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# Hyperfine structure in high spin multiplicity electronic states: Analysis of the $B^{4}\Pi - X^{4}\Sigma^{-}$ transition of gaseous NbO

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The (0,0) band of the B  ${}^{4}\Pi - X {}^{4}\Sigma^{-}$  transition of NbO, near 6600 Å, has been analyzed from spectra taken at sub-Doppler resolution. The transition is notable for the great width of its Nb nuclear hyperfine structure, which is caused principally by the unpaired  $5s\sigma$  electron in the ground state interacting with the large magnetic moment of the  $^{93}_{41}$ Nb nucleus (I=9/2). A fit to the ground-state combination differences, including four very precise microwave lines measured by Suenram et al. [J. Mol. Spectrosc. 148, 114 (1991)], has given a comprehensive set of rotational, spin, and hyperfine parameters. Prominent among these are the third-order spin-orbit distortions of the spin-rotation interaction and the Fermi contact interaction, which are large and well determined, reflecting different degrees of spin-orbit contamination of the the  ${}^{4}\Sigma_{1/2}^{-}$  and  ${}^{4}\Sigma_{3/2}^{-}$  components of the ground state. The  $\delta^{2}\pi B {}^{4}\Pi$  state was hard to fit, for a number of reasons. First, its spin-orbit structure is asymmetric, because of strong perturbations by a  ${}^{2}\Pi$  state which has been identified in this work, from among the various weak bands in the NbO spectrum near 7000 Å; the result is that many high order centrifugal distortion terms are needed in an effective Hamiltonian model for the rotation. Second, the hyperfine structure is perturbed, not only by this  ${}^{2}\Pi$  state, but by distant  $\Sigma$  and  $\Delta$  states at higher energy. The  $\delta^2 \sigma^* C \Delta^2 \Sigma^-$  state at 21 350 cm<sup>-1</sup> appears to be one of these. The distant states generate large apparent nuclear spin-rotation interactions, both within and between the  $\Lambda$  components of the  $\Pi$  state, as a result of cross terms between matrix elements of the operators  $-2BJ\cdot L$  and aI·L. Similar cross terms arising from the operators AL·S and aI·L produce corrections to the Fermi contact matrix elements and are responsible for the unexpected negative sign of the magnetic hyperfine parameter d. The "off-diagonal" quadrupole parameter  $e^2 Q q_2$  is very large, and causes some of the higher J line shapes of the B-X system to be noticeably asymmetric at Doppler limited resolution; its value is consistent with the electron configuration of the B <sup>4</sup> $\Pi$  state being  $\delta^2 \pi$ .

#### I. INTRODUCTION

Magnetic hyperfine structure is a valuable source of information about the bonding in simple free radicals because the hyperfine parameters are related to expectation values of the coordinates of the electrons near the spinning nuclei.<sup>1-5</sup> In most cases the relationship is given satisfactorily by the Frosch and Foley expressions,<sup>1</sup> since the matrix elements of the full Hamiltonian off-diagonal in electronic state are usually negligible. However, transition metal compounds, with their much greater densities of electronic states, sometimes show clear examples of where these off-diagonal elements are important. For instance, the two lowest electronic states of NbN,  $\sigma\delta a^{-1}\Delta$  and  $X^{-3}\Delta$ , interact strongly through both the spin-orbit and the Fermi contact operators;<sup>6</sup> the effect of the cross term between these operators is that the niobiurn hyperfine width in the  $a^{-1}\Delta$  state is reduced by a factor of 5 from what the expectation value  $\langle r^{-3} \rangle_{4d}$  for a niobium atom would suggest.<sup>7</sup> Naturally care has to be taken in such cases when the hyperfine parameters are interpreted in terms of electronic wave functions.

Spin-orbit contamination of the hyperfine parameters, of this type, obviously cannot be observed directly in singlet or doublet states, or even  ${}^{3}\Sigma$  states, because there are never more than three determinable parameters to be matched to the three Frosch and Foley parameters, *a*, *b*, and *c*. (For the moment we do not consider the "hyperfine  $\Lambda$ -doubling" parameter *d*.) Difficulties begin with orbitally degenerate triplet states, where a contaminated state in case (a) coupling may require as many as five magnetic hyperfine parameters, three

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for the  $\Delta\Omega=0$  matrix elements and two more for the  $\Delta\Omega=\pm 1$  elements.<sup>6</sup> In states of quartet and higher spin multiplicity each  $\Omega$  component needs its own magnetic hyperfine parameter in the general case, so that there are always more determinable parameters than the combinations of Frosch and Foley parameters can accommodate. Group theory arguments in fact show that additional parameters, representing the spin–orbit distortion, must arise.<sup>8</sup>

One of the aims of this work is to establish exactly what happens when the hyperfine structure of a high spin electronic state is distorted by such effects, using the electronic spectrum of NbO as a yardstick. What is found is that the optical and microwave<sup>9</sup> data for the  $X^{4}\Sigma^{-}$  ground state of NbO can be fitted very well, but the model must include the third-order spin-orbit distortions of the spin-rotation and Fermi contact interactions. The  $B^{4}\Pi$  excited state has unexpectedly disorganized hyperfine structure, which requires ten magnetic hyperfine parameters to describe it, including the hyperfine  $\Lambda$ -doubling parameter d. An unusually large nuclear spin-rotation interaction is shown to be a normal result of  $\Delta\Lambda = \pm 1$  interaction with nearby electronic states. It is independent of the distortions of the electron spin structure that arise from  $\Delta\Lambda = 0$  interaction.

A second aim of this work is to clarify the electronic states of NbO. Two low-lying <sup>4</sup>II states are expected in NbO,<sup>10,11</sup> just as in the 3*d* analog VO.<sup>12,13</sup> In VO it is easy to see, even from the Doppler limited hyperfine widths,<sup>14</sup> that the  $A^{4}\Pi$  state comes from the configuration  $\sigma\delta\pi$ , while the  $B^{4}\Pi$  state is now known<sup>15</sup> to come from  $\delta^{2}\pi$ . Only one <sup>4</sup>II state has been definitely identified in NbO, and this is shown from its hyperfine structure to correspond to the  $B^{4}\Pi$  state of VO. Another state lying just below it, originally thought to be the other expected <sup>4</sup>II state, is here reassigned as a <sup>2</sup>II state. The transition to it from the ground state has unusual spin structure, where only subbands coming from the  $X^{4}\Sigma_{1/2}^{-1}$  component appear.

#### **II. EXPERIMENTAL DETAILS**

NbO molecules were prepared in the gas phase by flowing a mixture of NbCl<sub>5</sub> vapor, argon, and oxygen through a 2450 MHz electrodeless discharge at a total pressure of about 1 Torr. The NbCl<sub>5</sub> vapor was produced by warming a small quantity of solid, contained in a side arm of the quartz discharge tube, to about 80 °C. The discharge was brilliant white in color, with a slight reddish tinge, and formed a long flame which was pumped through a fluorescence cell immediately downstream from the microwave cavity. Strong laserinduced fluorescence was excited by passing a laser beam through the tail of the flame: at this point most of the NbO molecules are in their ground electronic state, so that the fluorescence can be observed against a relatively dark background. The laser used was a Coherent Inc. model 599-21 standing wave dye laser, operating with the dye DCM.

Because of the complexity of the hyperfine structure it has been necessary to record almost the whole of the (0,0) band of the  $B^{4}\Pi - X^{4}\Sigma^{-}$  system at sub-Doppler resolution.



FIG. 1. Broadband laser-induced fluorescence spectrum of the NbO  $B \,{}^{4}\Pi - X \,{}^{4}\Sigma^{-}$  (0,0) band, showing the subband assignments.

This was a major undertaking, in which three continuous segments of about 120 cm<sup>-1</sup> each, centered near 14 840, 15 160, and 15 400 cm<sup>-1</sup>, were scanned by intermodulated fluorescence.<sup>16</sup> In these experiments the two chopper frequencies were in the ratio 7:9 and the sum frequency, near 1300 Hz, was used for demodulation. The NbO spectra were calibrated against the I<sub>2</sub> absorption spectrum,<sup>17</sup> and successive 1 cm<sup>-1</sup> scans were concatenated, using fringes from a passive Fabry-Perot interferometer, so as to average over a number of lines in the I<sub>2</sub> spectrum. The concatenation process used NbO lines that appeared on two adjacent scans to obtain the relative order numbers of the Fabry-Perot fringes, and to allow for any slight shifts caused by temperature, pressure, or alignment effects. It was usually only possible to assemble about 15  $cm^{-1}$  of truly "continuous" spectrum by this method, because there are often gaps in the rotational structure which halt the overlap procedure, and in any case it was almost never possible to concatenate spectra taken on different days. The principal difficulties we experienced with the calibration were always at places where two continuous spectra did not quite join. The measurement accuracy for small frequency intervals was normally about ±0.0003 cm<sup>-1</sup>, but over large intervals there were occasional inconsistencies of up to  $\pm 0.0015$  cm<sup>-1</sup>. The linewidths in our sub-Doppler experiments were limited by pressure broadening to about 50 MHz ( $0.0017 \text{ cm}^{-1}$ ).

# III. APPEARANCE OF THE *B* ${}^{4}\Pi - X {}^{4}\Sigma^{-}$ SYSTEM OF NbO

The (0,0) band of the  $B^{4}\Pi - X^{4}\Sigma^{-}$  system of NbO, as seen in broadband laser-induced fluorescence, consists of three groups of red-degraded heads, with accompanying rotational structure, in the region 6500-6750 Å. It is illustrated



FIG. 2. The  ${}^{T}R_{31}(7\frac{1}{2})$  line, from the  $B {}^{4}\Pi_{3/2} - X {}^{4}\Sigma_{1/2}^{-}$  (0,0) subband, illustrating the ten hyperfine components resulting from the I=9/2 nuclear spin of  ${}^{93}_{41}$ Nb. The upper state hyperfine width is essentially zero at this J value, so that all the observed splitting comes from the ground state.

in Fig. 1. Because both states are in case (a) coupling there are four allowed subbands, following the selection rule  $\Delta\Sigma=0$ , namely  ${}^{4}\Pi_{5/2} - {}^{4}\Sigma_{3/2}$ ,  ${}^{4}\Pi_{3/2} - {}^{4}\Sigma_{1/2}$ ,  ${}^{4}\Pi_{1/2} - {}^{4}\Sigma_{1/2}$ , and  ${}^{4}\Pi_{-1/2} - {}^{4}\Sigma_{3/2}$ . Two weak case (a)-forbidden subbands,  ${}^{4}\Pi_{5/2} - {}^{4}\Sigma_{1/2}$  and  ${}^{4}\Pi_{-1/2} - {}^{4}\Sigma_{1/2}$ , are induced by spinuncoupling effects. It was the recognition of the  ${}^{4}\Pi_{-1/2} - {}^{4}\Sigma_{1/2}$  subband that had proved the case (a) nature of the ground state,  ${}^{18}$  and led to the result that the second-order spin-orbit splitting between the  ${}^{4}\Sigma_{3/2}$  and  ${}^{4}\Sigma_{1/2}$  components is 62 cm<sup>-1</sup>. The reason why there are three groups of heads, rather than four, is that the spin structure of the *B*  ${}^{4}\Pi$  state is anomalous: the separation of the  ${}^{4}\Pi_{5/2}$  and  ${}^{4}\Pi_{3/2}$  substates is only 36 cm<sup>-1</sup>, while the other two spin-orbit intervals are about 250 cm<sup>-1</sup>.

The rotational structure of a B-X subband depends on whether the lower state is  ${}^{4}\Sigma_{1/2}$  or  ${}^{4}\Sigma_{3/2}$ , and on whether it is case (a)-allowed or forbidden. As is known from other examples of case (a)  ${}^{4}\Sigma$  states,  ${}^{19-21}$  the levels of a  ${}^{4}\Sigma_{3/2}$  state are grouped into parity doublets with the same value of J, as in a  ${}^{2}\Pi_{3/2}$  state;  ${}^{4}\Sigma_{1/2}$  states also consist of parity doublets, but the J values of the two close-lying levels differ by two units. Therefore, the branch structure of a  ${}^{4}\Pi - {}^{4}\Sigma_{3/2}$  subband is the familiar pattern of doubled P, Q, and R branches, but  ${}^{4}\Pi - {}^{4}\Sigma_{1/2}$  subbands appear to consist of S, R, Q, Q, P, and O form branches, and are therefore more spread out. Case (a)-forbidden subbands have no intensity at low J, and in this electronic transition of NbO they are first detectable at  $J \sim 10^{\frac{1}{2}}$ . Their intensity comes from the spin-uncoupling of the  ${}^{4}\Sigma$  (a) state towards case (b). Since spin-uncoupling effects become very large at higher multiplicities, the "forbidden" branches increase rapidly in strength; at  $J \sim 50\frac{1}{2}$  they are comparable in intensity to the allowed branches, indicating that the  ${}^{4}\Sigma$  state is almost fully uncoupled to case (b).

The  $F_1$  electron spin component of the  ${}^{4}\Sigma_{1/2}$  state (J=N+3/2) has particularly wide hyperfine structure, so that branches with  $F_1$  lower levels show well-resolved hyperfine patterns even in Doppler limited spectra. Figure 2 shows an example from the  ${}^{T}R_{31}$  branch at sub-Doppler resolution.

The upper state hyperfine width happens to be nearly zero at this J value, so that the structure reflects the ground-state splitting almost exactly. The ten hyperfine components resulting from the I=9/2 nuclear spin of  ${}^{93}_{41}$ Nb form a textbook pattern.

Hyperfine "satellite" lines with  $\Delta F \neq \Delta J$  are prominent at low J. They are valuable in the analysis because of the direct hyperfine combination differences they provide for both electronic states. The satellite lines die out beyond  $J \sim 7\frac{1}{2}$ , but the center dips (or crossover resonances) between them and the hyperfine "main" lines with  $\Delta F = \Delta J$  continue to at least  $J=22\frac{1}{2}$ . Center dips are an artifact of the intermodulated fluorescence technique, and have intensities proportional to the geometric mean of the intensities of the two transitions producing them. This implies that center dips should always be observable far beyond where the satellites themselves are too weak to be seen. In principle the center dips give information on how the hyperfine combination differences change at higher J, but in the present spectrum they usually lie so close to the main lines that their positions are affected by blending. When the upper state hyperfine split. tings are of the order of the linewidth, the center dips have the undesirable effect of broadening the bases of the main lines unsymmetrically. An exception occurs in the  ${}^{4}\Pi_{5/2} - {}^{4}\Sigma_{3/2}$  subband, where the center dips are well sepa rated from the main lines because of the large hyperfine splittings in the  ${}^{4}\Pi_{5/2}$  state.

Examples of hyperfine satellite lines and center dips are shown in Figs. 3 and 4. Figure 3 illustrates the first two  ${}^{S}Q_{31}$  lines and the first  ${}^{T}R_{31}$  line in the  ${}^{4}\Pi_{3/2} - {}^{4}\Sigma_{1/2}$  subband. At these low J values the full complement of ten hyperfine components in each state is not developed and, since the lower state hyperfine widths are much larger than the upper state widths, the structure separates into groups of lines with the same value of F''.

The  ${}^{S}Q_{31}(1\frac{1}{2})$  line shown in Fig. 3 has a clear hyperfineintensity cancellation,<sup>22</sup> where the F'-F''=4-4 component is missing. Such intensity cancellations occur in certain Qlines for which J is less than I, at F values where the angle between the vectors **F** and **J** in a classical picture is ~90°. Since the intensity of the rotational line is carried by the **J** vector, none of it can be projected onto the **F** vector if the two vectors are at right angles; as a result the intensity of that particular F hyperfine component becomes zero. All the low-J Q lines in the NbO spectrum show this effect, but it is most obvious when the lower state is  ${}^{4}\Sigma$ ,  $F_{1}$ , where the hyperfine structure is wide. Figure 1 of Ref. 22 shows some  ${}^{R}Q_{21}$  patterns from the  ${}^{4}\Pi_{1/2} - {}^{4}\Sigma_{3/2}$  subband of this system of NbO.

Figure 4 illustrates the  $R_4$  and  ${}^{S}R_{43}(1\frac{1}{2})$  lines, from the  ${}^{4}\Pi_{5/2} - {}^{4}\Sigma_{3/2}$  subband, with their extensive hyperfine structures. The two rotational lines are almost exactly blended; the  $\Lambda$ -doubling splitting between their upper levels is negligibly small, but their lower levels are the  $F_3$  and  $F_4$  components of  ${}^{4}\Sigma_{3/2}$ ,  $J=1\frac{1}{2}$ , separated by a small  $\Omega$  doubling which is of the order of the sub-Doppler linewidth. To be exact, the calculated  $\Omega$  doubling of the  $J''=1\frac{1}{2}$  levels varies with F'', from 27 MHz at F''=6 to 62 MHz at F''=3; the



FIG. 3. Some low-J lines from the  $B \,{}^{4}\Pi_{3/2} - X \,{}^{4}\Sigma_{1/2}^{-}(0,0)$  subband of NbO showing the  $\Delta F = 0, \pm 1$  hyperfine selection rule. An intensity cancellation (see the text) causes the F = 4 - 4 component of  ${}^{5}Q_{31}(1\frac{1}{2})$  not to appear. Various high-J lines also run through this region of the spectrum.

blending therefore makes the hyperfine linewidths apparently depend on F'', somewhat surprisingly.

