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Citation: J. Chem. Phys. 102, 4375 (1995); doi: 10.1063/1.469486

View online: http://dx.doi.org/10.1063/1.469486

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# High resolution rotational analysis of the $B^{3}\Pi-X^{3}\Delta$ (1,0) band of titanium monoxide

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(Received 3 October 1994; accepted 7 December 1994)

The  $B^3\Pi-X^3\Delta$  (1,0) band of titanium monoxide has been studied at sub-Doppler resolution (0.002 cm<sup>-1</sup>) by crossing a beam of TiO molecules with a cw tunable laser beam and by collecting the laser-induced fluorescence. The rotational structure of 42 branches belonging to the  ${}^3\Pi-{}^3\Delta$  transition has been analyzed up to rotational quantum numbers equal to 94. Spectroscopic data have been reduced to a set of 24 molecular constants, using a case (a) effective Hamiltonian. The rotational, spin-orbit and  $\Lambda$ -doubling constants are discussed in terms of the leading configurations which give rise to the  $X^3\Delta$  and  $B^3\Pi$  electronic states. It is shown that for the B state, existing *ab initio* calculations are not able to reproduce the second order spin-orbit effect and the  $\Lambda$  doubling effect. © 1995 American Institute of Physics.

#### I. INTRODUCTION

Titanium monoxide is the most abundant of the 3d oxides present in the spectra of cool M and S class stars. It is used for spectral classification of these stars on the MK system, the distribution of intensities in the rotational structure of TiO bands being a test to determine the temperature of stellar atmospheres. This great importance in astrophysics has led to numerous spectroscopic studies. TiO is also the simplest transition metal oxide known which involves d electrons in chemical bonding, justifying its interest in quantum chemistry.

Spectroscopy and bonding of the diatomic 3d transition metal oxides, including TiO, have been reviewed recently by Merer.<sup>6</sup> The observed electronic states are well represented by single configurations,  $(8\sigma)^2 (3\pi)^4 (9\sigma)^1 (1\delta)^1$  for the  $X^3\Delta$  ground state and  $(8\sigma)^2 (3\pi)^4 (1\delta)^1 (4\pi)^1$  for the  $B^3\Pi$  excited state.

Since its discovery by Cohen and Dunér in 1943,<sup>7</sup> the B-X (or  $\gamma'$ ) band system has been studied mainly by Hocking *et al.*<sup>8</sup> and by Gustavsson *et al.*<sup>9</sup> These two studies were Doppler-limited, restricting the assignment of rotational quantum numbers to  $J'' \le 55$ . Owing to the sub-Doppler resolution (0.002 cm<sup>-1</sup> or 60 MHz) and to the high signal-tonoise ratio achieved in the present experiment, the rotational analysis of the  $B^3\Pi-X^3\Delta$  (1,0) band has been extended up to J''=94. Most lines in the highly congested regions (heads in the sub-bands) are resolved for the first time, and the 3 sub-bands which are possible for a  ${}^3\Pi-{}^3\Delta$  transition are observed.

#### II. EXPERIMENTAL PROCEDURE

The experimental procedure has been described in detail in previous publications. <sup>10,11</sup> Briefly, an effusive beam of TiO molecules is produced by heating at 2200 K a tungsten crucible filled with TiO powder. The beam is perpendicularly crossed by a cw single mode tunable dye laser beam operating with Rh6G. The subsequent laser-induced fluorescence is collected by a parabolic mirror whose focus coincides with the crossing volume; it is then detected by a photomultiplier

through a series of broad band optical filters, whose role is to eliminate stray light in the collision chamber and part of the blackbody radiation emitted by the oven at high temperature. This radiation is further eliminated by chopping the laser beam and using a lock-in amplifier. The laser-induced fluorescence spectrum is recorded by tuning the laser frequency over the  $B^{3}\Pi - X^{3}\Delta$  (1,0) absorption band of TiO, by successive steps of 1 cm<sup>-1</sup> between 16 800 and 17 200 cm<sup>-1</sup>. The wave-number calibration is obtained through  $I_2$  absorption lines used as calibration standards<sup>12</sup> and by narrow reference fringes provided by a spherical Fabry-Perot etalon (free spectral range: 0.025 cm<sup>-1</sup>). The final resolution of the experiment (0.002 cm<sup>-1</sup>) is mainly due to the residual Doppler broadening associated with the angular aperture of the two beams (1°), to the finite lifetime of the excited level and to the jitter of the laser. At least four recordings of the same spectral region were performed to detect mode hops of the laser and to determine the internal coherence of the wave numbers  $(0.001 \text{ cm}^{-1})$ .

#### III. DESCRIPTION OF THE SPECTRA

Because of spin-orbit coupling, the  $B^3\Pi$  and  $X^3\Delta$  states of <sup>48</sup>Ti <sup>16</sup>O are split into three sub-states. Since the triplet splitting is much larger in the  $X^3\Delta$  state (101 cm<sup>-1</sup>) than in the  $B^3\Pi$  one (21 cm<sup>-1</sup>), a band consists in three distinct, case (a) allowed sub-bands labelled as  ${}^3\Pi_0 - {}^3\Delta_1$ ,  ${}^3\Pi_1 - {}^3\Delta_2$ , and  ${}^3\Pi_2 - {}^3\Delta_3$ . The  $\cdots$  (1 $\delta$ ) (4 $\pi$ )  ${}^1B^3\Pi$  state has such a small spin-orbit coupling because it is the difference between the one for 1 $\delta$  and for 4 $\pi$  electrons. As a consequence, the  $B^3\Pi$  state uncouples rapidly with increasing rotation to case (b), so that satellite branches ( $\Delta\Sigma$ =0) become allowed

Figure 1 shows a portion of the spectrum between 17 052.5 cm<sup>-1</sup> and 17 053 cm<sup>-1</sup>. It shows the band head of the  $R_{32f}$  satellite branch which occurs near J=29.

The branches are split into two components, noted as usually by (e) and (f),<sup>8</sup> as a result of  $\Lambda$  doubling in the  $B^3\Pi$  state. The  $\Lambda$ -doubling in the  $^3\Delta$  state was found negligible, even at the high resolution of the recorded spectra.

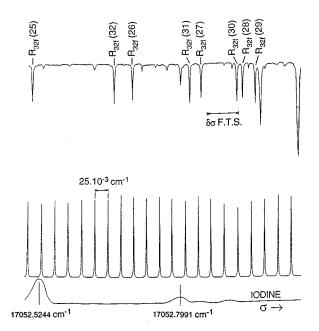


FIG. 1. Absorption spectrum of TiO between 17 052.5 cm<sup>-1</sup> and 17 053 cm<sup>-1</sup> (upper trace), with reference fringes  $25\times 10^{-3}$  cm<sup>-1</sup> apart (medium trace) and  $I_2$  absorption spectrum (lower trace). This section of the spectrum shows the band head of the  $R_{32}f$  branch, which occurs for  $J{=}29$ . The quantity noted  $\delta\sigma$  FTS represents the linewidth observed in the FTS measurements of Ref. 9. The label 1,2,3 is used in the B  $^3\Pi$  state to note the  $^3\Pi_{\Omega{=}0}$ ,  $^3\Pi_{\Omega{=}1}$ ,  $^3\Pi_{\Omega{=}2}$  sublevels and in X  $^3\Delta$  to indicate the  $^3\Delta_{\Omega{=}1}$ ,  $^3\Delta_{\Omega{=}2}$ ,  $^3\Delta_{\Omega{=}3}$  sublevels.  $R_{32}f(29)$  is written for the satellite line  $^3\Pi_{\Omega{=}2}(J'{=}30,f) \leftarrow ^3\Delta_{\Omega{=}2}(J''{=}29,f)$ .

Figure 2 shows directly the  $\Lambda$ -doubling in the  $B^3\Pi_2$  sublevel observed through the  $Q_3$  branches for  $J{=}26$  and through the  $P_3$  branches for  $J{=}10$ . In both figures, the quantity  $\delta\sigma$  FTS represents the linewidth of the spectrum recorded by Fourier transform spectroscopy<sup>9</sup> with Doppler-limited sources. These two spectra clearly show that the combination of sub-Doppler resolution and high signal to noise leads to detailed information about congested spectra.

#### IV. ENERGY MATRICES FITTING PROCEDURE

An effective Hamiltonian has been written using the  $\mathbb{R}^2$  formalism<sup>13,14</sup> where  $\mathbb{R}=J-L-S$  as

$$H_{\text{eff}} = H_{\text{rot}} + H_{\text{cd}} + H_{\text{so}} + H_{\text{cdso}} + H_{\text{sr}} + H_{\text{LD}} + H_{\text{cd}\Lambda D}$$
.

The five first terms are the rotational, centrifugal distortion, spin-orbit, centrifugal distortion of spin-orbit and spin-rotation components of the total Hamiltonian  $H_{\rm eff}$ . The last two terms are the  $\Lambda$ -doubling and its centrifugal distortion component. They have the following form: <sup>15</sup>

$$\begin{split} H_{\rm rot} &= B \mathbf{R}^2 \\ H_{\rm cd} &= -D \mathbf{R}^4 + H \mathbf{R}^6 \\ H_{\rm so} &= A L_z S_z + 2/3 \lambda (3 S_z^2 - \mathbf{S}^2) \\ H_{\rm cdso} &= 1/2 A_D [L_z S_z \,, \mathbf{R}^2]_+ + 1/3 \lambda_D [3 S_z^2 - \mathbf{S}^2, \mathbf{R}^2]_+ \\ &\quad + 1/2 A_H [L_z S_z \,, \mathbf{R}^4]_+ + 1/3 \, \lambda_H [S_z^2 - \mathbf{S}^2, \mathbf{R}^4]_+ \\ H_{\rm sr} &= \gamma \mathbf{R}. \mathbf{S} \end{split}$$

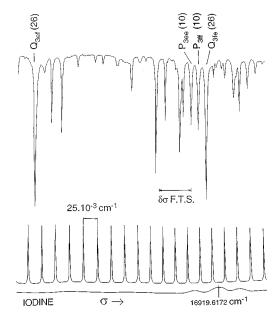


FIG. 2. Absorption spectrum of TiO around 16 919.5 cm<sup>-1</sup> (upper trace) with reference fringes and  $I_2$  absorption spectrum as in Fig. 1. This section of the spectrum shows the  $\Lambda$ -doubling observed in the  $Q_3$  branch for  $J{=}26$  and the  $\Lambda$ -doubling observed in the  $P_3$  branch for  $J{=}10$ . For main branches, only one subscript is used. For example  $P_{3ff}(10)$  means  ${}^3\Pi_{\Omega{=}2}(J'{=}9f) \leftarrow {}^3\Delta_{\Omega{=}3}(J''{=}10f)$ .

$$\begin{split} H_{\Lambda\mathrm{D}} &= 1/2(o+p+q)(S_{+}^{2}+S_{-}^{2}) - 1/2(p+2q) \\ &\times (J_{+}S_{+} + J_{-}S_{-}) + 1/2q(J_{+}^{2} + J_{-}^{2}) \\ H_{\mathrm{cd}\Lambda\mathrm{D}} &= 1/4D_{o+p+q}[S_{+}^{2} + S_{-}^{2}, \mathbf{R}^{2}]_{+} - 1/4D_{p+2q}[J_{+}S_{+} \\ &+ J_{-}S_{-}, \mathbf{R}^{2}]_{+} + 1/4D_{q}[J_{+}^{2} + J_{-}^{2}, \mathbf{R}^{2}]_{+} \\ &+ 1/4H_{o+p+q}[S_{+}^{2} + S_{-}^{2}, \mathbf{R}^{4}]_{+} - 1/4H_{p+2q}[J_{+}S_{+} \\ &+ J_{-}S_{-}, \mathbf{R}^{4}]_{+} + 1/4H_{q}[J_{+}^{2} + J_{-}^{2}, \mathbf{R}^{4}]_{+} \,. \end{split}$$

The symbol  $[x,y]_+$  is the anticommutator xy+yx which is necessary to preserve the Hermitian form of the matrices. The parameters in this effective Hamiltonian are

- (1) the rotational constant B with its first and second centrifugal distortion corrections D and H;
- (2) the first-order spin-orbit constant A, the second-order constant  $\lambda$  and the associated first and second centrifugal distortion corrections  $A_D$ ,  $A_H$  and  $\lambda_D$ ,  $\lambda_H$ ;
- (3) the spin-rotation constant  $\gamma$ ;
- (4) the lambda-doubling constants, introduced only for the  ${}^{3}\Pi$  electronic state, (o+p+q), (p+2q) and q with its first and second order centrifugal distortion corrections  $D_{o+p+q}$ ,  $H_{o+p+q}$ ,  $D_{p+2q}$ ,  $H_{p+2q}$  and  $D_{q}$ ,  $H_{q}$ .

