER, G. HUANG, A. S.-C. CHEUNG, AND A. W. TAYLOR, J. Mol. Spectrosc. 125, 465-503 (1987).
- 19. S. R. LANGHOFF AND C. W. BAUSCHLICHER, J. Chem. Phys., in press.
- 20. D. RICHARDS AND R. F. BARROW, Nature (London) 217, 842 (1968).
- 21. D. RICHARDS AND R. F. BARROW, Nature (London) 219, 1244-1245 (1968).