A characteristic feature of all the subbands is the presence of "hyperfine reversals." These are places where the frequency order of the hyperfine components changes sign at some particular J value in the lines of a branch, and they occur because the hyperfine widths vary quite rapidly with Jin the two electronic states. Specifically they occur because the hyperfine width of a rotational line is the difference of the widths in the upper and lower levels, so that should this difference happen to pass through zero the sense of the hyperfine splitting will reverse. At the point where the difference is exactly zero the hyperfine components all lie on top of each other, producing an enormous "spike" in the spectrum.

Hyperfine reversals occur in all branches of the B-X system except those with  $F_1$  lower states. The reason is that the upper state hyperfine widths are generally smaller than the lower state widths so that the hyperfine patterns mostly reflect the ground-state widths. Figure 5 shows these widths (as calculated from the final rotational constants) plotted against  $J - \frac{1}{2}$ . It can be seen that all the electron spin components of the ground state, except  $F_1$ , have hyperfine widths that pass through zero in the accessible range of J values.



= cross-over resonance (centre dip)

FIG. 4. The blended  $R_4(1\frac{1}{2})$  and  ${}^{S}R_{43}(1\frac{1}{2})$  lines of the  $B \, {}^{4}\Pi_{5/2} - X \, {}^{4}\Sigma_{3/2}^{-}$  (0,0) subband of NbO. The lower state  $\Omega$  doubling is less than the sub-Doppler linewidth, so that the two lines are almost exactly superimposed.



FIG. 5. Calculated hyperfine widths,  $\Delta E_{hfs} = E(F_{max} = J + I) - E(F_{min} = |J - I|)$ , of the four electron spin components of the  $X^{4}\Sigma^{-}$ , v = 0 level of NbO, plotted as a function of  $J - \frac{1}{2}$ .

The spikes seen in the branches of the B-X system occur close to these J values, though naturally the exact details depend on the upper state hyperfine widths.

Examples of hyperfine reversals in the  $Q_4$  and  ${}^{R}Q_{43}$ branches are illustrated in Fig. 6. The reversal is very rapid in the  $Q_4$  branch, where the more open side of the hyperfine pattern (the high values of F) is clearly different in the  $Q_4$  $(7\frac{1}{2})$  and  $(10\frac{1}{2})$  lines. The rapidity of the hyperfine reversal is governed by the slope of the variation shown in Fig. 5; as this figure predicts, the reversal occurs more slowly in the  ${}^{R}Q_{43}$  branch, where the "spiking" is spread over five rotational lines rather than two. These hyperfine reversals may turn out to be useful in the analysis of other electronic transitions of NbO involving the ground state because there should always be reversals in the  $F''_3$  and  $F''_4$  branches somewhere near  $J=10\frac{1}{2}$ , and a reversal in the  $F_2''$  branches near  $J=35\frac{1}{2}$ .

Closer examination of the spikes, e.g., the  ${}^{R}Q_{43}(8\frac{1}{2})$  line. shows that the hyperfine patterns do not collapse to symmetrical lines. Evidently the *F* dependence of the hyperfine energy is not the same in the two electronic states. Now the magnetic hyperfine energy is always proportional to F(F+1) in these two electronic states, because of the vector coupling J+I=F. Therefore, the asymmetry of the patterns implies a sizeable electric quadrupole contribution. It turns out that the B <sup>4</sup>II state is responsible, and that its quadrupole coupling parameters are surprisingly large: e.g.,  $e^{2}Qq_{2}=700$ MHz, e.g., is 700 MHz. The off-diagonal quadrupole effects are large enough to distort the line profiles noticeably even at Doppler limited resolution (see Fig. 7). This was a puzzle in the early stages of the analysis, and was one reason why we had to record the whole spectrum at sub-Doppler resolution.

Bandheads are a severe problem. Figure 8 illustrates the head of the  ${}^{s}Q_{31}$  branch (from the  ${}^{4}\Pi_{3/2} - {}^{4}\Sigma_{1/2}$  subband). The density of lines at the bandheads rises to something like 200 per  $cm^{-1}$ , and analysis becomes laborious. Because the upper state energy level pattern is very complicated it was not possible to write a sufficiently accurate predictor program for the line frequencies (good to within  $\pm 0.02$  cm<sup>-1</sup>) until the analysis was nearly complete. Instead, the method used was to extrapolate the frequencies of corresponding hyperfine components from line to line, starting in regions well away from the heads. Blended lines have to be recognized by their intensities, and weighted down in the extrapolation procedure. In the end, however, the analysis is unambiguous. and every line can be assigned. (A weak low- $J^{T}R_{31}$  line occurs near the middle of the figure but, since only one of its hyperfine components is unblended, it is not marked: it is left as an "exercise for the reader" to find.)



FIG. 6. Hyperfine reversals in the  ${}^{R}Q_{43}$  and  $Q_{4}$  branches of the  $B {}^{4}\Pi_{5/2} - X {}^{4}\Sigma_{3/2} (0,0)$  subband, resulting from the rapid variation of the hyperfine widths with J. A reversal in the sense of the hyperfine structure, where the relative energy order of the hyperfine components changes, occurs when the difference of the upper and lower state hyperfine widths passes through zero.



FIG. 7. Doppler limited tracing of the  ${}^{O}P_{12}(24\frac{1}{2})$  line of the  $B \,{}^{4}\Pi_{-1/2} - X \,{}^{4}\Sigma_{1/2}$  (0,0) subband, showing the asymmetric line shape caused by the off-diagonal quadrupole coupling constant  $e^{2}Qq_{2}$  of the  $B \,{}^{4}\Pi$  state.

Surprisingly, the  $B {}^{4}\Pi - X {}^{4}\Sigma^{-}$  system of NbO is almost entirely free of rotational perturbations. Only one has been found, and this is just a small anomaly within the hyperfine structure of a single rotational level, namely  $B {}^{4}\Pi_{5/2,f}$ ,  $J = 16\frac{1}{2}$ . This is discussed in more detail in Sec. V A.

# IV. DETERMINATION OF THE MOLECULAR CONSTANTS

perturbation Barring the just mentioned, the  $B^{4}\Pi - X^{4}\Sigma^{-}(0,0)$  band is free of local perturbations. At first sight it would seem ideally suited for fitting the lines of the spectrum to the differences between the eigenvalues of Hamiltonian matrices for the upper and lower states. We made strenuous efforts to fit the spectrum this way, but finally realized that the structure of the  $B^{4}\Pi$  state contains strong global perturbations by distant electronic states which produce systematic shifts of the rotational structure, but no local avoided crossings. The  ${}^{4}\Pi_{5/2}$  substate was particularly difficult to fit, though in hindsight the irregular spin-orbit pattern of Fig. 1 might have warned us.

The spectrum has therefore been fitted in two stages. First the ground state was fitted using combination differences; then the upper state parameters were obtained from the line frequencies, with the ground-state constants held fixed. In this way we could decouple the process of finding a suitable model for the upper state from the problems of correlation between the upper and lower state parameters.

#### A. Data for the ground state

The data set for the ground state contained 1906 combination differences from the optical spectrum, plus microwave



FIG. 8. Sub-Doppler spectrum of the  $B^{4}\Pi_{3/2} - X^{4}\Sigma_{1/2}^{-s}Q_{31}$  bandhead. The line density is nearly 200 per cm<sup>-1</sup> in this region. The weak line  ${}^{T}R_{31}(4\frac{1}{2})$ , not marked, lies near the middle of the figure; only one of its components, which lies just to the blue of the F = 23 component of  ${}^{s}Q_{31}(19\frac{1}{2})$ , is unblended.

measurements<sup>9</sup> of four hyperfine components of the  $R_1(\frac{1}{2})$  pure rotational line, which became available in the final stages of the fitting. It has been instructive to compare the parameters obtained with and without the inclusion of the extremely precise, but exiguous, microwave measurements.

The optical combination differences consisted of every possible ground-state interval that could be obtained from the unblended lines of the full data set, of the following types.

(i) Hyperfine combination differences, from the intervals between the main  $(\Delta F = \Delta J)$  and satellite  $(\Delta F \neq \Delta J)$  hyperfine components of the low-J rotational lines.

(ii)  $\Delta_1 F''$  and  $\Delta_2 F''$  hyperfine-rotational combination differences. In principle there are ten of these for each rotational interval because the ten hyperfine main branch lines  $(\Delta F = \Delta J)$  have different upper state hyperfine levels. The  $\Delta_2 F''$ 's mostly give information on the rotational and centrifugal distortion parameters, and are fairly insensitive to the hyperfine parameters; only at low J do the hyperfine patterns change rapidly enough with J for these combination differences to vary significantly with F. The  $\Delta_1 F''$  intervals establish the relative positions of the  $F_1''$  and  $F_2''$  electron spin components  $({}^{4}\Sigma_{1/2})$ , and also the  $F_{3}''$  and  $F_{4}''$  components  $({}^{4}\Sigma_{3/2})$ . They contain the principal information about the electron spin-rotation interaction and its centrifugal distortion, and also about the centrifugal distortion of the Fermi contact interaction. This can be understood from the e/fparities<sup>23</sup> of the electron spin components of a  ${}^{4}\Sigma^{-}$  state, where the  $F_1$  and  $F_3$  components are of *e* parity while the  $F_2$ and  $F_4$  components are of f parity. The selection rules for electric dipole radiation stipulate that R and P branches are of types *ee* or *ff*, while *Q* branches are *ef* or *fe*; therefore for any particular upper level the lower state e/f parity is different in the Q line compared to the R and P lines. Since  $\Delta_1 F''$ 

combination differences connect R lines and Q lines or Q lines and P lines, they must give the relative energies of the  $F_1$  and  $F_2$  or  $F_3$  and  $F_4$  electron spin components. The point is that when the  ${}^{4}\Sigma$  state approaches case (b) coupling the hyperfine energies in the four electron spin components are quite different, so that exact measurements of the energy differences between them give a very precise measure of the Fermi contact parameter and how it varies with J.

(iii) Hyperfine-rotational separations between corresponding lines of the electron spin satellite and main branches. These are of the type  ${}^{o}P_{12}(J) - {}^{M}P_{14}(J)$ , where one of the lines comes from a case (a)-forbidden subband (in this example the  ${}^{o}P_{12}$  branch, which belongs to the  ${}^{4}\Pi_{-1/2} - {}^{4}\Sigma_{1/2}$  subband), and the other is from a case (a)allowed subband. These combination differences connect the  $F_1''$  and  $F_3''$  components or the  $F_2''$  and  $F_4''$  components. Unfortunately the only reasonably intense case (a)-forbidden subbands are  ${}^{4}\Pi_{5/2} - {}^{4}\Sigma_{1/2}^{-}$  and  ${}^{4}\Pi_{-1/2} - {}^{4}\Sigma_{1/2}^{-}$ , with the former being too severely overlapped to give many useful data; as a result the separations of this type, which determine the second-order spin-orbit splitting  $\lambda({}^{4}\bar{\Sigma}^{-})$  and its centrifudistortion, come mostly from the gal subbands  ${}^{4}\Pi_{-1/2} - {}^{4}\Sigma_{1/2}^{-}$  and  ${}^{4}\Pi_{-1/2} - {}^{4}\Sigma_{3/2}^{-}$ .

#### B. Model for the ground state

The  $X {}^{4}\Sigma^{-}$  state of NbO has  $4\lambda = E({}^{4}\Sigma_{3/2}) - E({}^{4}\Sigma_{1/2}) = 62 \text{ cm}^{-1}$ , which is best described as case (a) coupling. To be sure, the increasing rapidity of spin uncoupling in higher multiplicity states<sup>24</sup> causes the  $X {}^{4}\Sigma^{-}$  state of NbO to be almost fully uncoupled to case (b) at the highest J values observed here (see Fig. 5); however, a case (b) basis, with its greater algebraic complexity, is not required in the present case since there are no internal hyperfine perturbations.<sup>25,26</sup>

The Hamiltonian has been taken in the form

$$\mathscr{H} = B(\mathbf{J} - \mathbf{S})^{2} + (2/3)\lambda(3S_{z}^{2} - \mathbf{S}^{2}) + \gamma(\mathbf{J} - \mathbf{S}) \cdot \mathbf{S} - D(\mathbf{J} - \mathbf{S})^{4} + (1/3)\lambda_{D}[(3S_{z}^{2} - \mathbf{S}^{2}), (\mathbf{J} - \mathbf{S})^{2}]_{+} + (1/2)\gamma_{D}[(\mathbf{J} - \mathbf{S}) \cdot \mathbf{S}, (\mathbf{J} - \mathbf{S})^{2}]_{+} + 10\gamma_{S}T^{3}(\mathbf{L}^{2}, \mathbf{J}) \cdot T^{3}(\mathbf{S}, \mathbf{S}, \mathbf{S})/[\sqrt{6}\langle\Lambda|T_{0}^{2}(\mathbf{L}^{2})|\Lambda\rangle] + b\mathbf{I} \cdot \mathbf{S} + cI_{z}S_{z} + (1/2)D_{b}[(\mathbf{I} \cdot \mathbf{S}), (\mathbf{J} - \mathbf{S})^{2}]_{+} + 10e^{2}Qq_{0}(3I_{z}^{2} - \mathbf{I}^{2})/[4I(2I - 1)] + 5\sqrt{14}b_{S}T^{1}(\mathbf{I}) \cdot T^{1}\{T^{2}(\mathbf{L}^{2}), T^{3}(\mathbf{S}, \mathbf{S}, \mathbf{S})\}/[3\langle\Lambda|T_{0}^{2}(\mathbf{L}^{2})|\Lambda\rangle].$$
(1)

The terms can be identified by their parameters. B,  $\lambda$ , and  $\gamma$  are the rotational constant and the spin-spin and spinrotation interactions, with their centrifugal distortion corrections D,  $\lambda_D$ , and  $\gamma_D$ . The operators in square brackets are the anticommutators  $[x,y]_+ = xy + yx$ , which are required to preserve the Hermitian form for the matrices. The term in  $\gamma_s$ is the spin-orbit distortion of the spin-rotation interaction,<sup>8</sup> in other words the "second gamma" introduced by Hougen<sup>27</sup> to account for various anomalies reported<sup>28</sup> in the  $a^{4}\Sigma^{-}$ state of SiF.<sup>29</sup> There still seems to be no agreed form for this term. Nelis *et al.*,<sup>30</sup> in their laser magnetic resonance study of the  $a^{4}\Sigma^{-}$  state of CH, reworked the effective operator of Brown and Milton<sup>8</sup> as

$$\mathscr{H}_{\text{spin-rot}}^{(3)} = CT^3(\mathbf{L}^2, \mathbf{N}) \cdot T^3(\mathbf{S}, \mathbf{S}, \mathbf{S}), \qquad (2)$$

where  $C = 10 \gamma_5 / [\sqrt{6} \langle \Lambda | T_0^2(\mathbf{L}^2) | \Lambda \rangle]$ . Their new form gives simpler matrix elements in case (b) coupling and also adds diagonal elements to the Hamiltonian matrix written in a case (a) basis. However, we find that it converges more slowly than the **J** form of Eq. (1) to the asymptotic expressions for high rotational quantum number. Since the reason for including this term for NbO is to allow the possibility of different spin-rotation parameters in the  ${}^{4}\Sigma_{1/2}$  and  ${}^{4}\Sigma_{3/2}$ components of the X  ${}^{4}\Sigma^{-}$  state it seems advisable to use the faster-converging form.