Taking the usually negligible  $\Lambda$ -doubling in the  $X^3\Delta$  state into account and using a case (a) basis set ( $|\Lambda; S\Sigma; J\Omega\rangle$ ), one obtains the matrix representation of the Hamiltonian for parity-independent elements:

$$\begin{split} \langle \Lambda, \Sigma = 1, J | H | \Lambda, \Sigma = 1, J \rangle &= T + A\Lambda + 2/3 \ \lambda - \gamma + (B + A_D \Lambda) \\ &+ 2/3 \ \lambda_D)(x - \Lambda^2 - 2\Lambda) - D[x^2 + 2x - 2\Lambda x(\Lambda + 2)] \\ &+ 2\Lambda(\Lambda - 1) + \Lambda^3(\Lambda + 4)]; \end{split}$$

$$\begin{split} \langle \Lambda, \Sigma = 0, J | H | \Lambda, \Sigma = 0, J \rangle \\ &= T - 4/3 \ \lambda - 2 \ \gamma + (B - 4/3 \ \lambda_D)(x - \Lambda^2 + 2) \\ &- D[x^2 + 8x - 2\Lambda^2(x + 4) + \Lambda^4 + 4)]; \\ \langle \Lambda, \Sigma = -1, J | H | \Lambda, \Sigma = -1, J \rangle \\ &= T - A\Lambda + 2/3 \ \lambda - \gamma + (B - A_D\Lambda + 2/3 \ \lambda_D) \\ &\times (x - \Lambda^2 + 2\Lambda) - D[x(x + 2) - 2\Lambda x(\Lambda - 2) \\ &+ 2\Lambda(\Lambda + 1) + \Lambda^3(\Lambda - 4)]; \\ \langle \Lambda, \Sigma = 0, J | H | \Lambda, \Sigma = 1, J \rangle \\ &= T - \sqrt{2[x - \Lambda(\Lambda + 1)]}[B - 1/2\gamma + 1/2A_D\Lambda - 1/3\lambda_D - 2D(x - \Lambda - \Lambda^2 + 1)]; \\ \langle \Lambda, \Sigma = -1, J | H | \Lambda, \Sigma = 1, J \rangle \\ &= T - 2D\sqrt{(x - \Lambda^2 + \Lambda)(x - \Lambda^2 - \Lambda)}; \\ \langle \Lambda, \Sigma = 1, J | H | \Lambda, \Sigma = 0, J \rangle \\ &= T - \sqrt{2[x - \Lambda(\Lambda - 1)]}[B - 1/2 \ \gamma - 1/2 \ A_D\Lambda - 1/3 \ \lambda_D - 2D(x + \Lambda - \Lambda^2 + 1)]; \end{split}$$

The following higher order elements have been used for the  ${}^{3}\Pi$  state, together with the parity-dependent matrix elements: (These matrix elements are comparable with the ones indicated in Ref. 15, but the elements relative to the hyperfine structure have been removed. We are indebted to Professor Merer for indicating a misprint in Table II of Ref. 15.)

where x = J(J+1).

$$\begin{split} &\langle \Lambda, \Sigma = 1, J | H | \Lambda, \Sigma = 1, J \rangle \\ &= H(x^3 - 3x^2 + 5x - 7) + A_H(x^2 - 5x + 7) \\ &\quad + 2/3 \ \lambda_H(x^2 - 7x + 11) + H_q x(x - 2); \\ &\langle \Lambda, \Sigma = 0, J | H | \Lambda, \Sigma = 0, J \rangle \\ &= H(x^3 + 15x^2 - 5x + 5) - 2A_H \\ &\quad - 2/3 \ \lambda_H(2x^2 + 5x + 1) \pm x[1/2q + D_{p + 2q} \\ &\quad + 1/2 \ D_q(x + 1)] + 1/2H_q x(x^2 + 6x - 5) \\ &\quad + H_{p + 2q} 2x(x + 1) + 2xH_{o + p + q}; \\ &\langle \Lambda, \Sigma = -1, J | H | \Lambda, \Sigma = -1, J \rangle \\ &= H(x^3 + 9x^2 + 9x + 1) - A_H(x^2 + 3x + 1) \\ &\quad + 2/3\lambda_H(x^2 + x + 1) \pm [(o + p + q) + D_{o + p + q}(x + 1) \\ &\quad + D_{p + 2q} x] + H_q x(x - 1) + H_{p + 2q} 2x(x + 1) \\ &\quad + H_{o + p + q}(x^2 + 4x + 1); \\ &\langle \Lambda, \Sigma = 0, J | H | \Lambda, \Sigma = 1, J \rangle \\ &= -\sqrt{2(x - 2)} [H(3x^2 - 2x + 3) + A_H(x - 2) \\ &\quad - 2/3\lambda_H(x + 2) \pm x/2 \ D_q + 1/2 \ H_q x(2x - 1) \end{split}$$

 $+1/2 xH_{p+2q}$ ];

TABLE I. TiO molecular parameters (in cm<sup>-1</sup>). Number of data points: 1207, root mean square of the fit:  $0.0021~\rm cm^{-1}$ . The numbers in parentheses are the uncertainties (one standard deviation) in units of the last quoted decimal digit. \**T* value constrained to zero in the matrix elements of the  $X^3\Delta$  (v=0) level.

	$X^{3}\Delta (v=0)$		$B^{3}\Pi (v=1)$	
$\overline{T}$	[0]*		17 010.830 92	(15)
A	50.650 947	(89)	20.813 35	(23)
λ	1.747 21	(10)	-0.93034	(23)
$10^2 \gamma$			2.4896	(52)
B	0.533 808	1(25)	0.502 855	8(52)
$10^7 D$	6.0274	(52)	6.8954	(55)
$10^4 A_D$	-0.26473	(79)	-1.148	(26)
$10^6 \lambda_D$	0.49	(10)	-3.74	(64)
$10^{13} H$			0.77	(10)
$10^9 A_H$			-6.47	(14)
$10^9 \lambda_H$			-0.61	(15)
o+p+q			-0.59192	(25)
$10^2 (p+2q)$			2.671 70	(94)
$10^{3} q$			0.296 54	(34)
$10^6 D_{o+p+q}$			1.40	(41)
$10^{7} D_{n+2a}$			1.082	(32)
$10^{10} D_a$			-7.86	(87)
$10^{10} H_{o+p+q}$			5.6	(10)

$$\begin{split} \langle \Lambda, \Sigma &= -1, J | H | \Lambda, \Sigma &= 1, J \rangle \\ &= \sqrt{x(x-2)} [H(6x-2) - 2/3\lambda_H \\ &\pm [1/2 \ q + 1/2 \ D_q(x-1)] + 1/2 \ H_q x^2 \\ &+ H_{p+2q}(x+1) + H_{o+p+q})]; \\ \langle \Lambda, \Sigma &= -1, J | H | \Lambda, \Sigma &= 0, J \rangle \\ &= -\sqrt{2x} [H(3x^2 + 10x - 1) - A_H(x+1) - 2/3\lambda_H(x+1) \\ &\pm [(1/2 \ (p+2q) + 1/2 \ D_q(x-1) \\ &+ 1/2 \ D_{p+2q}(x+1) + D_{o+p+q}] + 1/2 \ H_q(2x^2 - 1) \\ &+ 1/2 \ H_{p+2q}(x^2 + 4x + 1) + 3/2 \ H_{o+p+q}(x+1)]. \end{split}$$

The other matrix elements are derived to keep the matrix symmetrical.

To interpret the experimental spectrum, the line frequencies were fitted to the differences between the eigenvalues of the Hamiltonian matrices constructed as shown above. An iterative nonlinear least-square procedure was employed with 1207 wave numbers, yielding a standard deviation of  $0.0021~\rm cm^{-1}$  to compare with the two older works<sup>8,9</sup> where standard deviations of  $5\times10^{-3}~\rm cm^{-1}$  and  $10\times10^{-3}~\rm cm^{-1}$  were, respectively, obtained. Both  $\gamma$  and  $A_D$  parameters were found necessary to correctly reproduce the wave numbers. The derived constants are indicated in Table I. Generally speaking, more than one order of magnitude has been gained in the determination of the lower order constants. The rotational term energy values are collected in the Appendix.

If the relative ordering e/f were changed, only the  $\Lambda$ -doubling parameters o+p+q, p+2q and q and their centrifugal distortions would have a different sign, the other parameters would not be modified.

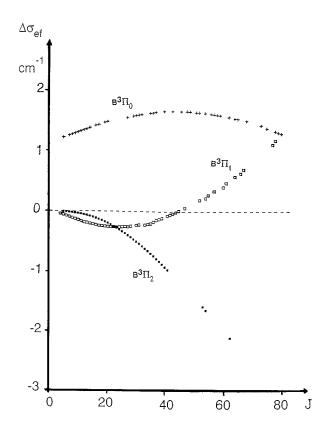


FIG. 3. Variation of the  $\Delta\sigma_{ef}$  quantity as a function of J in the B  $^3\Pi$  (v =1) level (experimental data).

#### V. $\Lambda$ -TYPE DOUBLING

As is well known,  $^8$  the absolute sign of the  $\Lambda$ -splitting would require a knowledge of the parity of the individual  $\Lambda$ -doublet components. This can be obtained experimentally, only through the observation of a transition involving a  $^{3}\Sigma$ state. As this is not the case in the present experiment, the notation (a) and (b) used by Merer et al.<sup>8</sup> has been kept, by setting (a) for the e parity and (b) for the f one. On the other hand, the relative signs of the  $\Lambda$ -doublet splittings can be determined. At high J, the coupling in the  ${}^{3}\Pi$  state transforms into case (b), then, the  $\Lambda$ -doubling in the  $B^{3}\Pi_{0}$  and  ${}^{3}\Pi_{2}$  substates becomes of the same magnitude, but its sign is opposite to that of the  ${}^{3}\Pi_{1}$  substate. Also, for small J, the sum of the  $\Lambda$ -doubling in  ${}^3\Pi_1$  and  ${}^3\Pi_0$  is constant. Using the above informations, it has been possible to plot the energy difference  $\Delta \sigma_{ef}$  between the e and f components for each of the three  $B^{3}\Pi$  substates, as a function of J (Fig. 3). In  ${}^{3}\Pi_{0}$ , this quantity is large at low J, grows toward a maximum near J=42 and then decreases. In  ${}^{3}\Pi_{2}$ , the  $\Lambda$ -doubling increases more rapidly with J than in  ${}^{3}\Pi_{0}$  and it never reverses. These variations are basically identical to those observed for lower J in the v = 0 level of the B state.<sup>8</sup>

In a recent paper, Balfour *et al.*<sup>15</sup> have compared the electronic structure of TiO with that of the isoelectronic molecule VN. A guessed energy level diagram showed that the lowest states of the  $(\delta)^2$  configuration have a  $^3\Sigma^-$  character at about 5000 cm $^{-1}$  and a  $^1\Sigma^+$  character at about 14 000 cm $^{-1}$ , both below the B  $^3\Pi$  state. As the  $\Lambda$ -doubling in the B  $^3\Pi_0$  component seems to be due mainly to spin—orbit interactions

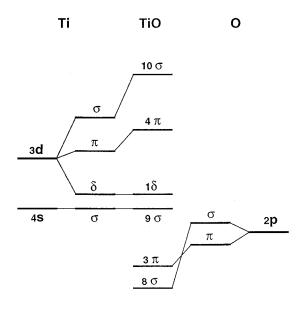


FIG. 4. The molecular orbital diagram of TiO (adapted from Ref. 6).

with the  $^3\Sigma_{0e}^-$  and  $^1\Sigma_e^+$  states (cf. Chap. VI), the B  $^3\Pi_{0e}$  component is shifted towards higher frequencies, leading to a positive  $\Delta\sigma_{ef}$  value, as represented in Fig. 3. Obviously, the spin–orbit interaction can occur with other electronic states arising from electron configurations such as  $\pi^2$ .