	$\left J\frac{1}{2}\frac{e}{f}\right\rangle$	$\left J\frac{3}{2}\frac{e}{f}\right\rangle$
$\left\langle J \frac{1}{2} \frac{e}{f} \right\rangle$	$-2\lambda - \frac{7}{2}\gamma + B(x+4) - \gamma_D(7x+16) - \frac{9}{4}\gamma_S - 2\lambda_D(x+4)$ $-D[(x+4)^2 + 7x+4] + \frac{W}{2J(J+1)} \left[ c_I + \frac{1}{4} (b+c-9b_S) \right]$ $-\frac{e^2 Qq_0 x [3W(W+1) - 4I(I+1)J(J+1)]}{8I(2I-1)J(J+1)(2J-1)(2J+3)}$ $\mp 2 \left( J + \frac{1}{2} \right) \left[ B - \frac{1}{2} \gamma - 2D(x+4) - 2\lambda_D + \frac{3}{2}\gamma_S - \frac{1}{2}\gamma_D(x+11) - (b-3b_S) \frac{W}{4J(J+1)} \right]$	Symmetric
$\left\langle J \frac{3}{2} \frac{e}{f} \right\rangle$	$-\sqrt{3x} \left\{ B - \frac{1}{2} \gamma - 2D(x+2) - \frac{1}{2} \gamma_D(x+7) - \gamma_S - (b+2b_S) \frac{W}{4J(J+1)} \right\}$ $\pm \left[ -\sqrt{3x} \left( J + \frac{1}{2} \right) (2D + \gamma_D) \right]$	$2\lambda - \frac{3}{2} \gamma + Bx - 3\gamma_D x + 2\lambda_D x - D(x^2 + 3x) + \frac{9}{4} \gamma_S + \left[c_I + \frac{9}{4} (b + c + b_S)\right] \frac{W}{2J(J+1)} + \frac{e^2 Qq_0(6-x)[3W(W+1) - 4I(I+1)J(J+1)]}{8I(2I-1)J(J+1)(2J-1)(2J+3)}$
$\left(J-1 \ \frac{1}{2} \ \frac{f}{e}\right)$	$-\frac{Y}{8J} \left\{ b + c - 9b_{S} + \frac{3e^{2}Qq_{0}[W+J+1]}{4I(2I-1)(J-1)(J+1)} \right\}$ $\mp \frac{Y}{4J} (b - 3b_{S})$	$\frac{Y}{8J} \sqrt{3(2J+3)/(2J-1)}(b+2b_s)$
$\left(J-1 \ \frac{3}{2} \frac{f}{e}\right)$	$-\frac{Y}{8J} \sqrt{3(2J-3)/(2J+1)}(b+2b_s)$	$-\frac{3Y}{8J} \sqrt{(4J^2-9)/(4J^2-1)} \left\{ (b+c+b_S) + \frac{3e^2Qq_0[W+J+1]}{4I(2I-1)(J-1)(J+1)} \right\}$
$\left\langle J-2 \ \frac{1}{2} \ \frac{e}{f} \right $ $\left\langle J-2 \ \frac{3}{2} \ \frac{e}{f} \right $ where	$e^2 Q q_0 \sqrt{J^2 - (1/4)} \sqrt{(J-1)^2 - (1/4)} Z$	0 $e^2 Q q_0 \sqrt{J^2 - (9/4)} \sqrt{(J-1)^2 - (9/4)} Z$
x = J(J+1) and $Z = Y \times \frac{3\sqrt{3}}{2}$	$\frac{3}{4}, W = F(F+1) - I(I+1) - J(J+1), Y = \sqrt{(I+J+F+I+J)(J-F+I-1)(F+I-J+2)}$ $\frac{(F-I+J-1)(F+I+J)(J-F+I-1)(F+I-J+2)}{16I(2I-1)J(J-1)(2J-1)\sqrt{(2J+1)(2J-3)}}$	$\overline{(J+I-F)(F+J-I)(F+I-J+1)},$

The hyperfine terms in Eq. (1) are Frosch and Foley's band c magnetic hyperfine parameters,<sup>1</sup> the centrifugal distortion correction to b ( $D_b$ ), which is at the limit of determinability, the electric quadrupole interaction ( $e^2Qq_0$ ), and finally the spin-orbit distortion of the Fermi contact interaction ( $b_s$ ).<sup>31</sup> There is no argument about the form of this operator, though in the present work we have recast it into a simpler form (with the same matrix elements) to show the parallel with the corresponding distortion of the spinrotation interaction: the different numerical factors reflect the different construction of the compound tensor for the hyperfine operator. The parameter  $b_s$  allows the effective Fermi contact interaction to be different in the  ${}^{4}\Sigma_{1/2}$  and  ${}^{4}\Sigma_{3/2}$  components, and is well determined in the ground state of NbO.

The matrix elements of the Hamiltonian in Eq. (1) are given in a case  $(a_\beta)$  basis in Table I. They are listed in algebraic form rather than as angular momentum coupling coefficients because in our experience the execution time for least-squares fitting increases by about a factor of 10 when subroutines for the Wigner n-j symbols are called. Even with free computer time the advantage of the algebraic forms is considerable when different models have to be tried out, or data sets debugged. The tensor expressions from which the matrix elements were derived are familiar<sup>32</sup> except for those for the spin-orbit distortions, which are

$$\langle \Lambda; S\Sigma'; J'\Omega'IF | \mathscr{H}_{spin-rotation}^{(3)} + \mathscr{H}_{Fermi \ contact}^{(3)} | \Lambda; S\Sigma; J\Omega IF \rangle$$

$$= \frac{1}{4} \sqrt{\frac{35}{3}} \left[ \gamma_S \delta_{JJ'} - (-1)^{J+I+F} \begin{cases} F & I & J' \\ 1 & J & I \end{cases} \sqrt{I(I+1)(2I+1)} b_S \right] \sum_q (-1)^q \begin{pmatrix} 2 & 3 & 1 \\ 0 & q & -q \end{pmatrix}$$

$$\times (-1)^{J'-\Omega'} \sqrt{(2J+1)(2J'+1)} \begin{pmatrix} J' & 1 & J \\ -\Omega' & q & \Omega \end{pmatrix} (-1)^{S-\Sigma'} \begin{pmatrix} S & 3 & S \\ -\Sigma' & q & \Sigma \end{pmatrix}$$

$$\times \sqrt{(2S-2)(2S-1)2S(2S+1)(2S+2)(2S+3)(2S+4)}.$$

$$(3)$$

For reference, the algebraic form for the diagonal matrix element of  $\mathcal{H}_{spin-rotation}^{(3)}$  is

$$\langle \mathscr{H}_{\text{spin-rotation}}^{(3)} \rangle = -\Omega \Sigma \gamma_{S} [3S(S+1) - 5\Sigma^{2} - 1].$$
(4)

#### C. Ground-state parameters

The final ground-state parameters are given in Table II. Two sets of constants are listed: first, those obtained from the full set of optical combination differences; then those that result on adding the four microwave lines of Suenram et al.<sup>9</sup> The microwave lines were given a weight of  $10^6$ , except for the  $R_1(\frac{1}{2})$  F = 5 - 4 component which was weighted 250 000. The microwave data<sup>9</sup> consist of the transitions  $R_1(\frac{1}{2})$ F=5-4, 4-4, 3-4, and 6-5. The first three have a common lower level, and therefore determine two of the  $F_1(J)$  $=1\frac{1}{2}$ ) hyperfine intervals directly; the fourth line shares no common levels with the other three. Interestingly, the microwave lines only improve the determination of the Fermi contact and dipolar interactions (b and c) by a factor of 2, presumably because of the large number of optical combination differences that also carry information about them. However, the microwave measurements improve the precision of the quadrupole parameter  $e^2 Q q_0$  by a factor of 70. The reason for the difference is that the influence of  $e^2 Q q_0$  on the energy levels dies out rapidly with J, so that these low-J microwave lines are particularly well suited for its determination while only a few of the optical combination differences are sensitive to it.

Another interesting comparison is that small higher order parameters, such as  $\gamma_D$ , change by up to five standard deviations when the microwave lines are included. It might be thought that low-J data would not affect the centrifugal distortion parameters, which are only important at high J; in fact the microwave measurements sharpen the values of the principal constants such as  $\gamma$ , so that higher order parameters that are strongly correlated to them become better determined.

#### D. Model for the $B^{4}\Pi$ upper state

The two lowest substates of the  $B^{4}\Pi$  state,  ${}^{4}\Pi_{1/2}$  and  ${}^{4}\Pi_{-1/2}$ , are well separated from the others and could be fitted satisfactorily to a simple rotational and hyperfine model. The other two substates,  ${}^{4}\Pi_{5/2}$  and  ${}^{4}\Pi_{3/2}$ , which are only 36 cm<sup>-1</sup> apart, could not be fitted by this model until many higher order terms had been added. This implies that the  $B^{4}\Pi$  state is globally perturbed, meaning that it interacts strongly with other states that are nearby, though not close enough to produce avoided crossing patterns. It also implies that extrapolation will be unreliable for energy levels beyond the range of J that has been fitted.

Table III lists the parameters that were used to fit the  $B^{4}\Pi$  state, grouping them according to their origins. It can be seen in this table that seven parameters are needed just to describe the rotational structure; this is almost equivalent to having a separate B and D value for each of the four  $\Omega$  substates, and is an indication of the extent of the global

	Optical data only	Microwave and optical data
λ	$15.580 8_{85} \pm 0.000 0_{66}$	15.580 825±0.000 057
В	$0.435\ 013_4 \pm 0.000\ 001_{68}$	$0.435\ 011_{50}\pm 0.000\ 001_{30}$
$10^7 D$	$3.433_5 \pm 0.009_9$	$3.423_3 \pm 0.008_3$
γ	$0.033990_0 \pm 0.00007_8$	$0.033978_2 \pm 0.000005_0$
$10^5 \lambda_D$	$0.54_{11} \pm 0.01_{32}$	$0.54_{60} \pm 0.01_{27}$
$10^7 \gamma_D$	$0.55_8 \pm 0.07_5$	$0.66_6 \pm 0.04_4$
$10^4 \gamma_s$	$0.763_0 \pm 0.016_2$	$0.757_2 \pm 0.016_1$
b	$0.052418_4 \pm 0.000033_6$	$0.052\ 368_2 \pm 0.000\ 018_8$
с	$-0.00359_0 \pm 0.00011_4$	$-0.00340_8 \pm 0.00005_2$
$10^7 D_b$	$-0.8_0 \pm 0.4_5$	$-0.30\pm0.31$
$e^2 Q q_0$	$-0.0014_5\pm0.0018_3$	$-0.00097_{73}\pm0.00002_{64}$
$b_s$	$-0.000\ 285_8^{\circ}\pm 0.000\ 008_4$	$-0.000293_7 \pm 0.000006_9$
r.m.s. error	$0.000 \ 6008 \ \mathrm{cm}^{-1}$	$0.000 \ 6108 \ cm^{-1}$

TABLE II. Rotational and hyperfine constants for the  $X \ ^4\Sigma^-$ , v = 0 level of NbO. Values in cm<sup>-1</sup>. Quoted error limits are three standard deviations:  $r_0 (X \ ^4\Sigma^-) = 1.6852_0$  Å.

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TABLE III.	Terms needed to fit	the rotational and hyp	erfine structure of the B	${}^{4}\Pi, v = 0$ state of NbO	, with their effective operators.	Matrix elements between
the two con	ponents of the $\Pi$ st	ate are given, with the	e standard spherical har	monic phase choice, as	$\langle \Lambda = \pm 1   \exp(\pm 2i\phi)   \Lambda = \mp 1$	$\rangle = -1.$

Substate origins	$T_{5/2} T_{3/2} T_{1/2} T_{-1/2}$	$T_{\Omega}$ 1				
Rotation	$B A_D \lambda_D \eta_D$	$B(\mathbf{J}-\mathbf{L}-\mathbf{S})^{2} + \frac{1}{2}A_{D}[L_{z}S_{z},(\mathbf{J}-\mathbf{L}-\mathbf{S})^{2}]_{+} + \frac{1}{3}\lambda_{D}[(3S_{z}^{2}-\mathbf{S}^{2}), (\mathbf{J}-\mathbf{L}-\mathbf{S})^{2}]_{+} + \frac{1}{2}\eta_{D}[L_{z}S_{z}(S_{z}^{2}-\{3\mathbf{S}^{2}-1\}/5),(\mathbf{J}-\mathbf{L}-\mathbf{S})^{2}]_{+}$				
Spin-rotation interaction	γ	$\gamma$ (J-L-S)·S				
Λ doubling	o+p+q p+2q q	$ \begin{array}{l} -\frac{1}{2}(o+p+q)(S_{+}^{2}e^{-2i\phi}+S_{-}^{2}e^{2i\phi})+\frac{1}{2}(p+2q)(J_{+}S_{+}e^{-2i\phi}\\ +J_{-}S_{-}e^{2i\phi})-\frac{1}{2}q(J_{+}^{2}e^{-2i\phi}+J_{-}^{2}e^{2i\phi}) \end{array} $				
Magnetic hyperfine	$h_{5/2} h_{3/2} h_{1/2} h_{-1/2}$	$h_{\Omega}I_{z}J_{z}/\Omega$				
	$d b_{53} b_{31} b_{1,-1}$	$+\frac{1}{2}d(I_{-}S_{-}e^{2i\phi}+I_{+}S_{+}e^{-2i\phi})+\frac{1}{2}b_{\Omega\Omega'}(I_{+}S_{-}+I_{-}S_{+})$				
Electric quadrupole	$e^2 Q q_0 \ e^2 Q q_2$	$\left[\sqrt{6}e^2 Q q_0 T_0^2(I,I) - e^2 Q q_2 T_{\pm 2}^2(I,I) e^{\pm 2i\phi}\right] / \left[4I(2I-1)\right]$				
Nuclear spin-rotation	c1 ξ	$c_{l}\mathbf{I}\cdot\mathbf{J}+\frac{1}{2}\xi(J_{+}I_{+}e^{-2i\phi}+J_{-}I_{-}e^{2i\phi})$				
Centrifugal distortion of						
rotation	$DA_{\mu}\lambda_{\mu}$	Operators are constructed as anticommutators of the lower rank				
A doubling	$\left. \begin{array}{c} D_{o+p+q} D_{p+2q} D_{q} \end{array} \right\}$	operators with $(J-L-S)^2$ ,				
Magnetic hyperfine	$D_b$	e.g., $-\frac{1}{4}D_{o+p+q}[(S_{+}^{2}e^{-2i\phi}+S_{-}^{2}e^{2i\phi}), (\mathbf{J}-\mathbf{L}-\mathbf{S})^{2}]_{+},$ where $[x,y]_{+}=xy+yx$ is the anticommutator.				

perturbations. Given this amount of disorganization it is not surprising that the magnetic hyperfine structure does not follow the normal case (a) patterns. In an unperturbed  ${}^{4}\Pi(a)$  state the four substates have low-*J* hyperfine patterns described by a combination of the Frosch and Foley parameters,

$$h = a\Lambda + (b+c)\Sigma; \tag{5}$$

the  ${}^{4}\Pi_{1/2}$  substate has different hyperfine patterns for its two  $\Lambda$ -doubling components, governed by the parameter d, while the patterns at high J depend on b, which appears in the  $\Delta \Omega = \pm 1$  "spin-uncoupling" matrix elements. We found that the maximum flexibility was needed for the  $B^{4}\Pi$  state of NbO, and therefore took four independent diagonal h parameters, one for each substate, with three different off-diagonal b parameters in the three spin-uncoupling matrix elements. These are labeled  $h_{\Omega}$  and  $b_{\Omega\Omega'}$  in Table III. The *h* parameters were found to require apparent centrifugal distortions, but it was later realized that these result from electronic perturbations by distant  $\Sigma$  and  $\Delta$  states, and are better described as nuclear spin-rotation interactions. There are two parameters of this type, a diagonal parameter,  $c_1$ , and a  $\Lambda$ -doubling parameter,  $\xi$ , representing interactions between the components of the  $\Pi$  state. A centrifugal distortion correction to the Fermi contact interaction, called  $D_b$ , has been introduced; it is at the limit of determinability.

Table III also lists the effective Hamiltonian operators for the various terms. The rotational and hyperfine matrix for a <sup>4</sup> $\Pi$  state can be derived from the algebraic and tensor expressions to be found in Refs. 32–35; it is given as Table IV. This table is set up for an unperturbed <sup>4</sup> $\Pi$  state, but the modifications needed to make it consistent with the operators of Table III are obvious. The matrix elements of the higher order centrifugal distortion terms are not shown. They can be obtained by straightforward, though lengthy, matrix multiplication. For example, the coefficients for  $D_q$  are the matrix product of those for *B* and those for *q*; they are listed in Ref. 14. It should be noted that the sign of a centrifugal distortion term is the same as that of its principal term, with the exception of that for D itself; in other words we write  $BJ(J+1)-DJ^2(J+1)^2$ , but the equivalent for all the other terms does not have the minus sign. The off-diagonal elements of the higher order terms have to be averaged in order to preserve the Hermitian forms of the matrices.