#### VI. DISCUSSION

The molecular orbital diagram of TiO, as reported by Merer, is shown in Fig. 4. The  $8\sigma$  and  $3\pi$  molecular orbitals (m.o.) are oxygen-based orbitals, slightly bonding combinations of O  $2p\sigma$  and O  $2p\pi$  atomic orbitals (a.o.) with Ti  $3d\sigma$  and Ti  $3d\pi$  a.o. respectively. The proportion of Ti 3d character is calculated to be about 15%. The  $9\sigma$  m.o. is essentially the Ti  $4\sigma$  a.o., while the  $4\pi$  m.o. is an antibonding combination of the Ti  $3d\pi$  and O  $2p\pi$  a.o., being largely Ti 3d in character. The  $(1\delta)$  m.o. is predicted to be essentially a pure Ti centered  $3d\delta$  a.o.

There have been two *ab initio* calculations on the low-lying electronic states of  $\text{TiO}^{16,17}$  indicating that the electron configuration giving rise to this  $X^3\Delta$  state is  $\cdots(8\sigma)^2 (3\pi)^4 (9\sigma)^1 (1\delta)^1$ . Based upon the intensity of the B-X system, it is most likely that the excited  $B^3\Pi$  electronic state configuration differs from that of the ground state, by the promotion of the  $9\sigma$  electron into a  $4\pi$  m.o., which is primarily a Ti centered  $3d\pi$  a.o. The primary configuration of the B state is then predicted to be mainly  $\cdots(8\sigma)^2 (3\pi)^4 (1\delta)^1 (4\pi)^1$ , although no population analysis of the orbitals was reported for this configuration. 17

In the following, the validity of the above mentioned electron configurations will be put into evidence by calculating the first-order spin-orbit constants, but it will be shown that the second-order spin-orbit and  $\Lambda$ -doubling parameters do not lead to a good agreement and that configuration mixing must be taken into account.

#### A. The first-order spin-orbit constants

Using the microscopic spin-orbit Hamiltonian  $H_{so} = \sum a_i$   $\mathbf{l_i.s_i}$  and a single configuration representation for the electronic states, it is possible to relate the observed spin-orbit parameters to the one-electron ones  $a_i$ .

In the absence of higher order effects, the spin-orbit intervals between the degenerate multiplet components are equal to  $A\Lambda$ . In the present study  $A\Lambda=101.30~{\rm cm}^{-1}$  for the X  $^3\Delta$   $(\Lambda=2)$  state and  $A\Lambda=20.81~{\rm cm}^{-1}$  for the B  $^3\Pi$   $(\Lambda=1)$  state (Table I). The wave functions for the X  $^3\Delta$   $\sigma^1$   $\delta^1$  and B  $^3\Pi$   $\delta^1$   $\pi^1$  electron configurations are  $|^3\Delta_{\Omega=3}\rangle=|\sigma\alpha\delta^+\alpha\rangle$  and  $|^3\Pi_{\Omega=2}\rangle=|\delta^+\alpha\pi^-\alpha|^{18}$  The diagonal matrix elements are then calculated as

$$\begin{split} &\langle {}^3\Delta_3|H_{\rm so}|{}^3\Delta_3\rangle = \hat{a}_{\delta},\\ &\langle {}^3\Pi_2|H_{\rm so}|{}^3\Pi_2\rangle = \hat{a}_{\delta} - (1/2)\hat{a}_{\pi}. \end{split}$$

The  $X^3\Delta$  state is well isolated, so that  $\hat{a}_{\delta} = A\Lambda = 101.302 \text{ cm}^{-1}$  to compare with the value 96 cm<sup>-1</sup> for the Ti<sup>+</sup> (3 $d^34s^1$ ) ion.<sup>6</sup>

In the  $B^3\Pi$  state, the separation for the  $\Omega=0$  and  $\Omega=2$  components is equal to  $2A-1/2(o+p+q)=\hat{a}_\delta-(1/2)\hat{a}_\pi$ . The numerical value of this quantity, based on the constants reported in Table I, is  $21.109~{\rm cm}^{-1}$  or  $20.517~{\rm cm}^{-1}$ , whether the quantity o+p+q is positive or negative. The parameter  $\hat{a}_\pi$  is then equal either to 160.386 or to  $161.570~{\rm cm}^{-1}$ , to be compared with  $156.70~{\rm cm}^{-1}$  for TiN.  $^{13}$ 

Thus, it is verified that the parameter  $\hat{a}_{\delta}$  is equivalent to the atomic  $\zeta 3d$  value, confirming that the electron configuration of the  $X^3\Delta$  state is  $\cdots (9\sigma)^1 \ (3d\delta)^1$ . Similarly, the values for  $\hat{a}_{\pi}$  in TiO and TiN indicate that the type of bonding occurring in the two molecules is almost the same, well described by the above mentioned configuration for the X state.

### B. The second-order spin-orbit constants

Equal splittings between the components of a multiplet state can occur only in the absence of higher-order spin-orbit effects or spin-spin interactions.

The principal higher-order spin-orbit effect in TiO results from the singlet-triplet interaction between states coming from the same electron configuration, the  $a^{-1}\Delta$  and  $X^{-3}\Delta$  states for the  $\sigma\delta$  configuration, or the  $(\delta\pi)^{-1}\Pi$  and  $B^{-3}\Pi$  states for the  $\delta\pi$  configuration.

In the first case  $(\sigma\delta)$  configuration, the central spin component of the triplet  $\Delta$  state, with  $\Omega=1$ , is shifted below its expected position by an amount  $2\lambda$ . The spin-orbit matrix element between the  $a^{-1}\Delta$  and  $X^{-3}\Delta$  states is calculated as  $-\hat{a}_{\delta}$ , 15 i.e., -101.3 cm<sup>-1</sup>. By use of the method of Balfour *et al.*, 15 the singlet-triplet separation  $\Delta E$  is represented by the expression:

$$\Delta E = 2\lambda + \hat{a}_{\delta}^2/2\lambda$$
.

With  $\lambda = 1.747~{\rm cm}^{-1}$  (Table I) and  $|\hat{a}_{\delta}| = 101.3~{\rm cm}^{-1}$ , one finds  $\Delta E = 2940.5~{\rm cm}^{-1}$ . The experimental value is about 3440 cm<sup>-1</sup>, indicating that some perturbation, in addition to the  $^{1}\Delta - ^{3}\Delta$  one, affects the ground state. In fact, the parameter  $\hat{a}_{\delta}$  should be increased by only 8% to correctly reproduce the observations.

A similar treatment carried out for the  $(\delta \pi)^{-1}\Pi - B^{-3}\Pi$  interaction gives a matrix element  $H_{12} = \langle {}^{1}\Pi|H_{\rm SO}|B^{-3}\Pi\rangle = -[(\hat{a}_{\delta} + 1/2(\hat{a}_{\pi})]]$  of about -181.7 cm<sup>-1</sup> (this value is, as expected, very close to the spin–orbit constant -173 cm<sup>-1</sup> of the  $A^{-3}\Phi$  state arising from the same  $\delta \pi$  configuration). The value for the mean energy of the  ${}^{3}\Pi_{2}$  and  ${}^{3}\Pi_{0f}$  components is

$$1/2[A + (2/3)\lambda - (A - (2/3)\lambda + o + p + q)]$$
  
= 1/2[(4/3)\lambda + o + p + q].

The difference of this mean energy with the energy of the  ${}^{3}\Pi_{1}$  component [equal to  $(4/3)\lambda$ ] is

$$s = 2\lambda + 1/2(o + p + q)$$
.

The quantity 1/2(o+p+q), which is equal to 0.296 cm<sup>-1</sup> in absolute value, is smaller than  $2\lambda = -1.86$  cm<sup>-1</sup>. So, whatever the sign of o+p+q, the quantity s is necessarily negative indicating that another interaction takes place between the B  $^3\Pi$  state and a new  $^1\Pi$  state located below the B  $^3\Pi$  state. The position of the two interacting electronic states is represented by the expression<sup>13</sup>

$$\Delta E = s + H_{12}^2/s$$
.

The derived  $\Delta E$  value, about  $-14\,000~{\rm cm}^{-1}$ , is clearly meaningless since no  ${}^{1}\Pi$  state of the same configuration is found below the B  ${}^{3}\Pi$  one. This fact indicates that perturbations are affecting the spin structure of the state. In particular the b  ${}^{1}\Pi$  state (of the  $9\sigma4\pi$  configuration) at  $14\,721~{\rm cm}^{-1}$  has some  $\delta\pi$  character. This will increase the energy of the central  ${}^{3}\Pi_{1}$  component of B  ${}^{3}\Pi$  and since the two states are close in energy, even a faint  $(\delta\pi)$  mixture will shift this state more than a pure  $(\delta\pi)$   ${}^{1}\Pi$  interaction. The small absolute value of  $\lambda$  is the result of two opposing tendencies, leading to difficult predictive values.

## C. The $\Lambda$ doubling

Generally speaking, in  ${}^3\Pi$  components the  $\Lambda$ -doubling results from rotational  $(B(R)J \cdot L \text{ from } B(R)R^2) \Pi \approx \Sigma$  interactions as well as through the spin-orbit operator and also through the  $S_x^2 - S_y^2$  part of the spin-spin operator.<sup>19</sup>

Following the method outlined by Balfour *et al.*, <sup>15</sup> the  $\Lambda$ -doubling in the B  $^3\Pi$  state must be due to the  $^1\Sigma^+$  and  $^3\Sigma^-$  states arising from electron configurations such as  $\pi^2$  and  $\delta^2$ . <sup>19</sup> For TiO, the states which are likely to contribute to the  $\Lambda$ -doubling are the  $^3\Sigma^-$  and  $^1\Sigma^+$  states arising from the configuration  $(1\delta)^2$ .

The interaction matrix elements are obtained as follows with the electronic wave functions for the  $\delta^2$  states:

$$\begin{split} &|\delta|^2, {}^1\Sigma^+\rangle = 1/2(|\delta^-\alpha\delta^+\beta| - |\delta^-\beta\delta^+\alpha|); \\ &|\delta|^2, {}^3\Sigma_0^-\rangle = 1/2(|\delta^-\alpha\delta^+\beta| + |\delta^-\beta\delta^+\alpha|); \\ &|\delta\pi, B^3\Pi_{0e}\rangle = 1/2(|\delta^+\beta\pi^-\beta| - |\delta^-\alpha\pi^+\alpha|). \end{split}$$

The following matrix elements for the spin-orbit operator are:

$$\langle \delta^{2} \, ^{1}\Sigma^{+} | H_{so} | B \, ^{3}\Pi_{0e} \rangle = -1/2 \langle \delta | \hat{a} | \delta \rangle 1 (1+1) - 2 = \hat{a}_{\delta};$$

$$\langle \delta^{2} \, ^{3}\Sigma_{0} \, ^{-} | H_{so} | B \, ^{3}\Pi_{0e} \rangle = 1/2 \langle \delta | \hat{a} | \delta \rangle 1 (1+1) - 2 = \hat{a}_{\delta};$$

TABLE II. See Appendix A.