# E. Molecular constants for the $B^{4}\Pi$ , v=0 state of NbO

Constants for the B  ${}^{4}\Pi$ , v=0 level were determined by a least-squares fit to the 7327 assigned hyperfine lines from the four spin-allowed ( $\Delta\Sigma=0$ ) subbands of the B-X transition; the 31 upper state parameters listed in Table III were floated. The ground state was not refined further. Its energy levels were calculated from the final constants of Table II. which were held fixed. There is no need to describe in detail how the upper state parameters were chosen. In essence we began with a simple model and added parameters in trialand-error fashion until the systematic trends in the leastsquares residuals had been eliminated. At the beginning we worked with limited data sets, where J ran to  $5\frac{1}{2}$  or to  $12\frac{1}{2}$ , in order to establish the  $T_{\Omega}$ 's and the hyperfine parameters, before tackling the high-J data. The final constants are given in Table V. All of them are well determined except for  $D_h$  and  $\xi$ , where the  $3\sigma$  error limits are comparable to the parameters themselves.

#### V. PERTURBATIONS IN THE *B*<sup>4</sup>II STATE—LOCAL AND GLOBAL

#### A. A local perturbation in B ${}^{4}\Pi_{5/2}$

The one small electronic perturbation occurring in the  $B^{4}\Pi$ , v = 0 level of NbO merely affects the hyperfine structure of the  $J = 16\frac{1}{2}$  level of  ${}^{4}\Pi_{5/2f}$ . The appearance of the

perturbation is illustrated by the  ${}^{R}Q_{43}(16\frac{1}{2})$  line, shown in Fig. 9. The lowest F hyperfine component is seen to be split into two nearly equally intense lines, and the nearby hyperfine structure is bunched. The lines going to this upper rotational level were omitted from the data set from which the  ${}^{4}\Pi$  constants were derived.

With just one rotational level affected the "window"

into the perturbing electronic state is too small to allow anything to be said about its nature, even though it is possible to deduce its hyperfine parameter. A similar situation was encountered in one of the spin components of the  $C^{4}\Sigma^{-}$  state of VO.<sup>25</sup> Our approach has been to assume that the interaction can be represented by a 2×2 matrix for each F value, of the form

TABLE IV. Matrix of the rotational and hyperfine Hamiltonian for a  ${}^{4}\Pi$  state in case  $(a_{\beta})$  coupling, where one spinning nucleus is present.

$$\frac{\left| \frac{1}{2} \frac{1}{2} \right\rangle}{\left| \frac{1}{2} \frac{1}{2} \right\rangle} \frac{\left| \frac{1}{2} \frac{1}{2} \right\rangle}{\left| \frac{1}{2} \frac{1}{2}$$

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: J. Chem. Phys., Vol. 100, No. 9, 1 May 1994 131.94.16.10 On: Mon. 22 Dec 2014 05:49:46 TABLE IV. (Continued.)

where  

$$\begin{aligned} z = \left(J + \frac{1}{2}\right)^2, \quad W = F(F+1) - I(I+1) - J(J+1), \quad G = \frac{3W(W+1) - 4I(I+1)J(J+1)}{8I(2I-1)J(J+1)(2J-1)(2J+3)}, \\ Y = (W+J+1)f[8I(2I-1)(J^2-1)], \quad V = \sqrt{(F+I+J+1)(F-I+J)(J+I-F)(F-J+I+1)}/(4J) \end{aligned}$$
There are  $\Delta J = \pm 2$  quadrupole matrix elements as follows:  

$$\left(J - 2 \Omega \frac{f}{e} \middle| H_e \middle| J\Omega \frac{f}{e} \right) = 3e^2 Q q_0 \frac{\sqrt{J^2 - \Omega^2} \sqrt{(J-1)^2 - \Omega^2}}{(2J-1)\sqrt{(2J-3)(2J+1)}} X, \quad \left\langle J - 2 \Omega' \frac{f}{e} \middle| H_e \middle| J\Omega \frac{f}{e} \right\rangle = \pm \frac{1}{8} e^2 Q q_2 Z_{\Omega'\Omega} X \end{aligned}$$
where  

$$X = \frac{\sqrt{(F+I+J+1)(F-I+J)(J+I-F)(F-J+I+1)} \sqrt{(F+I+J)(F-I+J-1)(I-F+J-1)(F+I-J+2)}}{4I(2I-1)4J(J-1)}, \\ Z_{5/2,-1/2} = \sqrt{(2J+3)(2J+5)/[(2J-1)(2J-3), \quad Z_{1/2,3/2} = \sqrt{(2J-5)/(2J-1)}, \\ Z_{3/2,1/2} = \sqrt{(2J+3)/(2J-1)}, \quad Z_{-1/2,5/2} = \sqrt{(2J-5)(2J-7)/[(2J-1)(2J+1)]}. \end{aligned}$$

$$\mathbf{H} = \begin{bmatrix} T(B^{-4}\Pi) + k(B^{-4}\Pi)F(F+1) & a \\ a & T_{\text{perturbing}}F(F+1) \end{bmatrix}.$$
(6)

There are five parameters to be determined, though with only one doubled line there is not enough experimental information to determine all five. However, the parameter  $k(B^{4}\Pi)$ can be obtained from the  $B^{4}\Pi$  energy levels calculated from the constants of Table V. The intercept  $T(B^{4}\Pi)$  can also be derived from the calculated levels, but was floated in the least-squares treatment in order to allow for possible calibration shifts. The analysis is summarized in Table VI. The interaction matrix element a is found to be 0.0144 cm<sup>-1</sup>. An electronic perturbation as small as this is not normally seen except with very precise data; it seems likely that the mechanism is a spin-orbit interaction where the Franck-Condon factor is very unfavorable. The k parameter for the perturbing state is -0.00044 cm<sup>-1</sup>, which is slightly smaller than that of the  $F_4$  component of the ground state at this J value. There are no signs of systematic trends in the least-squares residuals, so that the model appears to be adequate.

## B. Distortion of the spin–orbit structure of the B ${}^{4}\Pi$ state

The spin-orbit structure of the  $B^{4}\Pi$  state (see Fig. 1) does not follow the simple expression  $E_{spin-orbit}=A\Lambda\Sigma$ , but rather is crowded towards high frequencies. This immediately suggests that the low- $\Omega$  substates have been pushed down by a perturbing state above, or alternatively that the high- $\Omega$  substates have been pushed up by a state at lower energy. There are in fact two absorption bands near 7000 Å found in argon and neon matrices that have very similar intensity to the  $B^{4}\Pi - X^{4}\Sigma^{-}$  system;<sup>10,11</sup> these have been assigned as two of the spin-allowed subbands of another quartet system,  $A^{4}\Pi$  (a)- $X^{4}\Sigma^{-}$  (a), with the lower level being  $X^{4}\Sigma_{1/2}^{-}$ , since only this component is populated in the lowtemperature matrix.<sup>11</sup> These bands also appear weakly in our room temperature laser-induced fluorescence survey spectra, though they are overlapped by "hot" vibrational structure from the B-X system such that their assignment is not obvious.

Two close-lying  ${}^{4}\Pi$  states, such as A and B, could perturb each other's spin-orbit structure like this if they lie very close and have very different diagonal spin-orbit couplings, but in that case we should expect to see the full quartet structure of the other state. An alternative explanation is suggested by the MoN spectrum,<sup>21</sup> where the corresponding  $B {}^{4}\Pi$  state also shows a crowding of its spin-orbit structure, similar to that of NbO but in the opposite sense. Crowding of this type must presumably be a normal occurrence, indicating some simple interaction mechanism such as spin-orbit perturbation by a nearby  ${}^{2}\Pi$  state.

We have recently carried out experiments on the spectrum of supersonic jet-cooled NbO, prepared by the reaction of laser-ablated Nb metal with oxygen gas;<sup>36</sup> in these experiments the molecules are rotationally cold but "spin hot," meaning that the  $X \, {}^{4}\Sigma_{3/2}^{-}$  component is populated almost to the same extent as the  $X \, {}^{4}\Sigma_{1/2}^{-}$  component. The spectra show only two bands in the 7000 Å region, rather than the four expected for a second  ${}^{4}\Pi - X {}^{4}\Sigma$  transition. Since, from their consistent gas-to-matrix shifts, these are the same bands that appear in the magnetic circular dichroism experiments of Ref. 11, they must have orbitally degenerate upper states; we therefore conclude that the bands in the 7000 Å region have to be a  ${}^{2}\Pi - X {}^{4}\Sigma^{-}$  transition. In agreement with this, Pinchemel et al.<sup>37</sup> have analyzed the shorter wavelength band of the two, at 14 330  $\text{cm}^{-1}$ , and find that it is an  $\Omega = 3/2 - X \, {}^{4}\Sigma_{1/2}^{-}$  band, or  ${}^{2}\Pi_{3/2} - X \, {}^{4}\Sigma_{1/2}^{-}$  in our assignment. The longer wavelength band, at 13 551 cm<sup>-1</sup>, is presumably  ${}^{2}\Pi_{1/2} - X {}^{4}\Sigma_{1/2}^{-}$ .

A mechanism explaining the distortion of the  $B^{4}\Pi$  state, and which is consistent with the various observations,

TABLE V. Rotational and hyperfine constants for the  $B^{4}\Pi$ , v=0 level of NbO. Values in cm<sup>-1</sup>. Quoted error limits are three standard deviations.  $r_0(B^{4}\Pi) = 1.7278_6$  Å.

T <sub>5/2</sub>	15 414.627 8 <sub>3</sub>	±0.000 1 <sub>33</sub>	h <sub>5/2</sub>	-0.019 4 <sub>80</sub>	±0.000 1 <sub>12</sub>
$T_{3/2}$	15 378.833 6 <sub>8</sub>	$\pm 0.000 \ 1_{22}$	h <sub>3/2</sub>	0.018 7 <sub>37</sub>	±0.000 1 <sub>31</sub>
$T_{1/2}$	15 128.406 97	$\pm 0.000 \ 3_{04}$	$h_{1/2}$	0.023 9 <sub>33</sub>	$\pm 0.000 \ 3_{03}$
$T_{-1/2}$	14 863.608 9 <sub>1</sub>	$\pm 0.000 \ 2_{87}$	$h_{-1/2}$	0.054 8 <sub>52</sub>	$\pm 0.000 \ 2_{56}$
В	0.413 79355	$\pm 0.000\ 000_{20}$	b 53	-0.018 793	±0.000 0 <sub>60</sub>
$10^{6} D$	0.363 0 <sub>8</sub>	$\pm 0.000 \ 1_3$	b <sub>31</sub>	-0.019 0 <sub>65</sub>	$\pm 0.000 \ 1_{85}$
γ	0.162 346	$\pm 0.000 \ 1_{74}$	$b_{1,-1}$	-0.017 2 <sub>18</sub>	$\pm 0.000 2_{09}$
$A_D$	0.000 8968	$\pm 0.000\ 001_{39}$	d	$-0.00602_{82}$	$\pm 0.000\ 02_{84}$
$10^4 \lambda_D$	-0.16750	$\pm 0.011_{49}$	$e^2 Q q_0$	-0.002 036	$\pm 0.00041_{9}$
$10^{3} \eta_{D}$	-0.8145	$\pm 0.003_{2}$	$e^2 Q q_2$	0.02465	$\pm 0.009_{79}$
o+p+q	6.379 8 <sub>2</sub>	$\pm 0.0017_{7}$	$10^4 c_1$	$-0.152_{9}$	$\pm 0.005_{1}$
p+2q	0.062 3013	$\pm 0.000\ 008_1$	$10^{5} \xi$	1.199	±0.945
q	0.000 1168	$\pm 0.000\ 003_{9}$	$10^7 D_h$	-0.439	$\pm 0.6_{17}$
$D_{a+p+a}$	$-0.000036_{92}$	$\pm 0.000\ 000_{92}$	$10^7 A_H$	$-0.1828_{2}$	$\pm 0.001 2_8$
$10^5 D_{n+2a}$	$-0.2319_{2}$	$\pm 0.001 0_0$	$10^7 \lambda_H$	-0.115 54	$\pm 0.0009_{5}$
$10^{5} D_{q}$	-0.1008	±0.0215		•	·
		r.m.s. error = 0.000 7	786 4 cm <sup>-1</sup>		
P					

is that the two bands in the 7000 Å region comprise a spinorbit induced  ${}^{2}\Pi - X {}^{4}\Sigma^{-}$  transition. If it is assumed that their intensity comes from spin-orbit mixing of the  $B^{4}\Pi$ state into the  ${}^{2}\Pi$  state, with the selection rule  $\Delta\Omega=0$ , the case (a) spin selection rule  $\Delta \Sigma = 0$  for the  ${}^{4}\Pi - {}^{4}\Sigma^{-}$  transition (see Fig. 1) is transferred to the  ${}^{2}\Pi - {}^{4}\Sigma^{-}$  transition; the lower states of the new bands must then both be  $X^{4}\Sigma_{1/2}^{-}$ , in accord with the matrix spectra.<sup>10,11</sup>

We can test this proposed mechanism as follows. It is assumed that the spin structure of the  $B^{4}\Pi$  state would follow  $E_{\text{spin-orbit}} = A\Lambda\Sigma$  in the absence of the <sup>2</sup> $\Pi$  perturbation; also that the shifts caused by spin-orbit interaction are equal and opposite in the  $B^{4}\Pi$  and  $^{2}\Pi$  states. The energy level diagram that results is given in Fig. 10. Since the spin-orbit interaction is diagonal in  $\Omega$ , there will be a 2×2 matrix for each  $\Omega$  value, where we know the eigenvalues and the diagonal elements from the figure. We can calculate the offdiagonal elements from the formula<sup>6</sup>

$$|H_{12}| = \frac{1}{2} \sqrt{(\lambda_1 - \lambda_2)^2 - (H_{11} - H_{22})^2},$$
(7)

and find

$$|H_{12}|_{3/2} = 371 \text{ cm}^{-1}; |H_{12}|_{1/2} = 333 \text{ cm}^{-1}.$$
 (8)

In theory these two matrix elements should be the same whatever the electron configuration of the  $^{2}\Pi$  state, because the  $\Sigma$  dependence of the spin-orbit interaction follows from the Wigner-Eckart theorem,

$$\langle \Lambda S \Sigma \Omega | H_{\text{spin-orbit}} | \Lambda' S' \Sigma' \Omega \rangle$$
  
=  $(-1)^{S-\Sigma} \begin{pmatrix} S & 1 & S' \\ -\Sigma & q & \Sigma' \end{pmatrix} \langle \Lambda S || H_{\text{spin-orbit}} || \Lambda' S' \rangle, \quad (9)$ 

and the two 3-j symbols are the same for  $\Omega = 1/2$  and 3/2. The fact that the elements in Eq. (8) differ by only 11% suggests that we are on the right track.

On the other hand, the only low-lying  ${}^{2}\Pi$  states expected for NbO are the two from the same configuration,  $\delta^2 \pi$ , as the B  ${}^{4}\Pi$  state and the two from the configuration  $\sigma\delta\pi$  (corresponding to the A  ${}^{4}\Pi$  state of VO<sup>14</sup>). The  ${}^{2}\Pi$  states from the same configuration should lie above the  $B^{4}\Pi$  state,<sup>38</sup> while there should be no spin-orbit interaction possible between the  $\delta^2 \pi B^4 \Pi$  state and the  $\sigma \delta \pi^2 \Pi$  states, since the first electron would have  $\Delta \lambda = \pm 2$ . The mechanism of Fig. 10 might therefore seem to be impossible. The way around this impasse is provided by the hyperfine structure of the  $\Omega = 3/2$ upper state of the 14 330 cm<sup>-1</sup> subband. Although this has not been analyzed in detail yet, preliminary results<sup>37</sup> show that it has a magnetic hyperfine parameter

$$h_{3/2} = 0.047_1 \text{ cm}^{-1}$$
 (10)

According to Eq. (5), this is the sum of the Frosch and Foley a and  $\frac{1}{2}(b+c)$  parameters, where we expect a to be in the range 0.01-0.02 cm<sup>-1</sup>. Therefore,  $\frac{1}{2}(b+c)$  must be positive, which implies that the effects of an unpaired  $s\sigma$  electron must be present.

We next investigate what the Fermi contact parameters should be in the  ${}^{2}\Pi$  states from the configuration  $\sigma\delta\pi$ , where



FIG. 9. Sub-Doppler spectrum of NbO near 15 376.5 cm<sup>-1</sup>, illustrating the perturbed  ${}^{R}Q_{43}(16\frac{1}{2})$  line. A very small upper state perturbation doubles the F = 12 component of this line.

=

TABLE VI. Analysis of the hyperfine perturbation in the NbO B  ${}^{4}\Pi_{5/2f}$ , v=0,  $J=16\frac{1}{2}$  level.