	, par	222	P1 P	P19	mam	n1 n
		F2E	F1E	F3F	F2F	FIF
1 2			16991.4321 16993.3617			16990.2458 16992.1707
3	17035.8048	17018.5222	16996.2565	17035.8050	17018.5396	16995.0585
4						16998.9099
5		: 17027.4433 . 17033.3967				
7		17040.3476				
8		17048.2979				
9 10	17077.0432 17087.5776	17057.2491 17067.2028	17033.9309	17077.0582 17087 5988	17057.3546	17032.6535
11		17078.1603				
12	17111.7572	17090.1227	17065.8650	17111.7954	17090.2785	17064.5339
13 14		17103.0908 17117.0652				
15	17155.7629	17132.0465	17106.5734	17155.8383	17132.2460	17105.1866
16		17148.0349				
17 18		17165.0305 17183.0333				
19	17228.7806	17202.0432	17174.5573	17228.9279	17202.2834	17173.1000
		17222.0600				
21 22	17294.2352	17243.0832 17265,1125	17214.4430	17294.4521	17265.3679	17212.9537
23	17318.0814	17288.1475	17258.2678	17318.3244	17288.4051	17256.7489
24		17312.1877				
25 26		17337.2325 17363.2813				
27	17423.5714	17390.3337	17357.7559	17423.9317	17390.5860	17356.1863
28		17418.3889				
29 30		17447.4463 17477.5054				
31	17545.1748	17508.5653	17473.0531	17545.6716	17508.7918	17471.4438
32		17540.6256				
33 34		17573.6854 17607.7442				
35	17682.8261	17642.8011	17604.1726	17683.4764	17642.9833	17602.5345
36 37		17678.8556 17715.9068				
38		17753.9541				
39	17836.4650	17792.9967	17751.1124	17837.2845	17793.1182	17749.4560
40 41		17833.0338 17874.0648				
42	17962.1513	17916.0889	17871.6910	17963.1072	17916.1553	17870.0274
43	18006.0338	17959.1052	17913.8581	18007.0368	17959.1515	17912.1933
44 45		18003.1130 18048.1115	17957.0115	18051.9594	18003.1384	17955.3460 17999 4853
46	18143.6298	18094.0999	18046.2754	18144.7794	18094.0809	18044.6105
47		19141.0773				
48 49		18189.0429 18237.9960				
		18287.9355				
51	18392.7297	18338.8606	18286.6592	18394.1397	18338.7174	18285.0060
52 53		18390.7706 18443.6643				
54	18554.0122	18497.5410	18442.6750	18555.5877	18497.3144	18441.0357
55		18552.3997				
56 57		18608.2394 18665.0593	18551.5843	18668.1332	18664.7431	18549.9570
		18722.8583				
59		18781.6354				
60 61		18841.3897 18902.1201				
62	19027.2155	18963.8256	18901.7552	19029.2646	18963.3468	18900.1773
63		19026.5052				
64 65		19090.1578 19154.7822				
66	19287.2092	19220.3775	19154.6671	19289.5123	19219.7570	19153.1330
67		19286.9425				
		19354.4762 19422.9772				
70	19562.7025	19492.4446	19423.0781	19565.2706	19491.6726	19421.5964
71	19633.9889	19562.8771 19634.2735	19492.5947	19636.6250	19562.0657	19491.1274
73	19779.4487	19706.6327	19634.5169	19782.2228	19705.7408	19633.0801
74	19853.6197	19779.9535	19706.9201	19856.4638	19779.0204	19705.4994
75	19928.7497	19854.2345 19929.4746	19780.2833	19931.6645	19853.2597	19778.8792
77	20081,8817	20005.6724	19929.8848	20084.9399	20004.6125	19928.5153
78	20159.8810	20082.8268	20006.1205	20163.0120	20081.7234	20004.7692
		20160.9364 20239.9999				
		20320.0159				
82	20481.4032	20400.9832	20320.6018	20484.8317	20399.7003	20319.3283
		20482.9004 20565.7660				
85	20732.5073	20649.5788	20566.4417	20736.1660	20648.1553	20565.2320
		20734.3372				
87	20904,6329 20992.1083	20820.0399 20906.6855	20820.7947	20908.4484	20905.1165	20/33.9022
89	21080.5233	20994.2724	20907.4644	21084.4981	20992.6539	20906.3471
90	21169.8766	21082.7992	20995.0744	21173.9320	21081.1306	20993.9815
		21172.2644 21262.6665				
93	21443.5504	21354.0040	21263.5317	21447.8518	21352.1819	21262.5149
		21446.2753				
		21539.4790 21633.6134				
97	21821.4901	21728.6769	21634.5493	21826.1287	21726.6426	21633.6412
98	21918.2933	21824.6679 21921.5849	21729.6282	21923.0177	21822.5794	21728.7486
		21921.5849 22019.4261				

TABLE III. See Appendix B.

The color of the	TAB	LE III. See	Appendix I	3.
104,6354   7.3036   -96,9575   -93,7897   -93,7897   -89,5665   5 114,3435   12,6467   -84,2866   -84,2866   6 120,8154   19,0552   -77,9513   7 128,3656   26,5316   -70,5603   8 136,69940   35,0756   -62,1136   9 146,7005   44,6874   -52,6114   10 157,4849   55,3666   -42,0536   11 169,3470   67,1131   -30,4404   121,3976   108,7550   10,7305   12,275685   124,7691   26,5641   16 244,8158   141,8495   43,4525   17 263,1394   159,9660   61,3956   18 282,5389   179,2083   80,3931   19 303,0140   199,4663   100,4448   234,5454   232,8295   121,5506   21 347,1895   243,2377   143,7103   2370,8892   266,7106   66,9237   2370,8892   266,7106   66,9237   2370,8892   266,7106   66,9237   2370,8892   266,7106   66,9237   2370,8892   266,7106   66,9237   2370,8892   266,7106   66,9237   2370,8892   266,7106   66,9237   2370,8952   2478   191,1905   2448,4312   343,5139   242,8835   255,484,4312   343,5139   242,8835   256,895   30,6854   300,330   298,7873   28 535,6282   429,864   328,3175   326,66,8871   595,0754   331,539   358,8996   336,895   337 765,5595   666,8712   423,2181   363,24673   525,8172   339,5332   350,891,171   492,7790   390,5332   368,8334   762,3765   595,0754   491,7401   348,895   337 855,0122   746,3043   368,8334   776,5595   666,8712   566,8713   576,5790   386,8344   361,8325   706,9093   358,8996   378,550,122   746,3043   368,8344   378,8338   376,2376   595,0754   491,7401   378,895   377,5766   681,4167   399,77294   481,895   491,7401   378,895   377,5766   681,4167   399,77294   481,895   491,7401   391,895   391,7294   481,895   491,7401   391,895   3	J	F3	F2	F1
104,6354   7.3036   -96,9575   -93,7897   -93,7897   -89,5665   5 114,3435   12,6467   -84,2866   -84,2866   6 120,8154   19,0552   -77,9513   7 128,3656   26,5316   -70,5603   8 136,69940   35,0756   -62,1136   9 146,7005   44,6874   -52,6114   10 157,4849   55,3666   -42,0536   11 169,3470   67,1131   -30,4404   121,3976   108,7550   10,7305   12,275685   124,7691   26,5641   16 244,8158   141,8495   43,4525   17 263,1394   159,9660   61,3956   18 282,5389   179,2083   80,3931   19 303,0140   199,4663   100,4448   234,5454   232,8295   121,5506   21 347,1895   243,2377   143,7103   2370,8892   266,7106   66,9237   2370,8892   266,7106   66,9237   2370,8892   266,7106   66,9237   2370,8892   266,7106   66,9237   2370,8892   266,7106   66,9237   2370,8892   266,7106   66,9237   2370,8892   266,7106   66,9237   2370,8952   2478   191,1905   2448,4312   343,5139   242,8835   255,484,4312   343,5139   242,8835   256,895   30,6854   300,330   298,7873   28 535,6282   429,864   328,3175   326,66,8871   595,0754   331,539   358,8996   336,895   337 765,5595   666,8712   423,2181   363,24673   525,8172   339,5332   350,891,171   492,7790   390,5332   368,8334   762,3765   595,0754   491,7401   348,895   337 855,0122   746,3043   368,8334   776,5595   666,8712   566,8713   576,5790   386,8344   361,8325   706,9093   358,8996   378,550,122   746,3043   368,8344   378,8338   376,2376   595,0754   491,7401   378,895   377,5766   681,4167   399,77294   481,895   491,7401   378,895   377,5766   681,4167   399,77294   481,895   491,7401   391,895   391,7294   481,895   491,7401   391,895   3				-09 0604
3         104,6354         3.0336         -93,7897           4         108,9502         7.3061         -84,2866           5         114,3435         12,6467         -84,2866           6         120,8154         19,0552         -77,9563           7         128,3656         26,5316         -70,5603           8         136,7005         44,6874         -52,6114           10         157,4849         55,3666         -42,0336           11         169,3470         67,1131         -30,404           12         182,2867         79,9268         -17,7719           13         196,3306         93,8075         -4,0483           14         211,3976         108,7550         10,7305           15         227,5685         124,7691         26,5641           16         244,8158         141,895         34,3643           19         303,0140         199,4663         100,448           20         324,5643         220,8295         121,5506           21         347,1895         243,2377         143,7103           22         370,8962         266,7106         166,9237           3395,6630         291,2478         191,19	2			
5 114.3435 12.6467			3.0336	-93.7897
7 128.3656 26.5316 -70.5603 8 136.9940 35.0756 -62.1136 9 146.7005 44.6874 -52.6114 10 157.4849 55.3666 -42.0536 11 169.3470 67.1131 -30.4404 12 182.2867 79.9268 -17.7719 13 196.3036 93.8075 -4.0483 14 211.3976 108.7550 10.7305 15 227.5685 124.7691 26.5641 16 244.8158 141.8495 43.4525 17 263.1394 159.9960 61.3956 18 282.5389 179.2083 80.3931 19 303.0140 199.4863 100.4448 20 324.5643 220.8295 121.5506 21 347.1895 243.2377 143.7103 23 370.8892 2266.7106 166.9237 23 370.8892 2266.7106 166.9237 23 370.8892 2266.7106 166.9237 23 370.8892 2466.7106 166.9237 23 370.8992 246.7106 166.9237 23 575.4905 400.0330 299.7873 28 535.6282 429.8864 328.3175 29 566.8373 460.8019 358.8996 27 505.4905 400.0330 299.7873 28 535.6282 429.8864 328.3175 29 566.8871 492.7790 330.5332 31 632.4673 525.8172 432.32181 32 666.8871 559.9162 456.9538 33 702.3762 595.0754 491.7401 378.9338 631.2943 527.5766 36 815.2525 706.993 601.3986 37 855.0122 746.3043 641.3833 38 895.8381 786.7570 681.4167 39 937.7294 828.2667 722.4983 40 980.6854 870.8329 764.6276 41 1024.7055 914.4549 807.8043 41 115.9350 1004.8644 97.2976 41 1024.7055 914.4549 907.8043 42 1069.7890 959.1323 852.0277 43 1115.9352 1004.8644 97.2976 44 1163.1432 1051.6504 943.6133 48 1362.5790 1249.329 1139.3244 49 1415.0850 1301.3682 1199.8615 50 1468.6481 1354.4643 1243.4412 51 1523.2676 1408.6097 1297.0629 53 1635.6720 1520.0451 1407.4298 49 1415.0850 1301.3682 1199.8615 50 1468.6481 1354.4643 1243.4412 51 1523.2676 1408.6097 1297.0629 53 1635.6720 1520.0451 1407.4298 62 1293.5442 2073.2323 1955.4878 63 1293.3492 2276.3669 1293.0479 50 1468.6481 1354.4643 1243.4412 51 1523.2676 1408.6097 1297.0629 53 1635.6720 1520.0451 1407.4298 64 2293.3452 1379.3492 1399.3476 62 2193.4552 1577.3353 1464.1737 63 1293.4552 1577.3353 1464.1737 64 1227.3668 2139.9057 2021.5614 64 2480.9853 1481.9216 3054.6539 73 311.0553 3181.9216 3054.6539 73 3495.2688 3995.9554 3294.7663 74 3405.9859 4426.6074 3293.0306 74 3466.8861 3297.9553 2587.2640 74 3465.9855 4466.6618 3666 3366.662 74 3497.9906 3466.9373 3494.446		108.9502	12.6467	-89.5661
8 136.9940 35.0756 -62.1136 9 146.7005 44.6874 -52.6114 10 157.4849 55.3666 -42.0536 11 169.3470 67.1131 -30.4404 12 182.2867 79.9268 -17.7719 13 196.3036 93.8075 -4.0483 142.13976 108.7550 10.7305 15 227.5685 124.7691 26.5641 16 244.8158 141.8495 43.4525 17 263.1394 159.9960 61.3956 18 282.5389 179.2083 80.3931 193.03.0140 199.4863 100.4448 20 324.5643 220.8295 121.5506 21 347.1895 243.2377 243.7103 230.8952 266.7106 166.9237 23 3095.6630 291.2478 191.1905 244.215105 316.8490 216.5105 244.8312 343.5139 242.8835 266.7106 66.8237 25.5641 44.4312 343.5139 242.8835 266.646.4247 371.2420 270.3092 27 505.4905 400.0330 298.7873 28 535.6282 429.8864 228.3175 256.68373 460.8019 358.8996 30 599.1171 492.7790 390.5332 366.6867 3595.0754 491.7406 33 702.3762 595.0754 491.7406 33 702.3762 595.0754 491.7406 33 702.3762 595.0754 491.7406 33 702.3762 595.0754 491.7406 39 377.224 266.7506 681.5724 564.4629 36 815.2525 706.993 362.3986 37 855.0122 746.3043 641.3833 88 895.8381 786.7570 681.4167 39937.7294 428.6667 722.4983 40 980.6854 870.8329 764.6276 41 1024.7055 914.4549 807.8043 115.9352 1004.8644 897.2976 41 1024.7055 914.4549 807.8043 41 115.0850 1301.3682 1990.9743 41 163.1432 1051.6504 943.6133 45 1211.4124 1099.4899 990.9743 41 163.1432 1099.4899 990.9743 41 163.1432 1099.4899 990.9743 41 163.1432 1099.4899 990.9743 41 163.1432 1051.6504 943.6133 45 1211.4124 1099.4899 990.9743 41 163.1432 1075.66691 1521.9572 5158.4523 1635.6691 1521.9572 5158.4523 1635.6691 1521.9572 5158.8066 2468.7032 2488.8300 2364.6637 1293.6668 2666.0062 2561.7195 1393.4522 1578.3452 1393.4522 1579.3452 1393.4522 1578.3452 1393.4522 1579.3452 1393.4522 1579.3452 1393.4524 1393.4522	6	120.8154	19.0552	-77.9513
9 146.7005			26.5316	-70.5603
10 157.4849 55.3666 -22.0536 11 169.3470 67.1131 -30.4404 12 182.2867 79.9268 -17.7719 13 196.3036 93.8075 -4.0483 14 211.3976 108.7550 10.7305 15 227.5685 124.7691 26.5641 16 244.8158 141.8495 43.4525 17 263.1394 159.9960 61.3956 18 282.5389 179.2083 80.3931 9 303.0140 199.4863 100.4448 20 324.5643 220.8295 121.5506 21 347.1895 243.2377 143.7103 22 370.8892 266.7106 166.9237 23 395.6630 291.2478 191.1905 25 448.4312 343.5139 224.8835 24 421.5105 316.8490 216.5105 25 448.4312 343.5139 224.8835 26 476.4247 371.2420 270.3092 27 505.4905 400.0330 298.7873 28 535.6282 298.864 228.8175 29 566.8373 460.8019 338.8996 30 599.1171 492.7790 330.5332 1632.4673 525.8172 423.2181 32 666.8871 559.9162 456.9538 37 702.3762 595.0754 431.7401 38 895.8381 786.7570 681.4167 39 37.7294 828.2667 722.4983 40 980.6854 870.8329 764.6276 41 1024.7055 914.4549 807.8034 42 1069.7890 959.1323 852.0277 43 115.9352 1004.8644 877.2976 43 115.0850 1301.3662 190.9746 45 1211.4124 1099.4899 990.9743 45 1211.4124 1099.4899 990.9743 46 1260.7419 1148.3821 1039.3802 47 1311.1311 1198.3263 1088.8304 48 1362.5790 1249.3219 139.3244 49 1415.0850 1301.3662 1390.8715 51 1523.2676 1408.6097 1297.0629 52 1578.9425 1463.8035 1351.7259 53 1635.6720 1520.0451 1407.4298 1935.1071 1816.9404 1701.5374 62 2193.5442 2077.3232 199.9743 63 135.2172 1463.8035 1351.7259 64 1693.4552 1577.3335 1464.1737 65 1212.73647 2007.5961 1890.4478 64 229.0376 2207.6176 68 2612.5327 2488.800 2367.4064 68 2612.5327 2488.800 2367.4064 68 2612.5327 2488.800 2367.4064 68 2612.5327 2488.800 2367.4064 68 2612.5327 2488.800 2367.4064 68 2612.5327 2488.800 2367.4064 68 2612.5327 2488.800 2367.4064 68 2612.5327 2488.800 2367.4064 68 2612.5327 2488.800 2367.4064 69 2666.8671 2635.6661 1522.9509 77 3311.0553 3181.9216 3054.6539 78 393.1985.0711 1816.9404 1701.5374 69 2292.6483 2786.5795 2662.6030 73 290.2668 2668 2339.9057 2021.5614 68 2593.9374 2509.6663 3366.6622 69 273.1980 2466.6931 3472.2067 69 2686.0062 2561.7195 3289.6622 69 375.0008 4816.6424 477.9565 69 595.0008 4816.6424 477.9565		146.7005		-52.6114