Data (in cm <sup>-1</sup> )										
Line	F' = 21	20	19	18	17	16	15	14	13	12
$^{R}Q_{43}(16\frac{1}{2})$	15 376.8170	0.8019	0.7872	0.7737	0.7616	0.7502	0.7399	0.7311	0.7251	0.7223
$P_4(17\frac{1}{2})$	15 360.1740	0.1432	0.1135	0.0855	0.0590*	0.0340	0.0111	59.9894	0.9711	0.9654
*=blended line										
Upper state energy levels $Q$	15 535.1205	0.1140	0.1073	0.1012	0.0961	0.0910	0.0866	0.0833	0.0822	0.0840
Р	15 535.1198	0.1128	0.1060	0.1001	0.0947*	0.0899	0.0863	0.0828	0.0818	0.0833
Average	15 535.1202	0.1134	0.1066	0.1006	0.0954	0.0905	0.0864	0.0830	0.0820	0.0836
				Results	; 					0.0540
			T(B k(B T(perturk k(perturk r.m.s.	$T(B \ {}^{4}\Pi)$ 15 535.043 2±0.000 5 $k(B \ {}^{4}\Pi)$ 0.000 163 4± fixed $T(\text{perturbing})$ 15 535.138 1±0.018 7 $k(\text{perturbing})$ -0.000 438 3±0.000 120 6 $a$ 0.014 41±0.000 53r.m.s. error0.000 252 5 cm <sup>-1</sup>						

the  $\sigma$  orbital is predominantly Nb 5s $\sigma$ . It is not possible to calculate exact values because the two <sup>2</sup> $\Pi$  states cannot be treated separately, but we can estimate the ranges in which the parameters should lie. The starting point is the pair of linearly independent Slater determinant functions,

$$|^{2}\Pi_{3/2}; \delta\pi(^{1}\Pi) \times \sigma \rangle = (2)^{-1/2} \{ |\delta^{+}\overline{\pi^{-}}\sigma| - |\overline{\delta^{+}}\pi^{-}\sigma| \},$$

$$|^{2}\Pi_{3/2}; \delta\pi(^{3}\Pi) \times \sigma \rangle = (6)^{-1/2} \{ 2|\delta^{+}\pi^{-}\overline{\sigma}| - |\delta^{+}\overline{\pi^{-}}\sigma| - |\overline{\delta^{+}}\pi^{-}\sigma| \}.$$

$$(11)$$

The form of these functions assumes that the exchange splitting between the  $\delta \pi^{1}\Pi$  and  $^{3}\Pi$  states is large compared to the electrostatic interaction between the two  ${}^{2}\Pi$  states. The eigenvalues of the Fermi contact operator  $b_{F,\sigma} I_z s_{1z}$  for these two functions are  $\frac{1}{2}b_F \langle I_z \rangle$  and  $-\frac{1}{6}b_F \langle I_z \rangle$ , respectively, where  $\frac{1}{2}b_F \langle I_z \rangle$  is also the eigenvalue in the 3/2 component of the  $X^{4}\Sigma^{-}$  ground state. This means there should be a very large Fermi contact parameter for the first of the two  $^{2}\Pi$  functions which, from the ratio of the S values, should be three times that of the ground state, or  $b_F \sim 0.15_4$  cm<sup>-1</sup>. Since the real  $^{2}\Pi$  states must correspond to linear combinations of these functions, this value is an upper limit; electrostatic interaction between the two  $^{2}\Pi$  states must lower the actual value, but cannot reduce it below  $+\frac{1}{6}b_F\langle I_z\rangle = 0.05_1$  cm<sup>-1</sup>. The other  ${}^{2}\Pi$  state will have a smaller contact parameter, which must be less than  $0.05_1$  cm<sup>-1</sup>, but whose sign cannot be predicted by these arguments.

The  $h_{3/2}$  parameter of the 14 330 cm<sup>-1</sup> upper level given in Eq. (10) is therefore consistent with a <sup>2</sup> $\Pi$  state from the  $\sigma\delta\pi$  configuration. However, there must be configuration interaction (CI) occurring between the <sup>2</sup> $\Pi$  states from the  $\delta^2\pi$ and  $\sigma\delta\pi$  configurations, if the  $\delta^2\pi B$  <sup>4</sup> $\Pi$  state is to interact with one of the  $\sigma\delta\pi$ <sup>2</sup> $\Pi$  states, while at the same time the <sup>2</sup> $\Pi$  state that is seen lies *below* the *B* <sup>4</sup> $\Pi$  state. The spin-orbit matrix elements of Eq. (8) are consistent with what would be expected for a  $\delta^2 \pi {}^4 \Pi - {}^2 \Pi$  perturbation. Again there is the problem that two interacting  ${}^2 \Pi$ states arise from the configuration  $\delta^2 \pi$ , and we can therefore only give limiting values, which correspond to the  ${}^2 \Pi$  functions from the couplings  $\delta^2 ({}^1\Sigma^+) \times \pi$  and  $\delta^2 ({}^3\Sigma^-) \times \pi$ . Taking  $\Omega = 3/2$ , the relevant Slater determinant functions, including that for the  $B {}^4 \Pi$  state, are



FIG. 10. Energy level diagram illustrating the spin-orbit interaction between the  $\Omega = 3/2$  and 1/2 components of the  $\delta^2 \pi B^4 \Pi$  and  $(\sigma \delta \pi)^2 \Pi$  states of NbO.

$$|B^{4}\Pi_{3/2}\rangle = (3)^{-1/2} \{ |\overline{\delta^{+}} \delta^{-} \pi| + |\delta^{+} \overline{\delta^{-}} \pi| + |\delta^{+} \delta^{-} \bar{\pi}| \}, \\|^{2}\Pi_{3/2}; \delta^{2}({}^{1}\Sigma^{+}) \times \pi \rangle = (2)^{-1/2} \{ |\delta^{+} \overline{\delta^{-}} \pi| - |\overline{\delta^{+}} \delta^{-} \pi| \},$$
(12)  
$$|^{2}\Pi_{3/2}; \delta^{2}({}^{3}\Sigma^{-}) \times \pi \rangle = (6)^{-1/2} \{ 2 |\delta^{+} \delta^{-} \bar{\pi}| - |\delta^{+} \overline{\delta^{-}} \pi| - |\overline{\delta^{+}} \delta^{-} \pi| \},$$

from which we obtain the two possible values

$$\langle {}^{4}\Pi_{3/2} | H_{\text{spin-orbit}} | {}^{2}\Pi_{3/2} \rangle = \frac{4}{\sqrt{6}} a_{\delta} ({}^{1}\Sigma^{+}) \text{ or}$$
  
 $-\frac{1}{3} \sqrt{2} a_{\pi} ({}^{3}\Sigma^{-}).$  (13)

The value of  $a_{\delta}$  can be taken from the NbN spectrum, where the spin-orbit splitting of the  $\sigma \delta X^{3} \Delta$  ground state<sup>6</sup> gives  $a_{\delta}$  (Nb)=446 cm<sup>-1</sup>. We can obtain  $a_{\pi}$  by scaling the value from the corresponding  $B^{4}\Pi$  state of VO:<sup>13</sup> taking the spinorbit parameters for V<sup>+</sup> and Nb<sup>+</sup> from Ref. 39, we have

$$a_{\pi}(\text{NbO}, B^{4}\Pi) = a_{\pi}(\text{VO}, B^{4}\Pi) \times \zeta(\text{Nb}^{+})/\zeta(\text{V}^{+})$$
  
= 193.5 × 502/152 cm<sup>-1</sup>=639 cm<sup>-1</sup>.  
(14)

Substituting these numbers into Eq. (13), the limiting values for the electronic part of the spin-orbit matrix element are found to be 728 and  $-301 \text{ cm}^{-1}$ . The actual value will be reduced by the CI mixing of the previous paragraph and the vibrational overlap integral, but it is seen that the "experimental" value,  $\frac{1}{2}(371+333)=352 \text{ cm}^{-1}$ , from Eq. (8), is not inconsistent with the calculated range.

To sum up, Fig. 10 appears to provide a consistent explanation of the results. It is probable that the distortion in the spin structure of the  $B^{4}\Pi$  state is caused by a  ${}^{2}\Pi$  state lying below it, which appears weakly in the spectrum near 7000 Å, and where both  ${}^{2}\Pi_{1/2}$  and  ${}^{2}\Pi_{3/2}$  combine only with  $X {}^{4}\Sigma_{1/2}^{-}$ . This  ${}^{2}\Pi$  state is a CI mixture of  $\delta^{2}\pi$  and  $\sigma\delta\pi$ , where the sign of the Fermi contact parameter is positive.

## VI. INTERPRETATION OF THE MOLECULAR PARAMETERS

### A. Magnetic hyperfine parameters of the $\sigma \delta^2 X {}^4 \Sigma^-$ ground state

The Fermi contact interaction parameter for the ground state is consistent with the electron configuration  $\sigma\delta^2$ , where the  $\sigma$  electron is in a molecular orbital with about 80% Nb 5s atomic character. The argument goes as follows. The detailed analysis of the atomic beam spectrum of the  $4d^4$  5s ground configuration of the Nb atom<sup>40</sup> has given values for the contact parameter  $a_{nl}^{10}$  for both the 4d and the 5s electrons:

$$a_{4d}^{10} = -511.5 \pm 30.5$$
 MHz;  
 $a_{5s}^{10} = 6700 \pm 118$  MHz, (15)

where the negative value for the 4*d* electron is ascribed to spin polarization. The contact parameter for the ground state of NbO should therefore be  $(6700-2\times511.5)/3=1892$  MHz,

or 0.063 12 cm<sup>-1</sup>, assuming the atomic orbitals are unchanged in the molecule. The experimental value can be obtained from the *b* and *c* parameters of Table II,

$$b_F = b + (1/3)c = 0.051 \ 23_2 \ \mathrm{cm}^{-1}.$$
 (16)

Since the  $4d\delta$  molecular orbital has to be essentially identical in the atom and in the molecule, the difference must reflect the degree of contamination of the Nb 5s orbital in the molecule. Put another way, the percentage of Nb 5s atomic character in the "5s $\sigma$ " molecular orbital can be obtained by correcting the experimental value of  $b_F$  for the two  $\delta$  electrons, and dividing by the atomic contact parameter, which gives 84.0%.

The experimental Fermi contact parameter is also consistent with the *ab initio* calculations of  $\psi_{5s}^2(0)$ . The value for this quantity given by Froese's self-consistent field (SCF) calculations is 3.9784  $a_0^{-3}$ .<sup>41</sup> Using the expression<sup>1</sup>

$$b_F = \left(\frac{\mu_0}{4\pi hc}\right) \frac{8\pi}{3} gg_N \mu_B \mu_N \left(\frac{1}{2S}\right) \sum_i \langle \psi_i^2(0) \rangle_{nl}, \quad (17)$$

we find

$$b_F = 0.003 \ 186 \ 25 \ \mathrm{cm}^{-1}$$
  
  $\times \left(\frac{8\pi}{3}\right) \times \left(\frac{6.167}{9/2}\right) \times \frac{1}{3} \times 3.9784$   
  $= 0.048 \ 511 \ \mathrm{cm}^{-1}.$  (18)

Herman and Skillman's calculations<sup>42,43</sup> give the slightly higher value  $\psi_{5s}^2(0) = 4.736 \ a_0^{-3}$ , which translates as  $b_F = 0.05775 \ \text{cm}^{-1}$ .

The dipolar constant c can be compared in similar fashion to the atomic value. Büttenbach and Dicke<sup>40</sup> have derived the value  $\langle r_{12}^{-3} \rangle_{4d} = 2.119 a_0^{-3}$  from the atomic parameter  $a_{4d}^{12}$ . This is somewhat lower than the SCF calculations, which give 3.122  $a_0^{-3}$  (Ref. 41) and 3.494  $a_0^{-3}$ ,<sup>42,43</sup> respectively, and the disagreement has been ascribed<sup>40</sup> to configuration interaction. The dipolar parameter can be written<sup>1</sup>

$$c = \frac{3}{2} gg_N \mu_B \mu_N \left(\frac{\mu_0}{4\pi\hbar c}\right) \left(\frac{1}{2S}\right)$$
$$\times \sum_i \langle 3\cos^2\theta_i - 1 \rangle_{l\lambda} \langle r_i^{-3} \rangle_{nl}, \qquad (19)$$

which, for the configuration  $4d\delta^2 5s\sigma$ , becomes

 $c = 0.003 \ 186 \ 25 \ \mathrm{cm}^{-1}$ 

$$\times \frac{3}{2} \times \left(\frac{6.167}{9/2}\right) \times \frac{2}{3} \times \left(-\frac{4}{7}\right) \times 2.119$$
  
= -0.005 287 cm<sup>-1</sup>. (20)

The experimental value,  $c = -0.003 408 \text{ cm}^{-1}$ , is 64.5% of the theoretical.

There are considerable differences between the gas and matrix<sup>9</sup> values for these magnetic hyperfine parameters. For instance,

	Gas	Matrix,Ref.10	Matrix/gas
b	0.052 37	0.055 07	1.05
с	-0.003 41	-0.002 40	0.70

where the values are given in cm<sup>-1</sup>, and the comparison has been made with the Frosch and Foley<sup>1</sup> parameter b, rather than  $b_F$ . The gas-to-matrix shift for the contact parameter is typically of the order of 5%-10% for diatomic transition metal compounds. For example, in the ground state of MnH,<sup>44</sup> the gas phase value of the contact parameter is 11% smaller than the matrix value;<sup>45</sup> this has been rationalized<sup>44</sup> as partial suppression of the sp hybridization of the s $\sigma$  molecular orbital (MO) by the polarizing influence of the argon matrix, where the hybridization would otherwise push the unpaired electron density out behind the Mn nucleus and lower the contact parameter. The shift in the contact parameter is therefore not out of line with what happens in similar compounds. On the other hand, the 30% gas-to-matrix shift in the dipolar parameter is unexpectedly large. We are not aware of similar shifts in other systems.

# B. Electric quadrupole parameter of the $X {}^{4}\Sigma^{-}$ ground state

The magnetic hyperfine parameters of the ground state of NbO are reasonably well explained in terms of the atomic parameters and the parentage of the molecular orbitals. The quadrupole parameter  $e^2Qq_0$ , which includes a contribution from the paired valence electrons as well as the unpaired ones, is not so easy to interpret. The best we can do with the present data is to estimate the contribution of the unpaired electrons to  $e^2Qq_0$ .

The calculation goes as follows. The quantity  $e^2Qq_0$  is proportional to the same expectation values as the magnetic dipolar constant c:

$$\langle e^2 Q q_0 \rangle = -\frac{e^2 Q}{4 \pi \epsilon_0 h c} \sum_i \langle 3 \cos^2 \theta_i - 1 \rangle_{l\lambda} \langle r_i^{-3} \rangle_{nl}.$$
(21)

Substituting the value of the nuclear quadrupole moment, -0.22 barns ( $-0.22 \times 10^{-28}$  m<sup>2</sup>), from the atomic data tables<sup>46</sup> and Froese's value<sup>41</sup> for  $\langle r_i^{-3} \rangle_{4d}$ , we find

$$e^{2}Qq_{0}(X \ ^{4}\Sigma^{-}) = -0.007 \ 8376 \ \mathrm{cm}^{-1}$$
$$\times (-0.22) \left(-\frac{8}{7}\right) (3.122)$$
$$= -0.006 \ 152 \ \mathrm{cm}^{-1}. \tag{22}$$

The factor (-8/7) represents the two  $d\delta$  electrons, for which the expectation value  $\langle 3 \cos^2 \theta - 1 \rangle$  is -4/7.<sup>44</sup> The experimental value,  $-0.000 977 \text{ cm}^{-1}$ , is six times smaller than the calculated contribution from the unpaired electrons, though with the same sign.

There is still disagreement over the quadrupole moment of <sup>93</sup>Nb. The hyperfine structure of muonic <sup>93</sup>Nb gives<sup>47</sup>  $Q = -0.32 \times 10^{-28}$  m<sup>2</sup>, while Büttenbach and Dicke<sup>40</sup> have interpreted the atomic quadrupole coupling constants as giving  $Q = (-0.36 \pm 0.07) \times 10^{-28}$  m<sup>2</sup>. If we take their value, together with their derived expectation value  $\langle r_i^{-3} \rangle_{4d}$ , we predict an even larger contribution to the molecular quadrupole constant,  $e^2 Q q_0 = -0.006 83_3 \text{ cm}^{-1}$ .