14 211.3976 108.7550 10.7305 15 227.5685 124.7691 26.5641 16 244.8158 141.8495 43.4525 17 263.1394 159.9960 61.3956 18 282.5389 179.2083 80.3931 9 303.0140 199.4863 100.4448 20 324.5643 220.8295 121.5506 21 347.1895 243.2377 143.7103 22 370.8892 266.7106 166.9237 23 395.6630 291.2478 191.1905 25 448.4312 343.5139 242.8835 24 421.5105 316.8490 216.5105 25 448.4312 343.5139 242.8835 26 476.4247 371.2420 270.3092 27 505.4905 400.0330 298.7873 28 535.6282 429.8864 328.3175 29 566.8373 460.8019 338.8996 30 599.1171 492.7790 330.5332 26 666.8871 559.9162 456.9538 33 702.3762 595.0754 431.7401 32 370.8982 666.8871 559.9162 456.9538 33 702.3762 595.0754 431.7401 36 815.2525 766.9093 602.9986 36 855.0122 746.3043 661.3833 38 895.8381 786.7570 681.4167 39 937.7294 828.2667 722.4983 40 980.6854 870.8329 764.6276 41 1024.7055 914.4549 807.8043 42 1069.7890 959.1323 852.0277 43 1115.9352 1004.8644 877.2976 41 1024.7055 914.4549 807.8043 45 1211.4124 1099.4899 990.9743 41 1151.9352 1004.8644 877.2976 41 1624.7055 914.4549 807.8034 45 1211.4124 1099.4899 990.9743 46 1260.7419 1148.3821 1039.3802 47 1311.1311 1198.3263 1088.8304 48 1362.5790 1249.3219 139.3244 49 1415.0850 1301.3662 139.90.6712 51 578.9425 1463.8035 1351.7259 56 1812.1792 1695.0479 1580.7794 57 1998.1452 1879.4513 1763.4718 60 2062.2314 1943.0042 1826.4422 61 2273.5442 2073.2323 1955.4878 63 2260.7688 2139.9057 2021.5614 64 2299.0376 2276.6750 2266.6030 73 2990.2668 2665.733 2366.6622 81 373.5470 2077.5981 1890.4478 64 2299.0376 2277.6176 68 2612.2373.5442 2073.2323 1955.4878 60 2062.2314 1943.0042 1826.4422 61 2273.5442 2073.2323 1955.8878 63 323.666686 3139.9057 2021.5614 64 2299.0376 2276.6750 2296.1766 68 2686.0062 2561.7195 2439.6648 70 2760.5173 2635.6616 2512.9509 77 3311.0553 3181.9216 3054.6539 78 3393.8266 3264.0666 3156.2295 78 3393.8266 3264.0666 3156.2295 78 3393.8266 3264.0666 3156.2295 97 3475.6286 3295.9374 3383.2773 98 4756.9859 4426.0614 4676.2125 99 5160.1626 5017.8037 4876.5006 98 5263.2262 5120.1735 47978.1499 99 5476.2868 3997 4424.6071 4		157.4849	55.3666	-42.0536
14 211.3976 108.7550 10.7305 15 227.5685 124.7691 26.5641 16 244.8158 141.8495 43.4525 17 263.1394 159.9960 61.3956 18 282.5389 179.2083 80.3931 9 303.0140 199.4863 100.4448 20 324.5643 220.8295 121.5506 21 347.1895 243.2377 143.7103 22 370.8892 266.7106 166.9237 23 395.6630 291.2478 191.1905 25 448.4312 343.5139 242.8835 24 421.5105 316.8490 216.5105 25 448.4312 343.5139 242.8835 26 476.4247 371.2420 270.3092 27 505.4905 400.0330 298.7873 28 535.6282 429.8864 328.3175 29 566.8373 460.8019 338.8996 30 599.1171 492.7790 330.5332 26 666.8871 559.9162 456.9538 33 702.3762 595.0754 431.7401 32 370.8982 666.8871 559.9162 456.9538 33 702.3762 595.0754 431.7401 36 815.2525 766.9093 602.9986 36 855.0122 746.3043 661.3833 38 895.8381 786.7570 681.4167 39 937.7294 828.2667 722.4983 40 980.6854 870.8329 764.6276 41 1024.7055 914.4549 807.8043 42 1069.7890 959.1323 852.0277 43 1115.9352 1004.8644 877.2976 41 1024.7055 914.4549 807.8043 45 1211.4124 1099.4899 990.9743 41 1151.9352 1004.8644 877.2976 41 1624.7055 914.4549 807.8034 45 1211.4124 1099.4899 990.9743 46 1260.7419 1148.3821 1039.3802 47 1311.1311 1198.3263 1088.8304 48 1362.5790 1249.3219 139.3244 49 1415.0850 1301.3662 139.90.6712 51 578.9425 1463.8035 1351.7259 56 1812.1792 1695.0479 1580.7794 57 1998.1452 1879.4513 1763.4718 60 2062.2314 1943.0042 1826.4422 61 2273.5442 2073.2323 1955.4878 63 2260.7688 2139.9057 2021.5614 64 2299.0376 2276.6750 2266.6030 73 2990.2668 2665.733 2366.6622 81 373.5470 2077.5981 1890.4478 64 2299.0376 2277.6176 68 2612.2373.5442 2073.2323 1955.4878 60 2062.2314 1943.0042 1826.4422 61 2273.5442 2073.2323 1955.8878 63 323.666686 3139.9057 2021.5614 64 2299.0376 2276.6750 2296.1766 68 2686.0062 2561.7195 2439.6648 70 2760.5173 2635.6616 2512.9509 77 3311.0553 3181.9216 3054.6539 78 3393.8266 3264.0666 3156.2295 78 3393.8266 3264.0666 3156.2295 78 3393.8266 3264.0666 3156.2295 97 3475.6286 3295.9374 3383.2773 98 4756.9859 4426.0614 4676.2125 99 5160.1626 5017.8037 4876.5006 98 5263.2262 5120.1735 47978.1499 99 5476.2868 3997 4424.6071 4		169.3470	67.1131	-30.4404
14 211.3976 109.7550 10.7305 15 227.5685 124.7691 26.5641 16 244.8158 141.8495 43.4525 17 263.1394 159.9960 61.3956 18 282.5389 179.2083 80.3931 19 303.0140 199.4683 100.4448 20 324.5643 220.8295 121.5506 21 347.1895 243.2377 143.7103 22 370.8892 266.7106 166.9237 22 370.8892 266.7106 166.9237 24 421.5105 316.8490 216.5105 25 448.4312 343.5139 242.8835 26 476.4247 371.2420 270.3092 27 505.4905 400.0330 289.87873 28 535.6282 429.8864 328.3175 29 566.8373 460.8019 358.8996 30 599.1171 492.7790 339.5332 31 632.4673 525.8172 423.2181 32 666.8871 559.9162 365.6533 33 702.3762 595.0754 491.7401 34 738.9338 631.2943 527.5766 35 776.5595 668.5724 564.4629 36 815.2525 706.9093 602.3986 37 855.0122 746.3043 641.3833 38 895.8381 786.7570 681.4167 39 937.7294 828.2667 722.4983 40 980.6854 870.8329 764.6276 41 1024.7055 914.4549 807.8043 42 1069.7890 959.1323 852.0277 44 1163.1432 1051.6504 943.6133 45 1211.4124 1099.4899 990.9743 41 115.9352 1004.8644 897.2976 44 1163.1432 1051.6504 943.6133 45 1211.4124 1099.4899 990.9743 46 1260.7419 1148.3821 1039.3802 47 1311.1311 1198.3263 1088.8304 48 1362.5790 1249.3219 139.3244 49 1415.0850 1301.3682 1190.8615 50 1468.6481 1354.4643 123.4412 51 523.2676 1408.6097 1297.0629 52 1578.9425 1463.8035 1351.7259 53 1635.6720 1520.0451 1407.429 54 1693.4552 1577.3335 1464.1737 55 1752.2913 1635.6681 1521.9572 52 1578.9425 1463.8035 1351.7259 53 1635.6720 1520.0451 1407.397 57 1873.1182 1755.4723 1646.3537 57 1998.1452 1879.4513 1763.4718 60 2062.2314 1943.0042 1826.4422 2193.5442 2073.2323 1986.680 61 2249.3980 2374.6157 2225.9764 62 2293.5442 2073.2323 1980.47663 63 2240.7688 2139.9057 1580.7794 63 2250.7686 2666.795 2662.6030 73 393.8266 3264.0666 3136.1285 74 3311.9553 3161.9216 3394.7663 75 2398.3894 2276.3669 6262.6330 74 3068.9164 2941.6353 2866.662 62 488.7032 2396.6667 2225.9764 64 2462.8688 2399.957 9541 3924.7663 65 2398.3949 2766.6863 3136.1285 67 3479.9809 3779.341 3924.7663 67 2590.2658 866.666 3136.628 67 375.7896 5250.2073 4393.2773 67 3476.9809 3778.3775 3666.662 68 2612.53	13	196.3036	93.8075	-4.0483
16       244,8158       141,8495       43,4525         17       263,1394       159,9960       61,3956         18       282,5389       179,2083       80,3931         19       303,0140       199,4863       100,4448         20       324,5643       220,8295       121,5506         21       347,1895       243,2377       143,7103         23       395,6630       291,2478       191,1905         24       421,5105       316,8490       216,5105         25       448,4312       343,5139       242,8835         26       476,4247       371,2420       270,3092         27       505,4905       400,0330       298,7873         28       535,6282       429,8864       328,3175         29       566,8371       550,919       338,8996         30       599,1171       492,7790       390,5332         31       632,4673       525,8172       423,2181         34       738,9338       631,2943       527,5766         357,65595       668,5724       564,4629         36       815,2525       706,9093       662,3986         37,76,5595       668,574       36,813       895	14	211.3976	108.7550	10.7305
17         263.1394         159.9960         61.3956           18         282.5389         179.2003         80.3931           19         303.0140         199.4863         100.4448           20         324.5643         220.8295         121.5506           21         347.1895         243.2377         143.7103           22         370.8992         266.7106         166.9237           23         395.6630         291.2478         191.1905           24         421.5105         316.8490         216.5105           24         421.5105         316.8490         2270.3092           27         505.4905         400.0330         299.873           28         535.6282         429.8864         328.3175           29         566.8373         460.8019         358.8996           30         599.1171         492.7790         330.5332           31         632.4673         525.8172         426.5938           33         702.3762         595.0754         491.7401           34         738.9338         631.2943         527.5766           35         776.5595         668.5724         564.4629           36         815.2525		227.5685	124.7691	26.5641 43.4525
199 303.0140 199.4663 100.44468 20 324.5643 220.8295 121.5506 21 347.1895 243.2377 143.7103 22 370.8892 266.7106 166.9237 244 221.5105 316.8490 216.5105 25 448.4312 343.5139 242.8835 26 476.4247 371.2420 270.3092 27 505.4905 400.0330 289.87873 28 535.6282 429.8864 328.3175 28 535.6282 429.8864 328.3175 29 566.8373 460.8019 358.8996 30 599.1171 492.7790 390.5332 31 632.4673 525.8172 423.2181 32 666.8871 559.9162 365.6533 37 02.3762 595.0754 491.7401 34 738.9338 631.2943 527.5766 355.855.855 668.5724 566.5538 38 776.5595 668.5724 566.5538 38 895.8381 786.7570 661.3467 39 937.7294 828.2667 722.4983 40 980.6854 870.8329 746.6276 46.276		263.1394	159.9960	61.3956
20				
21 347.1895 243.2377 143.7103 22 370.8892 266.7106 166.9237 23 395.6630 291.2478 191.1905 25 448.4312 343.5139 242.8835 26 476.4247 371.2420 270.3092 27 505.4905 400.0330 298.7873 28 535.6282 429.8864 328.3175 29 566.8373 460.8019 338.8996 30 599.1171 492.7790 339.5332 31 632.4673 525.8172 423.2181 32 666.8871 559.9162 358.8996 33 702.3762 595.0754 491.7401 34 738.9338 631.2943 327.5766 35 776.5595 668.5724 564.4629 36 815.2525 706.9093 602.3986 37 7855.0122 746.3043 661.3833 38 895.8381 786.7570 681.4167 39 937.7294 828.2667 722.4983 38 895.8381 786.7570 681.4167 39 937.7294 828.2667 722.4983 41 1024.7055 914.4549 807.8043 42 1069.7890 959.1323 492.2027 41 1103.1432 1051.6504 493.6133 45 1211.4124 1099.4899 990.9743 41 1163.1432 1051.6504 493.6133 45 1211.4124 1099.4899 990.9743 46 1260.7419 1148.3821 1039.3802 47 1311.1311 1198.3263 1088.8304 48 1362.5790 1249.3219 1199.3244 49 1415.0850 1301.3682 1199.8615 50 1468.6481 1354.4643 1243.4412 51 1523.2676 1408.6097 1297.0629 52 1578.9425 1463.8035 1351.7259 53 1635.6720 1520.0451 1407.429 54 1693.4552 1577.3335 1464.1737 55 1752.2913 1635.6681 1521.9572 52 1578.9425 1463.8035 1351.7259 54 1693.4552 1577.3335 1464.1737 55 1752.2913 1635.6681 1521.9572 56 1612.1792 1695.0479 1580.7794 57 1873.1182 1755.4723 1640.6397 58 1935.1071 1816.9404 1701.5374 59 1998.1452 1879.4513 163.4718 60 2062.2314 1941.0042 186.4422 2193.5442 2073.2323 1955.4878 61 2249.3294 2276.3669 1656.8066 62 268.0062 2561.7195 2429.6648 70 2760.5173 2635.6616 512.9509 71 2836.0651 2710.5593 2862.6070 72 2912.6483 2786.5795 2662.6030 73 3110.5553 3161.9216 3386.6622 2373.51710 3602.8643 3472.2067 3477.6251 3347.2345 3328.6220 3735.1771 3602.8643 3422.2077 34 3068.9164 2941.6353 2816.3551 75 3148.5990 3020.7048 2894.7663 78 2292.6458 8263.5932 2739.9567 79 3311.0553 3161.9216 3398.2773 34 371.9803 3778.3775 3664.3389 37 377.9262 8698 397.9541 399.302.136 88 4277.8241 4141.841 4009.399.999 90 4466.8361 4329.2574 4193.0001 91 4562.8599 4466.6124 977.6269 9 5567.2896 5223.5406 5080.7748				
23 395.6630 291.2478 191.1905 24 421.5105 316.8490 216.5105 25 448.4312 343.5139 242.8835 26 476.4247 371.2420 270.3092 27 505.4905 400.0330 298.7873 28 535.6282 429.8864 238.3175 29 566.8373 460.8019 358.8996 30 599.1171 492.7790 390.5332 31 632.4673 525.8172 432.2181 32 666.8871 559.9162 456.9538 33 702.3762 595.0754 491.7401 34 738.9338 631.2943 527.5766 35 776.5595 668.5724 564.629 36 815.2525 706.993 602.3986 37 855.0122 746.3043 641.3833 38 895.8381 786.7570 681.4167 39 937.7294 828.2667 722.4983 30 895.8381 786.7570 681.4167 39 937.7294 828.2667 722.4983 40 980.6854 870.8329 764.6276 41 1024.7055 914.4549 807.8043 42 1069.7890 959.1232 852.0277 43 1115.9352 1004.8644 897.2976 44 1163.1432 1051.6504 493.6133 45 1211.4124 1099.4899 990.9743 45 1211.4124 1099.4899 990.9743 46 1260.7419 1148.3821 1039.3802 47 1311.1311 1198.3263 1088.8304 48 1362.5790 1249.3219 1393.3244 51 211.4124 1099.4899 979.9743 46 1260.7419 1148.3821 1039.3802 47 1311.1311 1198.3263 1088.8304 48 1362.5790 1249.3219 1393.2244 51 145.0850 1301.3682 1190.8615 50 1468.6481 1354.4663 1293.4412 51 1523.2676 1408.6097 1297.0629 52 1578.9425 1463.8035 1351.7259 53 1635.6720 1520.0451 1407.4298 54 1693.4552 1577.3335 1464.1737 556 1812.1792 1695.0479 1580.7794 57 1873.1182 1755.4723 1606.6397 59 1998.1452 1879.4513 1763.4718 60 2062.2314 1943.0042 1826.4422 61 2127.3647 2007.5981 1890.4478 62 2193.5442 2073.2323 1955.4878 66 2468.7032 2346.1527 2225.9764 67 2540.0980 2416.9740 2296.1766 68 2612.5327 2488.8300 2367.4064 69 2686.0062 2561.7195 2439.6648 70 2760.5173 2683.5646 2512.9509 71 2836.0651 2710.553 2887.2640 72 2912.6483 2786.5795 2662.6030 71 2836.0651 2710.5953 2887.2640 72 2912.6483 2786.5795 2662.6030 73 3110.9553 3181.9216 3356.122.9509 74 3068.9164 2941.6353 2816.3551 75 3148.5990 3020.7048 2894.7663 84 3711.9853 3161.9216 3354.6539 93 3477.6251 3347.2345 3328.6220 93 3479.6258 3937.9541 393.0031 94 4865.9859 3716.6692 4379.9910 94 4466.8361 3399.9577 2625.6766 95 2698.8039 3799.571 4299.6698 95 377.6698 3937 4924.6071 4297.6366 9		347.1895	243.2377	143.7103
24         421.5105         316.8490         216.5105           25         448.4312         371.2420         270.3092           27         505.4905         400.0330         288.3873           28         535.6282         429.8864         328.3175           29         566.8373         460.8019         338.8996           30         599.1171         492.7790         390.5332           31         632.4673         525.8172         423.2181           32         666.8871         559.9162         456.5538           33         702.3762         595.0754         491.7401           34         738.9338         631.2943         527.5766           35         776.5595         668.5724         564.4629           36         815.2525         706.9093         602.3986           37         855.0122         746.3043         641.3833           38         895.8381         786.7570         681.4167           39         37.7294         828.2667         722.4983           40         980.6854         870.8329         764.6276           41         1024.7055         914.4549         807.8043           42         1069.7890			266.7106	
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29         566.8373         460.8019         338.8996           30         599.1171         492.7790         390.5332           31         632.4673         525.8172         423.2181           32         666.8871         559.9162         436.5533           33         702.3762         595.0754         491.7401           34         738.9338         631.2943         527.5766           35         776.5595         668.5724         564.4629           36         815.2525         706.9093         602.3986           37         855.0122         746.3043         641.3833           38         895.8381         786.7570         681.4167           39         937.7294         828.2667         722.4983           40         980.6854         870.8329         764.6276           41         1024.7055         914.4549         807.8043           42         1069.7890         959.1323         852.0277           43         1115.9352         1004.8644         897.2976           44         1163.1432         1051.6504         943.6133           45         1211.4124         1099.4899         990.9743           45         1211.5			429.8864	328.3175
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32 666.8871 559.9162 456.9538 33 702.3762 595.0754 491.7401 34 738.9338 631.2943 527.5766 35 776.5595 668.5724 564.46293 36 815.2525 706.9093 602.3983 37 855.0122 746.3043 661.3833 38 895.8381 786.7570 661.4167 39 937.7294 828.2667 722.4983 40 980.6854 870.8329 764.6276 41 1024.7055 914.4549 807.8043 42 1069.7890 959.1323 852.0277 43 115.9352 1004.8644 897.2976 44 1163.1432 1051.6504 943.6133 45 1211.4124 1099.4899 990.9743 45 1260.7419 1148.3221 1039.3802 47 1311.1311 1198.3263 1088.8304 48 1362.5790 1249.3219 1139.3244 49 1415.0850 1301.3662 1190.8615 50 1468.6481 1354.4643 1243.4412 51 1523.2676 1408.6097 1297.0629 52 1578.9425 1463.8035 1351.7259 53 1635.6720 1520.0451 1407.4298 54 1693.4552 1577.3335 1464.1737 55 1752.2913 1635.6681 1521.9572 56 1812.1792 1695.0479 1580.7794 57 1873.1182 1755.4723 1640.6397 58 1935.1071 1816.9404 1701.5374 60 2062.2314 1943.0042 1626.4422 61 2127.3647 2007.5981 1890.4742 62 2193.5442 2073.2323 1955.4878 63 2260.7688 2139.9057 2021.5614 64 2229.0376 2207.6176 2088.6680 65 2398.3494 2276.3669 1266.4226 67 2540.0980 2416.9740 2296.1766 68 2612.5327 2488.8300 2367.4064 68 2612.5327 2488.8300 2367.4064 68 2612.5327 2488.8300 2367.4064 68 2612.5327 2488.8300 2367.4064 68 2612.5327 2488.8300 2367.4064 68 2612.5327 2488.8300 2367.4064 68 2612.5327 2488.8300 2367.4064 68 2612.5327 2488.8300 2367.4064 68 2612.5327 2488.8300 2367.4064 69 2886.0062 2561.7195 2439.6648 70 2760.5173 2635.6416 512.9509 77 3311.0553 3181.9216 3054.6539 78 3393.8266 3264.0666 3366.622 83 735.1710 3602.8643 3472.2067 83 393.8266 3264.0666 336.622 84 3735.1710 3602.8643 3472.2067 83 393.8266 3264.0666 3366.622 84 3735.1710 3602.8643 3472.2067 83 393.8266 3264.0666 3366.622 84 3735.1710 3602.8643 3472.2067 83 393.8266 3264.0667 3366.622 84 3735.1710 3602.8643 3472.2067 83 393.8266 3264.0666 3366.622 84 3735.1710 3602.8643 3472.2067 83 393.8266 3264.0666 3366.622 84 3735.1710 3602.8643 3472.2067 83 393.8266 3264.0666 3366.622 84 3735.1710 3602.8643 3472.2067 85 306.8668 3264 3477.9264 4499.9369 94 4466.8361 43		599.1171	492.7790	390.5332
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36 815.2525 706.9093 602.3986 37 855.0122 746.3043 661.3833 38 895.8381 786.7570 661.4163 39 937.7294 828.2667 722.4983 40 980.6854 870.8329 764.6276 41 1024.7055 914.4549 807.8043 42 1069.7899 959.1323 852.0277 43 1115.9352 1004.8644 897.2976 44 1163.1432 1051.6504 943.6133 45 1211.4124 1099.4899 990.9743 46 1260.7419 1148.3221 1039.3802 47 1311.1311 1198.3263 1088.8304 48 1362.5790 1249.3219 1139.3244 49 1415.0850 1301.3662 1190.8615 50 1468.6481 1354.4643 123.4412 51 1523.2676 1408.6097 1237.0625 52 1578.9425 1463.8035 1351.7259 53 1635.6720 1520.0451 1407.4298 54 1693.4552 1577.3335 1464.1737 55 1752.2913 1635.6681 1521.9572 56 1812.1792 1695.0479 1580.7794 57 1873.1182 1755.4723 1640.6397 58 1935.1071 1816.9404 1701.5374 60 2062.2314 1943.0042 1826.4422 61 2127.3647 2007.5981 1890.4427 61 2127.3647 2007.5981 1890.4427 62 2193.5442 2073.2323 1955.4878 63 2260.7688 2139.9057 2021.5614 64 2229.0376 2207.6176 2088.6680 65 2398.3494 2276.3669 2156.8066 66 2468.7032 2374.61527 2225.9764 67 2540.0980 2416.9740 2296.1766 68 2612.5327 2488.8300 2367.4064 68 2612.5327 2488.8300 2367.4064 68 2612.5327 2488.8300 2367.4064 68 2612.5327 2488.8300 2367.4064 68 2612.5327 2488.8300 2367.4064 68 2612.5327 2488.6300	33	702.3762	595.0754	491.7401
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42 1069,7890 959,1323 852.0277 43 1115,9352 1004.8644 897.2976 44 1163.1432 1051.6504 943.6133 45 1211.4124 1099,4899 990.9743 46 1260,7419 1148.3221 1039.3802 47 1311.1311 1198.3263 1088.8304 48 1362.5790 1249.3219 1139.3204 49 1415.0850 1301.3662 1190.8615 50 1468.6481 1354.4643 1243.4412 51 1523.2676 1408.6097 1297.0629 52 1578.9425 1463.8035 1351.7259 53 1635.6720 1520.0451 1407.4298 54 1693.4552 1577.3335 1464.1737 55 1752.2913 1635.6681 1521.9572 56 1812.1792 1695.0479 1580.7794 57 1873.1182 1755.4723 1640.6397 1873.1182 1755.4723 1640.6397 58 1935.1071 1816.9404 1701.5374 60 2062.2314 1943.0042 1626.4422 61 2127.3647 2007.5981 1899.4478 62 2193.5442 2073.2323 1955.4878 63 2260.7688 2139.9057 2021.5614 64 2329.0376 2207.6176 2088.6680 65 2398.3949 2276.3669 1265.80668 66 2468.7032 2346.1527 2225.9766 67 2540.0980 2416.9740 2296.1766 68 2612.5327 2488.8300 2367.4064 69 2686.0062 2561.7195 2439.6648 70 2760.5173 2635.6416 512.9509 71 2836.0651 2710.5953 2587.2640 67 2590.2658 2863.5932 2738.9670 72 2912.6483 2786.5795 2662.6030 73 2990.2658 2863.5932 2738.9670 74 3036.9164 2941.6353 2816.3551 75 3148.5990 3020.7048 2894.7663 83 3393.8266 3264.0666 3136.1285 76 3129.3123 3100.8006 2974.1995 77 3311.0553 3181.9216 3354.6523 80 3562.4495 3431.4242 3302.1336 81 3648.2985 3516.6346 3322.1336 83 393.8266 3264.0666 3136.1285 79 3477.6251 3347.2345 3328.6220 80 3562.4495 3431.4242 3302.1336 81 3648.2985 3516.6346 3386.6622 82 3735.1710 3602.8643 3472.2067 83 393.8266 3264.0666 3136.1285 79 3477.6251 3347.2345 3328.6220 80 3562.4495 3431.4242 3302.1336 81 3648.2985 3516.6346 3326.3537 83 393.8266 3264.0666 3136.1285 93 3471.8237 3244.1607 392.1286 84 371.9808 3778.3775 3646.3389 85 4001.9157 3867.6585 3734.9244 89 4371.8237 4234.9160 4099.3692 90 4466.8361 4329.2574 4193.0001 91 4562.8599 4424.6071. 4297.6366 92 4659.8937 4520.9637 4383.2773 93 4757.6361 4324.2617 93 4765.986 9377 4306.4466.2125 90 5368.1003 9416.4327 4775.865 95 5495.2062 5223.5406 5080.7748	40	980.6854	870.8329	764.6276
43 1115.9352 1004.8644 97.2976 44 1163.1432 1099.4899 990.9743 45 1211.4124 1099.4899 990.9743 46 1260.7419 1148.3821 1099.3809 47 1311.1311 1196.3263 1088.8304 48 1362.5790 1249.3219 1139.3244 49 1415.0850 1301.3682 1190.8615 50 1468.6481 1354.4643 1243.4412 51 1523.2676 1408.6097 1297.0629 52 1578.9425 1463.8035 1351.725 53 1635.6720 1520.0451 1407.4298 54 1693.4552 1577.3335 1464.1737 55 1752.2913 1635.6681 1521.9572 56 1812.1792 1695.0479 1580.7794 57 1873.1182 1755.4723 1640.6397 57 1873.1182 1755.4723 1640.6397 58 1935.1071 1816.9404 1701.5374 59 1998.1452 1879.4513 1763.4718 60 2062.2314 1943.0042 1826.4422 61 2127.3647 2007.5981 1899.4478 62 2193.5442 2073.2323 1955.4878 63 2260.7688 2139.9057 2021.5614 64 2329.0376 2207.6176 2088.6680 65 2398.3494 2276.3669 2156.8066 65 2468.7032 2346.1527 2225.9764 67 2540.0980 2416.9740 2296.1766 68 2612.5327 2488.8300 2367.4064 69 2686.0062 2561.7195 2439.6648 70 2760.5173 2635.66116 2512.9509 71 2836.0651 2710.5953 2587.2640 72 2912.6483 2786.5795 2662.6037 73 301.0553 3181.9216 3794.7663 73 2990.2658 8263.5932 2738.9670 74 3068.9164 2941.6353 2816.3551 73 348.5990 3020.7048 2894.7663 78 393.8266 2964.0666 3136.1285 79 3477.6251 3347.2345 3218.6220 80 3562.4495 3311.0553 3181.9216 3154.2563 81 3648.2985 3516.6346 3386.6622 82 3735.1710 3602.8643 3472.2067 83 3932.3655 3690.1124 3558.7660 84 277.8241 4141.5941 4006.7449 84 371.8237 4234.9160 4099.3692 94 4466.8361 4329.2574 4993.0001 91 4562.8599 4424.6071 4287.6366 84 277.8241 4141.5941 4006.7449 84 371.8237 4234.9160 4099.3692 94 4466.8361 4329.2574 4993.0001 91 4562.8599 4424.6071 4287.6366 92 4659.8937 4520.9637 4393.2773 93 4757.9360 4618.3260 4479.9210 90 4466.8361 4329.2574 4993.0001 91 4562.8599 4424.6071 4287.6366 92 4659.8937 4520.9637 4393.2773 93 4757.9360 4618.3260 4479.9210 90 4466.8361 4329.2574 4993.0001 91 4562.8599 4424.6071 4287.6366 92 4659.8937 4520.9637 4393.2773 93 4757.9360 4618.3260 479.9210 90 4466.8361 4329.2574 4993.3001 91 4562.8599 4716.6624 4577.5665 95 5958.1003 4916.4327 4775.8576 97		1024.7055	914.4549	807.8043