## C. Third-order spin–orbit distortion of the Fermi contact interaction in the X $^{4}\Sigma^{-}$ ground state

The parameter for the third-order spin-orbit distortion of the Fermi contact interaction,<sup>31</sup>  $b_s$ , is very well determined in the  $X^{4}\Sigma^{-}$  state, but unfortunately there is no simple interpretation for it. When this parameter is nonzero it means that the effective Fermi contact interactions in the  $X^{4}\Sigma_{1/2}^{-}$ and  $X^{4}\Sigma_{3/2}^{-}$  components are slightly different. Now the  $b_{S}$ parameter is a sum of products of spin-orbit and Fermi contact matrix elements<sup>31</sup> with distant electronic states. We should therefore look for large spin-orbit matrix elements between the ground state and various excited states. The strongest spin-orbit interaction felt by the ground state will almost certainly be with the  ${}^{2}\Sigma^{+}$  state from the same configuration,  $\sigma\delta^2$ . The position of this state is not known yet. Wherever it may be, it turns out that its contribution to  $b_s$ must be very small because this has to be proportional to the difference between the Fermi contact interactions in the  $X^{4}\Sigma^{-}$  and  ${}^{2}\Sigma^{+}$  states.<sup>31</sup> Since these two states both come from the configuration  $\sigma\delta^2$ , it is easy to show that their Fermi contact parameters should be the same, barring the factor of 3 from the spin multiplicity, so that the  ${}^{2}\Sigma^{+}$  state cannot contribute to  $b_s$ . Another way of looking at this is that spinorbit mixing of the  ${}^{2}\Sigma^{+}$  state into X  ${}^{4}\Sigma_{1/2}^{-}$  mixes foreign character into the ground state, but the foreign state has the same hyperfine parameters as the ground state. More detailed investigation shows that the Fermi contact matrix element between X  ${}^{4}\Sigma_{1/2}^{-}$  and  ${}^{2}\Sigma_{1/2}^{+}$  is identically zero, as can be seen by writing the electronic wave functions as Slater determinants, so that no third-order contribution to the  $b_s$  parameter is possible. Evidently in the present case the  $b_s$  parameter arises from a more complicated mechanism which we have not so far elucidated.

#### D. A doubling in the $B^{4}\Pi$ state

There is remarkably good agreement for the  $\Lambda$ -doubling parameters of the  $B^{4}\Pi$  state with the "pure precession," or "unique perturber," relations. Assuming that a distant  ${}^{4}\Sigma^{-}$ state is the only state responsible for the  $\Lambda$  doubling we should have

$$o + p + q = -\frac{1}{2} \frac{\langle {}^{4}\Pi | (A + 2B)L_{+} | {}^{4}\Sigma^{-} \rangle^{2}}{\Delta E_{\Pi\Sigma}}, \qquad (23)$$

$$p+2q=-2 \frac{\langle {}^{4}\Pi | (A+2B)L_{+} | {}^{4}\Sigma^{-} \rangle \langle {}^{4}\Pi | BL_{+} | {}^{4}\Sigma^{-} \rangle}{\Delta E_{\Pi\Sigma}}, \qquad (24)$$

$$q = -2 \frac{\langle {}^{4}\Pi | BL_{+} | {}^{4}\Sigma^{-} \rangle^{2}}{\Delta E_{\Pi\Sigma}} .$$
<sup>(25)</sup>

The ratios of these parameters are found to be

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Calculated Observed

$$(o+p+q)/(p+2q) = (A+2B)/(4B)$$
 111.5 102.4  
 $(p+2q)/q = (A+2B)/B$  446 523

where we take A as  $\frac{1}{3}$  (551 cm<sup>-1</sup>)=183.7 cm<sup>-1</sup> and B = 0.413 79 cm<sup>-1</sup>, from Table V.

The positive signs of the  $\Lambda$ -doubling parameters suggest that  $\Delta E_{\Pi\Sigma}$  must be negative, since the other quantities are all positive, and point, not to the ground state, but to the  $C^{4}\Sigma^{-}$ state<sup>48</sup> at 21 436 cm<sup>-1</sup> as the state responsible. In this case we have an interaction between  $4d\delta^{2} 4d\pi B^{4}\Pi$  and  $4d\delta^{2}$  $4d\sigma C^{4}\Sigma^{-}$ , where the pure precession relations should hold quite well if the amount of oxygen atomic character mixed into the " $4d\sigma$ " and " $4d\pi$ " orbitals is not unduly great. All the same we should never expect the agreement to be as good as is found for hydrides.

The full consequences of pure precession in quartet states have not so far been investigated. We defer the detailed discussion to Sec. VIE, because it is necessary to consider the magnetic hyperfine structure as well. A prediction that can be tested here concerns the various  $\gamma$  parameters. (In lighter molecules, where the effects of spin-orbit interaction are less, these would be called spin-rotation parameters. In heavier molecules the second-order cross term between the spin-orbit and orbit-rotation interactions becomes important; it has the same operator form as the spin-rotation interaction and is indistinguishable from it, so that the experimental  $\gamma$  parameter represents their sum.) According to the unique perturber model the  $\gamma$ 's in the  $4\Sigma$  and  $4\Pi$  states should be the same, and equal to half the  $\Lambda$ -doubling parameter p+2q of the <sup>4</sup> $\Pi$  state. The prediction is not borne out by experiment; the calculated value for the two  $\gamma$ 's is 0.0311<sub>5</sub> cm<sup>-1</sup>, whereas experimentally they are  $-0.0157 (C^{4}\Sigma^{-})$ and 0.162 cm<sup>-1</sup> ( $B^{4}\Pi$ ), respectively. However, as we shall see, very good agreement is found for the value of  $\gamma (B^{4}\Pi)$ if the effects of perturbing  $\Delta$  states are also included.

The value of  $\gamma$  (B <sup>4</sup>\Pi) is nearly 40% of the rotational constant B. Since it appears in the case (a) Hamiltonian matrix, Table IV, as a correction to the B value in the  $\Delta\Omega = \pm 1$  (spin-uncoupling) matrix elements, its size is surprising at first sight. In light molecules, where the  $\gamma$  parameter is dominated by the true spin-rotation interaction, a correction of this magnitude is not feasible but, as spin-orbit effects become relatively more important,  $\gamma$  can easily become of the order of B, or even larger. In particular, if the manifold of possible perturbing states is fairly dense, it must become very important. Its effect on the energy levels in this case is to "soften" the spin uncoupling, so that the transition from case (a) coupling to case (b) occurs less rapidly than expected; a negative  $\gamma$  has the effect of intensifying the spin uncoupling.

#### E. Magnetic hyperfine structure of the B<sup>4</sup>II state

The principal magnetic hyperfine parameters of the  $B^{4}\Pi$  state are shown plotted against  $\Omega$  in Fig. 11. In pure case (a) the  $h_{\Omega}$ 's should fall on a straight line, while the three  $b_{\Omega\Omega'}$ 's should be identical. The  $b_{\Omega\Omega'}$ 's are the same to within 0.0018 cm<sup>-1</sup>, but the  $h_{\Omega}$ 's show a pronounced zig-



FIG. 11. The magnetic hyperfine parameters  $h_{\Omega}$  and  $b_{\Omega\Omega'}$  of the  $B^{4}\Pi v=0$  state of NbO plotted against  $\Omega$ . The parameters  $h_{\Omega}$  appear in the matrix elements diagonal in  $\Omega$ , and in theory should be equal to  $a\Lambda + (b + c)\Sigma$ , such that a plot of  $h_{\Omega}$  against  $\Omega$  should be a straight line. The  $b_{\Omega\Omega'}$  parameters appear in the  $\Delta\Omega = \pm 1$  spin-uncoupling matrix elements, as the effective coefficients of  $(I_+S_-+I_-S_+)$  acting between  $|\Omega\rangle$  and  $|\Omega' = \Omega \pm 1\rangle$ . The value of  $h_{1/2}$  has been lowered, and that of  $h_{3/2}$  raised, by spin-orbit interaction with the  $(\sigma\delta\pi)^2\Pi$  state, which has a positive Fermi contact parameter, unlike the  $B^{4}\Pi$  state.

zag pattern. The explanation of the zig-zag is that the  ${}^{4}\Pi_{3/2}$  and  ${}^{4}\Pi_{1/2}$  components are mixed by spin-orbit interaction with the  ${}^{2}\Pi$  state lying 1100 cm<sup>-1</sup> below (see Sec. V B). The  ${}^{2}\Pi$  state has a positive Fermi contact parameter  $b_F$ , so that the  ${}^{2}\Pi_{3/2}$  and  ${}^{2}\Pi_{1/2}$  components have, respectively, positive and negative  $h_{\Omega}$  values. The spin-orbit mixing therefore raises and lowers the  $h_{\Omega}$  values of  ${}^{4}\Pi_{3/2}$  and  ${}^{4}\Pi_{1/2}$ , respectively. The relative amounts of the raising and lowering can be estimated from the eigenvectors of the 2×2 matrices whose off-diagonal elements are given as Eq. (8). A simple calculation shows that  $h_{3/2}$  should be raised by 3.0 times as much as  $h_{1/2}$  is lowered; the experimental ratio is 2.2, which is in satisfactory agreement considering the crudeness of the model.

Values of a and (b+c) can be obtained from the unperturbed  ${}^{4}\Pi_{5/2}$  and  ${}^{4}\Pi_{-1/2}$  states:

$$a = \frac{1}{2}(h_{5/2} + h_{-1/2}) \approx 0.0176_9 \text{ cm}^{-1},$$
  
(b+c) =  $\frac{1}{3}(h_{5/2} - h_{-1/2}) \approx -0.0247_8 \text{ cm}^{-1}.$  (26)

Assuming the molecular orbitals are unchanged from those of the Nb atom, the value of a should be (5/3) times the atomic parameter  $a_{4d}^{01}$ , which is 351.7 MHz,<sup>40</sup> leading to the value a=0.019 55 cm<sup>-1</sup>. If we take b as the average of the  $b_{\Omega\Omega'}$ 's, i.e.,  $-0.0183_6$  cm<sup>-1</sup>, c is obtained as  $-0.0064_2$ cm<sup>-1</sup>. This value seems high because, applying Eq. (19) for the configuration  $\delta^2 \pi$ , the calculated value is  $-0.0039_7$ cm<sup>-1</sup>. On the other hand the Fermi contact parameter is given as

$$b_F = b + (1/3)c \approx -0.020 \ 50 \ \mathrm{cm}^{-1},$$
 (27)

only slightly larger than the atomic contact parameter  $a_{4d}^{10}$ , which is  $-0.0170_6$  cm<sup>-1</sup> [see Eq. (15)]. These estimates may

in fact be unreliable, because the same electronic perturbations that cause the magnetic hyperfine d parameter to be negative, as we discuss below, also give a correction to the  $b_{\Omega\Omega'}$  parameters.

Two of the anomalous features of the magnetic hyperfine structure of the  $B^{4}\Pi$  state are this negative sign for d, and the unusually large value of the nuclear spin-rotation parameter  $c_{I}$ . We can discount the  ${}^{2}\Pi$  state that distorts the spin-orbit structure as a cause of these effects, because it is easy to show that it can only have very small hyperfine matrix elements with the  $B^{4}\Pi$  state. To be exact, if we write the Fermi contact operator in the microscopic form

$$H_{\rm FC} = \sum_{i} b_i \mathbf{I} \cdot \mathbf{s}_i, \qquad (28)$$

and take the electronic wave functions as in Eq. (12), we obtain

$$\langle {}^{4}\Pi_{3/2}; JIF | H_{FC} | {}^{2}\Pi_{3/2}; JIF \rangle = \frac{1}{3} \sqrt{2} (b_{\delta} - b_{\pi}) \frac{\Omega W(FIJ)}{2J(J+1)}, \qquad (29)$$

where the quotient at the end represents the matrix element of the operator  $I_z$ . If it is possible to define a contact interaction for a non- $\sigma$  electron caused by spin polarization, as is done for atoms,<sup>49</sup> it can be seen that the matrix element of Eq. (29) must be very small, as it is the difference of the contact parameters for  $d\delta$  and  $d\pi$  electrons; these can only be different to the extent that the  $d\pi$  molecular orbital has some oxygen character mixed in while the  $d\delta$  molecular orbital does not.

However, prompted by the unique perturber patterns shown by the  $\Lambda$  doubling, we have investigated the effects of  $\Delta\Lambda = \pm 1$  perturbations on the magnetic hyperfine structure. It appears that they can explain a number of the observed anomalies, as we now show. The effects of perturbing  ${}^{4}\Sigma$  and  ${}^{4}\Delta$  states can be worked out by taking the interaction Hamiltonian as

$$H' = \frac{1}{2}a(I_{+}L_{-} + I_{-}L_{+}) + \frac{1}{2}(A + 2B)(L_{+}S_{-} + L_{-}S_{+})$$
  
-B(J\_{+}L\_{-} + J\_{-}L\_{+}), (30)

where *a* is the electron orbit-nuclear spin interaction constant, in the Hamiltonian  $H=a\mathbf{I}\cdot\mathbf{L}$ . Specifically we have considered perturbing  ${}^{4}\Sigma^{-}$  and  ${}^{4}\Delta$  states, and the calculations can be done separately for the two types of state. For perturbing  ${}^{4}\Sigma^{-}$  states, the basis set consists of the 12 functions  $|\Lambda;S\Sigma;J\Omega IF\rangle$  for the  ${}^{4}\Sigma^{-}$  and  ${}^{4}\Pi$  states, with  $\Lambda=0$  and  $\pm 1$ . Evaluation of the matrix elements is standard, although the matrix elements of  $I_{\pm}$  may be unfamiliar:

$$\langle J\Omega \mp 1IF | I_{\pm} | J\Omega IF \rangle = \frac{\sqrt{J(J+1) - \Omega(\Omega \pm 1)}}{2J(J+1)} \quad W(FIJ),$$
(31)

where W(FIJ) = F(F+1) - I(I+1) - J(J+1). The 12×12 matrix is symmetric about both diagonals, so that it can be factorized by taking sums and differences of the basis functions (a Wang transformation). The form of the coupling block that results is given in Table VII. Next a Van Vleck

TABLE VII. Matrix of coupling elements between a <sup>4</sup>II state and a unique perturber <sup>4</sup> $\Sigma^-$  state. t = W(FIJ)/[2J(J+1)] and  $z = (J + \frac{1}{2})^2$ ;  $L_+$  represents the orbital matrix element  $\langle {}^4\Pi | L_+ | {}^4\Sigma^- \rangle$ . Upper and lower signs correspond to the Wang sum and difference functions, respectively, which for a  ${}^4\Sigma^-$  perturbing state give the *f* and *e* levels. They must be inverted for a unique perturber  ${}^4\Sigma^+$  state.

	$ ^{4}\Sigma_{3/2}\rangle$	$ ^{4}\Sigma_{1/2}\rangle$
$\langle {}^{4}\Pi_{5/2}  $	$(\frac{1}{2}at - B)\sqrt{z-4}L_+$	0
( <sup>4</sup> Π <sub>3/2</sub>	$\frac{1}{2}(A + 2B)\sqrt{3}L_+$	$(\frac{1}{2}at - B)\sqrt{z-1}L_+$
$\langle {}^{4}\Pi_{1/2}$	. 0	$(A+2B)L_{+} \mp (\frac{1}{2}at-B)(J+\frac{1}{2})L_{+}$
( <b>711</b> 1/2	$\mp (\frac{1}{2}at - B)\sqrt{z - 1}L_+$	$\mp \frac{1}{2}(A + 2B)\sqrt{3L_+}$

transformation is applied, in order to fold the coupling elements into the effective Hamiltonian matrix of the  ${}^{4}\Pi$  state. Many elements are generated, as summarized in Table VIII.

<sup>4</sup> $\Delta$  states give contributions of the same general form to the elements of Table VIII, but only for the terms without double signs. This means that the expressions in the table have different meanings depending on whether they carry double signs or not, being sums over  $\Sigma^-$  states only, or sums over  $\Sigma^-$  and  $\Delta$  states. What they describe can be understood by comparing this table with the complete Hamiltonian in Table IV. For instance the terms labeled  $\mp \tilde{A}^2$ ,  $\pm \tilde{A}B$ , and  $\mp B^2$  become the  $\Lambda$ -doubling parameters o+p+q, p+2q, and q, where the relative signs come from the effective Hamiltonian of Ref. 35. (See also Table III.) Equations (23)– (25) then follow at once.

The other terms in Table VIII can be identified as follows. The terms in  $\mathbf{a}^2$  and  $\mp \mathbf{a}^2$  are, roughly speaking, contributions to the quadrupole parameters  $e^2 Q q_0$  and  $e^2 Q q_2$ , respectively. They will be small compared to the quadrupole parameters themselves, and we do not consider them further. The  $\mathbf{B}^2$  terms on the diagonal give a contribution to the rotational constant B which, if perturbing  $\Delta$  states are ignored, is equal to  $-\frac{1}{2}q$ ; similarly the  $\tilde{A}^2$  terms on the diagonal are small corrections to the spin-orbit intervals, or in other words contributions to the higher order spin-orbit constants  $\lambda$  and  $\eta$ . The unsigned **AB** term in the spin-uncoupling matrix elements gives rise to the  $\gamma(^{4}\Pi)$  term; the  $\Sigma^{-}$  contribution to it is related to the  $\Lambda$ -doubling parameter p + 2q, as we described above. The magnetic hyperfine effects resulting from the  $\Delta \Lambda = \pm 1$  perturbations are represented by the terms in aA and aB. The aA terms are obviously electronic corrections to the b and d parameters, but the **aB** terms have no counterpart in the Frosch and Foley Hamiltonian;<sup>1</sup> instead they represent nuclear spin-rotation interactions.

Nuclear spin-rotation interactions are familiar in microwave spectra of closed-shell molecules,<sup>3</sup> and are known to arise in linear molecules from second-order cross terms between the operators  $-2BJ\cdot L$  and  $aI\cdot L$ , as we have here. The most detailed accounts for open-shell molecules have been given for OH by Meerts and Dymanus<sup>50</sup> and Brown *et al.*<sup>51</sup> There are two terms needed in the effective Hamiltonian, one for the sum over  $\Sigma$  and  $\Delta$  states, which is parityindependent, and the other for the sum over  $\Sigma$  states only, which contributes to the  $\Lambda$  doubling. These terms can be written

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TABLE VIII. Corrections to the Hamiltonian matrix for a  ${}^{4}\Pi$  state perturbed by a  ${}^{4}\Sigma^{-}$  state, to second order.<sup>a</sup>

	$ ^{4}\Pi_{5/2} angle$	4II <sub>3/2</sub> >	<sup>4</sup> Π <sub>1/2</sub> >	<sup>4</sup> ∏ <sub>−1/2</sub> ⟩
( <sup>4</sup> Π <sub>5/2</sub>	$(z-4)\left(\frac{1}{4} \mathbf{a}^2 t^2 - \mathbf{a}\mathbf{B}t + \mathbf{B}^2\right)$	$-\sqrt{3(z-4)}\left(-\frac{1}{4} \tilde{\mathbf{A}}\mathbf{a}t+\frac{1}{2} \tilde{\mathbf{A}}\mathbf{B}\right)$	0	$\pm\sqrt{(z-1)(z-4)}\left(-\frac{1}{4}\mathbf{a}^{2}t^{2}+\mathbf{a}\mathbf{B}t-\mathbf{B}^{2}\right)$
$\langle {}^4\Pi_{3/2}  $		$\frac{3}{4}  \tilde{\mathbf{A}}^2 + (z-1) \left( \frac{1}{4}  \mathbf{a}^2 t^2 - \mathbf{a} \mathbf{B} t + \mathbf{B}^2 \right)$	$-2\sqrt{z-1}\left(-\frac{1}{4} \tilde{\mathbf{A}}\mathbf{ar}+\frac{1}{2} \tilde{\mathbf{A}}\mathbf{B}\right)$	$\pm \sqrt{3(z-1)} \left( \frac{1}{2}  \tilde{\mathbf{A}}\mathbf{a}t - \tilde{\mathbf{A}}\mathbf{B} \right)$
			$\pm\sqrt{z(z-1)}\left(-\frac{1}{4}\mathbf{a}^{2}t^{2}+\mathbf{a}\mathbf{B}t-\mathbf{B}^{2}\right)$	
⟨ <sup>4</sup> Π <sub>1/2</sub>			$\tilde{\mathbf{A}}^2 + z \left( \frac{1}{4} \ \mathbf{a}^2 t^2 - \mathbf{a} \mathbf{B} t + \mathbf{B}^2 \right)$	$-\sqrt{3z}\left(-\frac{1}{4} \tilde{\mathbf{A}}\mathbf{a}t+\frac{1}{2} \tilde{\mathbf{A}}\mathbf{B}\right)\mp\frac{1}{2} \sqrt{3}\tilde{\mathbf{A}}^2$
			$\mp \sqrt{z}(\tilde{\mathbf{A}}\mathbf{a}t - 2\tilde{\mathbf{A}}\mathbf{B})$	
⟨ <sup>4</sup> ∏ <sub>- 1/2</sub>	2 Symmetric			$\frac{3}{4}  \tilde{\mathbf{A}}^2 + (z-1) \left( \frac{1}{4}  \mathbf{a}^2 t^2 - \mathbf{a} \mathbf{B} t + \mathbf{B}^2 \right)$

 $a_{Z} = (J + \frac{1}{2})^{2}$ ; t = [F(F+1) - I(I+1) - J(J+1)]/[2J(J+1)]. The other symbols, **a**,**B**, and  $\tilde{A}$  (where  $\tilde{A} = A + 2B$ ) are matrix elements of  $L_{+}$ , e.g.,  $a = \langle {}^{4}\Pi | aL_{+} | {}^{4}\Sigma^{-} \rangle$ , and when taken in pairs they indicate second order perturbation expressions, such as

 $\tilde{\mathbf{A}}\mathbf{B} = \langle {}^{4}\Pi | \tilde{A}L_{+} | {}^{4}\Sigma^{-} \rangle \langle {}^{4}\Pi | BL_{+} | {}^{4}\Sigma^{-} \rangle / \Delta E_{\Pi\Sigma^{-}},$ 

 $\mathbf{B}^2 = \langle {}^4\Pi | BL_+ | {}^4\Sigma^- \rangle^2 / \Delta E_{\Pi\Sigma^-} \,.$ 

 $^{4}\Delta$  states give analogous corrections, but only to those terms without double signs; in other words they do not contribute to the  $\Lambda$ -doubling effects. Therefore when the perturbation expressions are equated to the experimental parameters, different symbols are required depending on whether the sum is over  $\Sigma^{-}$  states only, or  $\Sigma^{-}$  and  $\Delta$  states. For example,

with double sign:  $\mathbf{aB} = \langle {}^{4}\Pi | aL_{+} | {}^{4}\Sigma^{-} \rangle \langle {}^{4}\Pi | BL_{+} | {}^{4}\Sigma^{-} \rangle / \Delta E_{\Pi\Sigma^{-}} = -\frac{1}{2} \xi;$ 

no double sign: 
$$\mathbf{aB} = \sum_{\Lambda = \Sigma^{-}, \Delta} \langle {}^{4}\Pi | aL_{\pm} | {}^{4}\Lambda \rangle \langle {}^{4}\Pi | BL_{\pm} | {}^{4}\Lambda \rangle / \Delta E_{\Pi\Lambda} = -c_{I}.$$

Upper and lower signs correspond to f and e levels, respectively.

$$H_{nsr} = c_I \mathbf{I} \cdot \mathbf{J} + \frac{1}{2} \xi (J_+ I_+ e^{-2i\phi} + J_- I_- e^{2i\phi}), \qquad (32)$$

where the  $\xi$  notation is taken from Ref. 52. The exact definitions of  $c_1$  and  $\xi$  are given below Table VIII. (The definition of the parity-dependent term  $\xi$  is opposite in sign to that given in Ref. 52 because we consider perturbing  $\Sigma^-$  states rather than  $\Sigma^+$ ; the same considerations apply to the  $\Lambda$ -doubling parameters, as explained in Ref. 35.)

Given these preliminaries, it is possible to establish various pure precession relations. The corrections to the *b* and *d* magnetic hyperfine parameters, caused by perturbing  $\Sigma^{-}$  states, are

$$\Delta d = 2\Delta b = \frac{\langle 4\Pi | (A+2B)L_+ | 4\Sigma^- \rangle \langle 4\Pi | aL_+ | 4\Sigma^- \rangle}{\Delta E_{\Pi\Sigma}} .$$
(33)

The net effect is that the "true" d value is altered by an amount:

$$\Delta d = -2 \frac{a}{A+2B} (o+p+q) = -0.001 \ 23_8 \ \mathrm{cm}^{-1}.$$
(34)

This correction is about a factor of 5 smaller than the observed d parameter but, significantly, it is negative, which agrees with the experimental sign of d. Evidently perturbations by  $\Sigma$  states can reverse the sign of the apparent d hyperfine parameter, even though the true d is proportional to the expectation value  $\langle \sin^2 \theta \rangle$ , which should be a positive number:

$$d = \frac{3}{2} gg_N \mu_B \mu_N \left(\frac{\mu_0}{4\pi hc}\right) \left(\frac{1}{2S}\right) \sum_i \langle \sin^2 \theta_i \rangle_{l\lambda} \langle r_i^{-3} \rangle_{nl}.$$
(35)

The usual explanation for a negative value of d is configuration interaction;<sup>53</sup> here is a case where it seems we can say how this configuration interaction might occur. The discrepancy in the magnitude of the correction suggests that further perturbation mechanisms, as yet unknown, must be operating.

The correction to the Fermi contact parameter given in Eq. (33) arises because the second-order cross term  $(I \cdot L)(L \cdot S)$  looks like a term in  $I \cdot S$ . Equation (33) is not the whole story, and if we include perturbing  ${}^{4}\Delta$  states, we find that there is a simple relation between  $\Delta b$  and  $\gamma$ , which gives

$$\Delta b = -a \gamma/2B = -0.003 \ 47 \ \mathrm{cm}^{-1}. \tag{36}$$

However the relation may not be very useful in the present instance because there will be additional corrections to the  $b_{\Omega\Omega'}$ 's coming from the  ${}^{4}\Pi/{}^{2}\Pi$  interaction described in Sec. V B. This spin-orbit mixing is presumably the reason why the three  $b_{\Omega\Omega'}$  values are not quite the same; we do not pursue this point.

Further pure precession relations also hold for the nuclear spin-rotation parameters  $c_1$  and  $\xi$ . There should be a simple relation between  $c_1$  and  $\gamma$ <sup>4</sup>II), because both arise from perturbing  $\Sigma$  and  $\Delta$  states:

$$c_l = -\gamma a/A, \tag{37}$$

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TABLE IX. Low J rotational and hyperfine energies of the v = 0 levels of the  $X^{4}\Sigma^{-}$  and  $B^{4}\Pi$  states of NbO, calculated from the constants of Tables II and V. Values in cm<sup>-1</sup>.

	<i>F</i> =	J+9/2	J+7/2	J+5/2	J+3/2	J+1/2	J-1/2	J-3/2	J-5/2	J-7/2	J-9/2
$\overline{X^{4}\Sigma^{-}}$											
$J = \frac{1}{2}$	F.	-30.1805	-30.62102								
2	F 26	-28.7939	-28.5379								
$J = \frac{3}{7}$	$F_{1,\epsilon}^{2}$	$-29.7142_{0}^{2}$	-29.9424	$-30.0925_{0}$	$-30.2038_{6}$						
-	F.	-26.7362	-26.5890	-26.4740	-26.3857						
	F3.	32.6243	32.45296	32.3133	32.20342						
	$F_{4f}$	32.6252	32.45416	32.31492	32.20548						
$J = \frac{5}{2}$	Fie	-28.40434	-28.56574	$-28.6909_{3}^{-1}$	$-28.7893_{1}$	$-28.8651_{1}$	$-28.9205_{7}$				
-	$F_{2f}$	-23.79145	-23.67663	$-23.5841_7$	-23.50870	-23.44970	$-23.4061_{7}$				
	$F_{3e}$	34.78169	34.7069 <sub>0</sub>	34.6393 <sub>2</sub>	34.58099	34.53321	34.49679				
_	$F_{4f}$	34.78596	34.71174	34.6448 <sub>3</sub>	34.58723	34.5401 <sub>5</sub>	34.5043 <sub>3</sub>				
$J = \frac{7}{2}$	$F_{1e}$	-26.2434	-26.3761	-26.4860	-26.5766	-26.6500	-26.7076	-26.7502	-26.7783		
	$F_{2f}$	19.9838	-19.8878	-19.8064	-19.7383	-19.6827	-19.6389	-19.6064	-19.5849		
	F <sub>3e</sub>	37.8490	37.8052	37.7653	37.7299	37.6995	37.6748	37.6559	37.6432		
~	$F_{4f}$	37.8605	37.8177	37.7788	37.7445	37.7152	37.6913	37.6732	37.6610		
$J = \frac{9}{2}$	Fie	-23.2287	-23.3460	-23.4466	-23.5322	-23.6041	-23.6630	-23.7096	-23.7442	-23.7671	-23.7786
	$F_{2f}$	-15.3209	-15.2363	-15.1630	-15.1002	-15.0472	-15.0037	-14.9692	- 14.9436	-14.9266	-14.9181
	F <sub>3e</sub>	41.8119	41.7835	41.7574	41.7338	41.7131	41.6955	41.6811	41.6702	41.6629	41.6592
	$F_{4f}$	41.8359	41.8090	41.7843	41.7623	41.7430	41.7267	41.7135	41.7035	41.6968	41.6934
<i>Β</i> ⁴Π											
$J = \frac{1}{2}$	-1/2f	14 863.9271	864.1031								
- 2	1/2f	15 130.4567	130.3455								
	-1/2e	14 863.8287	864.0209								
	1/2 <i>e</i>	15 130.6433	130.5966								
$J = \frac{3}{2}$	-1/2f	14 865.2499	865.2995	865.3341	865.3547						
-	1/2f	15 131.5724	131.5433	131.5140	131.4873						
	3/2f	15 380.9642	380.9190	380.8813	380.8511						
	-1/2 <i>e</i>	14 865.0529	865.1153	865.1557	865.1764						
	1/2 <i>e</i>	15 131.9745	131.9715	131.9689	131.9670						
	3/2 <i>e</i>	15 380.9642	380.9190	380.8813	380.8511						
$J = \frac{5}{2}$	-1/2f	14 867.3719	867.3952	867.4135	867.4276	867.4380	867.4453				
	1/2f	15 133.5182	133.4998	133.4827	133.4675	133.4547	133.4447				
	3/2f	15 382.9805	382.9603	382.9427	382.9279	382.9160	382.9070				
	5/2f	15 416.2780	416.3150	416.3465	416.3727	416.3936	416.4092				
	-1/2e	14 867.0782	867.1104	867.1344	867.1517	867.1638	867.1718				
	1/2 <i>e</i>	15 134.1379	134.1399	134.1420	134.1440	134.1458	134.1472				
	3/2e	15 382.9806	382.9603	382.9427	382.9280	382.9161	382.9071				
	5/2 <i>e</i>	15 416.2780	416.3150	416.3465	416.3727	416.3936	416.4092				

where  $\tilde{A} = A + 2B$ . Similarly  $\xi$  should be related to the perturbation correction  $\Delta d$  of Eq. (33), and to the  $\Lambda$ -doubling parameter q:<sup>52</sup>

$$\xi = -2\Delta dB/\tilde{A} = qa/B. \tag{38}$$

To check these relations it is assumed that the observed value of d comes entirely from the electronic perturbation, such that  $\Delta d = d = -0.006 \ 02_8 \ \text{cm}^{-1}$ , and that  $\tilde{A} = 184.5 \ \text{cm}^{-1}$ , from  $T_{5/2}$  and  $T_{-1/2}$  in Table V. The comparison is as follows:

Calculated Observed  

$$c_{I} = -1.56 \times 10^{-5} = -1.53 \times 10^{-5} \text{ cm}^{-1},$$
  
 $\xi = 2.7 \times 10^{-5} = 1.2 \times 10^{-5}$   
 $5.0 \times 10^{-6}.$  (39)

The agreement for  $c_1$  is excellent, and confirms the large value of  $\gamma({}^4\Pi)$ . The parameter  $\xi$  is not well determined, though it is seen to lie between the two calculated values.

It seems that Eq. (37) may give a useful method for breaking the least-squares correlation between  $\gamma$  and the centrifugal distortion parameter  $A_D$ , which complicates the fitting of rotational data for doublet and triplet II states.<sup>54</sup> Normally one of  $\gamma$  or  $A_D$  has to be set to zero but, if the nuclear spin-rotation parameter  $c_I$  can be measured, an estimate of  $\gamma$ becomes available. This particular correlation does not occur in quartet states because there are more substates available to provide data; the equivalent indeterminacy for quartets is the strong, but not total, correlation between  $\gamma$  and  $\eta_D$ .

#### F. Quadrupole parameters of the $B^{4}\Pi$ state

As in Sec. VI B, above, the diagonal quadrupole parameter  $e^2Qq_0$  sums the contributions to the field gradient tensor from all the electrons, both paired and unpaired;<sup>3</sup> it is not easy to estimate the effect of the electrons in closed shells, while the effect of the unpaired electrons is given by Eq. (21). The parameter  $e^2Qq_2$  is easier to interpret because it represents the contribution of the single unpaired  $\pi$  electron to the nonspherical charge distribution, and there is no need to include the paired electrons. Given the quadrupole coupling constant of the Nb atom,<sup>40</sup>  $b^{02}$  ( $4d^45s$ ) = -232.0  $\pm 0.2$  MHz, we can estimate  $e^2Qq_2$  (NbO),  $\delta^2\pi$ ) from the relation<sup>52</sup>

$$e^2 Q q_2 = -3b^{02}. (40)$$

The comparison between experiment and estimate for the quadrupole parameters, with the values given in  $cm^{-1}$ , is

$$\begin{array}{ccc} & \text{Calculated} & \text{Observed} \\ e^2 Q q_0 & -0.005 \ 12 & -0.0020_4 \\ e^2 Q q_2 & 0.023 \ 22 & 0.024_{65} \end{array}$$

The estimate for  $e^2Qq_2$  is well within the error limits of the experimental determination, and indicates that the charge distribution near the Nb nucleus in the  $\pi$  molecular orbital is not unduly altered from that in a Nb 4d atomic orbital by the bonding to oxygen. The agreement for  $e^2Qq_0$  is not expected to be as good since the effects of the paired electrons are not included.

#### VII. DISCUSSION AND SUMMARY

The analysis of the  $B^{4}\Pi - X^{4}\Sigma^{-}$  (0,0) band of NbO presented in this work demonstrates how complex the hyperfine structures of high multiplicity states can become when the atoms involved are moderately heavy. The X  ${}^{4}\Sigma^{-}$  ground state is well behaved, but requires a total of 12 parameters to account for its rotational and hyperfine structure. The thirdorder spin-orbit distortions of the spin-rotation and contact hyperfine interactions are essential in modeling the energy levels correctly, and are well determined in the least-squares treatment. For instance, the parameter  $b_S$ , for the third-order distortion of the contact term, is only a factor of 10 smaller than the dipolar parameter. The reason why these terms are needed is that spin-orbit interaction with distant states can contaminate the two case (a) components,  ${}^{4}\Sigma_{1/2}^{-}$  and  ${}^{4}\Sigma_{3/2}^{-}$ , differently, so that the two components have slightly different spin-rotation and contact parameters. These third-order parameters are not simple to interpret, because cancellation effects may occur such that the largest off-diagonal spinorbit matrix elements do not necessarily generate important third-order terms.

The B <sup>4</sup> $\Pi$  state is more difficult to fit. For a start its spin-orbit structure is crowded towards high frequencies, with the  $\Omega = 5/2$  and 3/2 components only 36 cm<sup>-1</sup> apart, out of a total spin-orbit width of 551 cm<sup>-1</sup>. The reason for the crowding is that there is a <sup>2</sup> $\Pi$  state about 1100 cm<sup>-1</sup> below, whose wave function is a configuration interaction mixture of  $\delta^2 \pi$  and  $\sigma \delta \pi$ ; spin-orbit interaction between the <sup>2</sup> $\Pi$  and <sup>4</sup> $\Pi$  states has the effect of pushing the two middle components of the quartet state upwards, and altering their *h* hyperfine parameters. The main effect is on the rotational structure, where we have had to introduce a number of higher order centrifugal distortion terms to account for the mixing of <sup>2</sup> $\Pi$  character into the <sup>4</sup> $\Pi$  state, and the consequent breakdown of the <sup>4</sup> $\Pi$  spin-uncoupling formalism. Obviously the fit is somewhat artificial, and it is likely that extrapolation of the <sup>4</sup> $\Pi$  energy levels beyond the observed range of *J* will be unsatisfactory; as an indication of this, a preliminary fit just to the lower two spin-orbit components gave a root-meansquare (rms) error that was two-thirds of the best we achieved for the full data set. The alternative solution, a simultaneous fit to the <sup>2</sup> $\Pi$  and <sup>4</sup> $\Pi$  states, is not practical at present since only the  $\Omega=3/2$  component of the <sup>2</sup> $\Pi$  state has been analyzed rotationally.<sup>37</sup>

Nevertheless the hyperfine structure of the  $B^{4}\Pi$  state is quite severely distorted. One of the reasons is suggested by the  $\Lambda$ -doubling parameters, which are consistent with a "pure precession" model. A probable perturbing state is the  $\delta^{2}\sigma C^{4}\Sigma^{-}$  state at 21 436 cm<sup>-1</sup>. We have calculated the effect of distant  ${}^{4}\Sigma$  and  ${}^{4}\Delta$  states on the rotational and hyperfine structure of the  $B^{4}\Pi$  state, and find that it reproduces the distortions qualitatively, making various predictions that can be verified experimentally. In particular it explains the large size of the apparent spin-rotation parameter  $\gamma(B^{4}\Pi)$ , and the unexpected negative sign for the *d* hyperfine parameter. To our knowledge it has not been appreciated how electronic perturbations by distant  $\Sigma$  states with the same multiplicity can act so as to reverse the expected sign of *d* in a  $\Pi$  state.

To cope with the distortions we had to use a total of 13 hyperfine parameters for the  $B^{4}\Pi$  state. These include four diagonal magnetic hyperfine parameters,  $h_{\Omega}$ , one for each  $\Omega$  substate, and three off-diagonal contact parameters,  $b_{\Omega\Omega'}$ , instead of Frosch and Foley's *a*, *b*, and *c*. The values of these magnetic hyperfine parameters are shown, plotted as a function of  $\Omega$ , in Fig. 11. The zig-zag pattern of the  $h_{\Omega}$  parameters seen in this figure arises because of the spin-orbit interaction with the <sup>2</sup>\Pi state lying just below. The Fermi contact parameter of the  $B^{4}\Pi$  state is negative, as shown by the negative slope for the  $h_{\Omega}$ 's, while that of the <sup>2</sup>\Pi state is positive; the spin-orbit mixing therefore locally reduces the negative Fermi contact parameter for the <sup>4</sup>\Pi\_{3/2} and <sup>4</sup>\Pi<sub>1/2</sub> components.

Approximate values can be derived for the Frosch and Foley parameters, and these are in quite good agreement with what would be expected for the configuration  $\delta^2 \pi$  from the Nb atomic spectrum. The quadrupole parameters of the  $B^{4}\Pi$  state are very large, with  $e^2Qq_2$  being so large that the higher-J line profiles are asymmetric at Doppler limited resolution, rather like the spectrum of I<sub>2</sub>. It is interesting how this asymmetry grows in at higher J, because of the way  $e^2Qq_2$ only appears in J-dependent matrix elements off-diagonal in  $\Omega$  in Table IV. The  $e^2Qq_2$  parameter is nicely consistent with the configuration  $\delta^2 \pi$ , but  $e^2Qq_0$  clearly must include a sizeable contribution from the electrons in closed shells.

A large diagonal nuclear spin-rotation parameter,  $c_I$ , is shown to arise from  $\Delta \Lambda = \pm 1$  perturbations by distant <sup>4</sup> $\Sigma$  and <sup>4</sup> $\Delta$  states. There is a simple relation between  $c_I$  and the "spin-rotation" parameter  $\gamma$ , which is obeyed very well in the present instance. The relation should be general for all  $\Pi$ states, and measurement of  $c_I$  may provide a valuable way of estimating  $\gamma$  in a <sup>2</sup> $\Pi$  state, where the total least-squares correlation<sup>54</sup> with  $A_D$  permits only a combination of the two to be determined. A parity-dependent nuclear spin-rotation





FIG. 12. Calculated hyperfine widths,  $\Delta E_{\text{hfs}} = E(F_{\text{max}}) - E(F_{\text{min}})$ , for the  $B^{4}\Pi$ , v = 0 state of NbO, plotted as a function of  $J - \frac{1}{2}$ .

parameter is also needed for the  $B^{4}\Pi$  state of NbO; it results from perturbations by distant  $\Sigma$  states.

In view of the complexity of the energy level formulas and the widths of the hyperfine patterns we list the low-J energy levels, both for the ground state and the  $B^{4}\Pi$  state, in Table IX. It is expected that these will be useful in jetcooled laser ablation experiments, either in the visible region or in the microwave. To illustrate the patterns at higher J values, Figs. 5 and 12 show the hyperfine widths plotted as a function of J for the ground state and the  $B^{4}\Pi$  state, respectively. The figures have been calculated from the final leastsquares constants of Tables II and V. We also give the calculated  $\Lambda$  doubling of the  $B^{4}\Pi$  state, plotted as a function of J, in Fig. 13.

The configuration interaction between the  ${}^{2}\Pi$  states of  $\delta^{2}\pi$  and  $\sigma\delta\pi$  is interesting; it permits the  $\delta^{2}\pi B {}^{4}\Pi$  state to





interact with a <sup>2</sup> $\Pi$  state lying below it, and which possesses the hyperfine hallmark of the  $\sigma\delta\pi$  configuration. It seems that such configuration interaction is turning out to be more common than expected in the low-lying states of the early transition metal diatomics; similar examples have recently been found in NbN<sup>7</sup> and VN,<sup>55</sup> where it is the reason for the small size of the matrix element between the  $\delta\pi C$  <sup>3</sup> $\Pi$  and  $\delta^{2}$  <sup>1</sup> $\Sigma^+$  states. Clearly the single configuration approximation is starting to break down earlier than had been thought, and suggests that it will be a formidable task to interpret the spectra of such molecules as FeO and CoO in detail.

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- <sup>1</sup>R. A. Frosch and H. M. Foley, Phys. Rev. 88, 1337 (1932).
- <sup>2</sup>G. C. Dousmanis, Phys. Rev. 97, 967 (1955).
- <sup>3</sup>C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (Dover, New York, 1975).
- <sup>4</sup>P. Christiansen and L. Veseth, J. Chem. Phys. 84, 2711, 6336 (1986).
- <sup>5</sup>E. Hirota, *High Resolution Spectroscopy of Transient Molecules* (Springer, Berlin, 1985).
- <sup>6</sup>Y. Azuma, J. A. Barry, M. P. J. Lyne, A. J. Merer, J. O. Schröder, and J. L. Féménias, J. Chem. Phys. **91**, 1 (1989).
- <sup>7</sup>Y. Azuma, G. Huang, M. P. J. Lyne, A. J. Merer, and V. I. Srdanov, J. Chem. Phys. (in press).
- <sup>8</sup>J. M. Brown and D. J. Milton, Mol. Phys. 31, 409 (1976).
- <sup>9</sup>R. D. Suenram, G. T. Fraser, F. J. Lovas, and C. W. Gillies, J. Mol. Spectrosc. **148**, 114 (1991).
- <sup>10</sup> J. M. Brom, C. H. Durham, and W. Weltner, J. Chem. Phys. **61**, 970 (1974).
- <sup>11</sup>M. Vala, R. D. Brittain, and D. Powell, Chem. Phys. 93, 147 (1985).
- <sup>12</sup> A. J. Merer, G. Huang, A. S.-C. Cheung, and A. W. Taylor, J. Mol. Spectrosc. **125**, 465 (1987).
- <sup>13</sup>A. J. Merer, Annu. Rev. Phys. Chem. 40, 407 (1989).
- <sup>14</sup> A. S.-C. Cheung, A. W. Taylor, and A. J. Merer, J. Mol. Spectrosc. **92**, 391 (1982).
- <sup>15</sup>G. Huang, D. J. Clouthier, and A. J. Merer, J. Mol. Spectrosc. **153**, 32 (1992).
- <sup>16</sup>M. S. Sorem and A. L. Schawlow, Opt. Commun. 5, 148 (1972).
- <sup>17</sup>S. Gerstenkorn and P. Luc, Atlas du Spectre d'Absorption de la Molécule d'Iode (Editions du C.N.R.S., Paris, 1978); Rev. Phys. Appl. 14, 791 (1979).
- <sup>18</sup> J. L. Féménias, G. Cheval, A. J. Merer, and U. Sassenberg, J. Mol. Spectrosc. **124**, 348 (1987).
- <sup>19</sup>L. Klynning, B. Lindgren, and N. Åslund, Ark. Fys. **30**, 141 (1965).
- <sup>20</sup>R. W. Martin and A. J. Merer, Can. J. Phys. **51**, 125 (1973).
- <sup>21</sup> R. C. Carlson, J. K. Bates, and T. M. Dunn, J. Mol. Spectrosc. **110**, 215 (1985).
- <sup>22</sup> A. J. Merer, U. Sassenberg, J. L. Féménias, and G. Cheval, J. Chem. Phys. 86, 1219 (1987).

- <sup>23</sup> J. M. Brown, J. T. Hougen, K.-P. Huber, J. W. C. Johns, I. Kopp, A. J. Merer, D. A. Ramsay, J. Rostas, and R. N. Zare, J. Mol. Spectrosc. 55, 500 (1975).
- <sup>24</sup> U. Sassenberg, A. S.-C. Cheung, and A. J. Merer, Can. J. Phys. 62, 1610 (1984).
- <sup>25</sup>D. Richards and R. F. Barrow, Nature (London) 219, 1244 (1968).
- <sup>26</sup> A. S.-C. Cheung, R. C. Hansen, and A. J. Merer, J. Mol. Spectrosc. 91, 165 (1982).
- <sup>27</sup> J. T. Hougen, Can. J. Phys. 40, 598 (1962).
- <sup>28</sup> R. D. Verma, Can. J. Phys. **40**, 586 (1962).
- <sup>29</sup> R. W. Martin and A. J. Merer, Can. J. Phys. 51, 634 (1973).
- <sup>30</sup>T. Nelis, J. M. Brown, and K. M. Evenson, J. Chem. Phys. **92**, 4067 (1990).
- <sup>31</sup>A. S.-C. Cheung and A. J. Merer, Mol. Phys. 46, 111 (1982).
- <sup>32</sup> J. M. Brown, I. Kopp, C. Malmberg, and B. Rydh, Phys. Scr. 17, 55 (1978).
- <sup>33</sup>A. Carrington, P. N. Dyer, and D. H. Levy, J. Chem. Phys. 47, 1756 (1969).
- <sup>34</sup> J. M. Brown and J. E. Schubert, J. Mol. Spectrosc. 95, 194 (1982).
- <sup>35</sup> J. M. Brown and A. J. Merer, J. Mol. Spectrosc. 74, 488 (1979).
- <sup>36</sup>M. Barnes, P. G. Hajigeorgiou, and A. J. Merer (unpublished).
- <sup>37</sup>B. Pinchemel, C. Dufour, A. J. Merer, J. L. Féménias, and G. Cheval (unpublished).
- <sup>38</sup>J. Raftery, P. R. Scott, and W. G. Richards, J. Phys. B 5, 1293 (1972).
- <sup>39</sup>H. Lefebvre-Brion and R. W. Field, Perturbations in the Spectra of Diatomic Molecules (Academic, Orlando, 1986).

- <sup>40</sup>S. Büttenbach and R. Dicke, Z. Phys. A 275, 197 (1975).
- <sup>41</sup>C. Froese, Department of Mathematics, Internal Report, University of British Columbia, 1966.
- <sup>42</sup> F. Herman and S. Skillman, Atomic Structure Calculations (Prentice-Hall, Englewood Cliffs, 1963).
- <sup>43</sup> W. Weltner, Jr., Magnetic Atoms and Molecules (Van Nostrand Reinhold, New York, 1983).
- <sup>44</sup>T. D. Varberg, R. W. Field, and A. J. Merer, J. Chem. Phys. **95**, 1563 (1991).
- <sup>45</sup> R. J. Van Zee, D. A. Garland, and W. Weltner, Jr., J. Chem. Phys. 85, 3237 (1986).
- <sup>46</sup>G. H. Fuller, J. Phys. Chem. Ref. Data 5, 835 (1976).
- <sup>47</sup>H. P. Povel, Nucl. Phys. A 217, 573 (1976).
- <sup>48</sup>G. Cheval, J. L. Féménias, A. J. Merer, and U. Sassenberg, J. Mol. Spectrosc. 131, 113 (1988).
- <sup>49</sup>P. G. H. Sandars and J. Beck, Proc. R. Soc. London Ser. A 289, 97 (1965).
- <sup>50</sup>W. L. Meerts and A. Dymanus, J. Mol. Spectrosc. 44, 320 (1972).
   <sup>51</sup>J. M. Brown, M. Kaise, C. M. L. Kerr, and D. J. Milton, Mol. Phys. 36,
- 553 (1978). <sup>52</sup> I. Burshardt I. P. Zink, D. A. Elatohar, and I. M. Brown, Mol. Phys. 67
- <sup>52</sup> I. Burghardt, L. R. Zink, D. A. Fletcher, and J. M. Brown, Mol. Phys. 67, 1401 (1989).
- 53 T. Amano, J. Mol. Spectrosc. 144, 454 (1990).
- <sup>54</sup> J. M. Brown, E. A. Colbourn, J. K. G. Watson, and F. D. Wayne, J. Mol. Spectrosc. 74, 294 (1979).
- <sup>55</sup> W. J. Balfour, A. J. Merer, H. Niki, B. Simard, and P. A. Hackett, J. Chem. Phys. 99, 3320 (1993).