44 1163.1432 1051.6504 943.6133 45 1211.4124 1099.4899 990.9743 46 1260.7419 1148.3821 1039.3802 47 1311.1311 1198.3263 1088.8304 48 1362.5790 1249.3219 1139.3244 49 1415.0850 1301.3682 1199.8615 50 1468.6481 1354.4643 1243.4412 51 1523.2676 1408.6097 1297.0629 52 1578.9425 1463.8035 1351.7259 53 1635.6720 1520.0451 1407.4298 54 1693.4552 1577.3335 1464.1737 55 1752.2913 1635.6681 1521.9572 56 1812.1792 1695.0479 1580.7794 57 1873.1182 1755.4723 1640.6397 58 1935.1071 1816.9404 1701.5374 59 1998.1452 1879.4513 1763.4718 60 2062.2314 1943.0042 1826.4422 61 2127.3647 2007.5981 1890.4478 62 2193.5442 2073.2323 1955.4878 63 2260.7688 2139.9057 64 2329.0376 2207.6176 2088.6680 65 2398.3494 2276.3669 2156.8066 66 2468.7032 2346.1527 2225.9764 67 2540.0980 2416.9740 2296.1766 68 2612.5327 2488.8300 2367.4064 69 2686.0662 2561.7195 2439.6648 70 2760.5173 2635.6616 512.9509 71 2836.0651 2710.5953 2587.2640 69 2686.0662 2561.7195 2439.6648 70 2760.5173 2635.6616 522.9509 71 2836.0651 2710.5953 2587.2640 69 2686.0662 2561.7195 2439.6648 70 2760.5173 2635.6616 512.9509 71 2836.0651 2710.5953 2587.2640 69 2686.0662 2561.735 28439.6648 70 2760.5173 2635.6616 512.9509 71 2836.0651 3710.5953 2587.2640 69 2686.0662 2561.735 2439.6648 73 2299.3123 3100.8006 2974.1995 73 3118.0553 3181.9216 3054.6539 73 3793.8266 3264.0666 3136.1285 79 3477.6251 3347.2345 3218.6220 80 3562.4495 3431.4242 3302.1336 81 3648.2985 3516.6346 3386.6622 82 3735.1710 3602.8643 3472.2067 83 3823.0655 3690.1124 3558.7660 84 4277.8241 4141.5841 4006.7449 89 4371.8237 4234.9160 4099.3692 90 4466.8361 4329.2574 4193.0001 91 4562.8599 4424.6071 4287.6366 92 4659.8937 4520.9637 4393.2773 93 4757.9360 4618.3260 4479.9210 94 4465.8959 4716.6624 4577.5665 95 5058.1003 4916.4327 4775.8576 97 5160.1626 5017.8037 4876.5006 98 5267.2266 5122.1735 6978.1748		1115.9352		
46 1260.7419 11446.3821 1039.3802 47 1311.1311 1198.3263 1088.8304 48 1362.5790 1249.3219 1139.3244 49 1415.0850 1301.3682 1190.8615 50 1466.6481 1354.4643 1243.4412 51 1523.2676 1408.6097 1297.0629 52 1578.9425 1463.8035 1351.7259 53 1635.6720 1520.0451 1407.4298 54 1693.4552 1577.3335 1464.1737 55 1752.2913 1635.6681 1521.9572 56 1812.1792 1695.0479 1580.7794 57 1873.1182 1755.4723 1640.6397 58 1935.1071 1816.9404 1701.5374 59 1998.1452 1879.4513 1763.4718 60 2062.2314 1943.0042 1826.4422 61 2127.3647 2007.5981 1890.4478 62 22193.5442 2073.2323 1955.4878 62 262.2314 1943.0042 1826.4622 66 2468.7032 2346.1527 2225.9764 67 2240.0980 2416.9740 2896.1766 68 2612.5327 2488.8300 2367.4064 69 2686.0062 2561.7195 2439.6648 70 2760.5173 2635.6616 2512.9509 71 2836.0651 2710.5953 2587.2640 72 2912.6483 2786.5795 2662.6030 72 2912.6483 2786.5795 2662.6030 73 2990.2658 2863.5932 2738.9670 74 3068.9164 2941.6353 2816.3551 75 3148.5990 3020.7048 2894.7663 76 3229.3123 3100.8006 2974.1995 77 3311.0553 3181.9216 3154.6529 78 3477.6251 3347.2345 3218.6220 80 3562.4495 3314.2423 3302.1336 81 3648.2985 3516.6346 3336.6622 82 3735.1710 3602.8643 3472.2067 88 4277.8241 4141.5941 4006.7449 89 4371.8237 4234.9160 4999.3692 90 4466.8361 4329.2574 4193.0001 91 4562.8599 4424.6071 4287.6366 92 4659.8937 4520.9637 4393.2773 93 4757.9360 4618.3260 4479.9210 90 4466.8361 4329.2574 4193.0001 91 4562.8599 4424.6071 4287.6366 92 4659.8937 4520.9637 4393.2773 93 4757.9360 4618.3260 4479.9210 90 4466.8361 4329.2574 4193.0001 91 4562.8599 4424.6071 4287.6366 92 4659.8937 4520.9637 4393.2773 93 4757.9360 4618.3260 4479.9210 94 4466.8361 4329.2574 4193.0001 94 4465.8959 4716.6652 4577.5665 95 5058.1003 9416.4227 4775.8576 97 5160.1626 5017.8037 4876.5006	44	1163.1432	1051.6504	943.6133
48 1362.5790 1249.3219 1139.3244 49 1415.0850 1301.3682 1190.8615 50 1468.6481 1354.4643 1243.4412 51 1523.2676 1408.6097 1297.0629 52 1578.9425 1463.8095 1351.7259 53 1635.6720 1520.0451 1407.4298 54 1693.4552 1577.3335 1464.1737 55 1752.2913 1635.6681 1521.9572 56 1812.1792 1695.0479 1580.7794 57 1873.1182 1755.4723 1640.6397 58 1935.1071 1816.9404 1701.5374 59 1998.1452 1879.4513 1763.4718 60 2062.2314 1943.0042 1826.4422 61 2127.3647 2007.5981 1890.4478 62 2193.5442 2073.2323 1955.4878 63 2260.7688 2139.9057 2021.5614 64 2229.0376 2207.6176 2088.6680 65 2398.3494 2276.3669 2156.8066 66 2468.7032 2346.1527 2225.9766 67 2540.0980 2416.9740 2296.1766 68 2612.5327 2488.8300 2367.4064 69 2686.0062 2361.7195 2439.6648 70 2760.5173 2635.6416 512.9509 71 2936.6651 2710.5953 2587.2640 72 2912.6483 2786.5795 2662.6030 73 2990.2658 2863.5932 2738.9670 74 3068.9164 2941.6353 2816.3551 75 3148.5990 3020.7048 2894.7663 78 3393.8266 3264.0666 3366.622 87 3735.1710 3602.8643 3472.2067 83 3393.8266 3264.0666 3366.622 82 3735.1710 3602.8643 3472.2067 83 3491.9808 3778.3775 3646.3389 85 4001.9157 3867.6595 3734.9244 86 4092.8688 3957.9541 3824.5214 87 4184.8387 4049.2630 3915.1286 88 4277.9241 4141.5841 406.7449 89 4371.8237 4234.9160 4099.3692 90 4466.8361 4329.2574 4193.0001 91 4562.8599 4424.6071 4287.6366 92 4659.8937 4520.9637 4383.2773 93 477.6251 3347.2345 3228.6220 90 4466.8361 4329.2574 4193.0001 91 4562.8599 4424.6071 4287.6366 92 4659.8937 4520.9637 4383.2773 93 477.6251 3347.2345 3228.6220 90 4466.8361 4329.2574 4193.0001 91 4562.8599 4424.6071 4287.6366 92 4659.8937 4520.9637 4383.2773 93 4757.9360 4618.3260 4479.9210 90 4465.8596 4424.6071 4287.6366 95 5605.800.7748 4816.6018 4676.2125 97 5160.1626 5017.8037 4876.5006 98 5267.2266 5120.1735 4978.1007.748		1211.4124		990.9743
48 1362.5790 1249.3219 1139.3244 49 1415.0850 1301.3682 1190.8615 50 1468.6481 1354.4643 1243.4412 51 1523.2676 1408.6097 1297.0629 52 1578.9425 1463.8035 1351.725 53 1635.6720 1520.0451 1407.4298 54 1693.4552 1577.3335 1464.1737 55 1752.2913 1635.6681 1521.9572 56 1812.1792 1695.0479 1580.7794 57 1873.1182 1755.4723 1640.6397 58 1935.1071 1816.9404 1701.5374 59 1998.1452 1879.4513 163.4718 60 2062.2314 1943.0042 1826.4422 61 2127.3647 2007.5981 1899.4478 62 2219.35442 2073.2323 1955.4878 62 222.3346 1297.3232 1955.4878 63 2260.7688 2139.9057 2021.5614 64 2329.0376 2207.6176 2088.6680 65 2398.3494 2276.3669 2156.8066 66 2468.7032 2346.1527 2225.9764 67 2540.0980 2416.9740 2296.1766 68 2612.5327 2488.8300 2367.4064 69 2686.0062 2561.7195 2439.6648 70 2760.5173 2635.6416 2512.9509 71 2836.0651 2710.5953 2587.2640 72 2912.6483 2786.5795 2662.6037 73 2990.2658 2863.5932 2738.9670 74 3068.9164 2941.6353 2816.3551 75 3148.5990 3020.7048 2894.7663 76 3229.3123 3100.8006 2974.1995 77 3311.0553 3181.9216 3054.6539 78 3937.8266 2264.0666 3136.1285 79 3477.6251 3347.2345 3218.6220 80 3562.4495 3431.4242 3302.1336 81 3648.2985 3516.6346 3386.6622 82 3735.1710 3602.8643 3472.2067 83 3923.0655 3690.1124 3558.7660 84 277.8241 4141.5941 4006.7449 84 371.8237 4234.9160 4099.3692 94 466.8361 4329.2574 4193.0001 94 4866.8961 4241.6561 4479.9210 90 4466.8361 4329.2574 4193.0001 91 4562.8599 4424.6071 4287.6366 92 4659.8937 4243.6071 4287.6366 92 4659.8937 4243.6071 4287.6366 92 4659.8937 4243.6071 4287.6366 92 4659.8937 4243.6071 4287.6366 92 4659.8937 4243.6071 4287.6366 92 4659.8937 4243.6071 4287.6366 92 4659.8937 4243.6071 4287.6366 92 4659.8937 4246.6071 4287.6366 92 4659.8937 4246.6071 4287.6366 92 4659.8937 4246.6071 4287.6366 92 4659.8937 4246.6071 4287.6366 92 4659.8937 4243.6071 4287.6366 92 4659.8937 4243.6071 4287.6366 93 5260.2265 5120.1735 4978.8100				
50         1468.6481         1354.4643         1243.4412           51         1523.2676         1408.6097         1297.0629           52         1578.9425         1463.8035         1351.7259           53         1635.6720         1520.0451         1407.4298           54         1693.4552         1577.3335         1464.1737           55         1752.2913         1635.6681         1521.9572           56         1812.1792         1695.0479         1580.7794           57         1873.1182         1755.4723         1640.6397           58         1935.1071         1816.9404         1701.5374           60         2062.2314         1943.0042         1826.4422           61         2127.3647         2007.5981         1890.4478           62         2193.5442         2073.2323         1955.878           63         2260.7688         2139.9057         2021.5614           64         2329.0376         2207.6176         2088.6680           65         2398.3494         2276.3669         2156.8066           66         2468.7032         2346.1527         2225.9764           67         2540.0980         2416.9740         2296.1766      <	48	1362.5790	1249.3219	1139.3244
51         1523.2676         1408.6097         1297.0629           52         1578.9425         1463.8035         1351.7259           53         1635.6720         1520.0451         1407.4298           54         1693.4552         1577.3335         1464.1737           55         1752.2913         1635.6681         1521.9572           56         1812.1792         1695.0479         1580.7794           57         1873.1182         1755.4723         1640.6337           58         1935.1071         1816.9404         1701.5374           59         1998.1452         1879.4513         1763.4718           60         2062.2314         1943.0042         1826.4422           61         2127.3647         2007.5981         1890.4478           62         2293.3764         2073.2323         1955.4878           63         2260.7688         2139.9057         2021.5614           64         2329.0376         2207.6176         2088.6680           65         2398.3494         2276.3669         2156.8066           62         2468.7032         2346.1527         2225.9764           63         2260.5617.32         2488.8300         2367.4064				
52         1578.9425         1463.8035         1351.7259           53         1635.6720         1520.0451         1407.4298           54         1693.4552         1577.3355         1464.1737           55         1752.2913         1635.6681         1521.9572           56         1812.1792         1695.0479         1580.7794           57         1873.1182         1755.4723         1640.6397           58         1935.1071         1816.9404         1701.5374           60         2062.2314         1943.0042         1826.4422           61         2127.3647         2007.5981         1890.4478           62         2123.5442         2073.2323         1955.4878           63         2260.7688         2139.9057         2021.5614           64         2229.0376         2207.6176         2088.6680           65         2398.3494         2276.3669         2156.8066           66         2468.7032         2346.1527         2225.976           67         2540.0980         2416.9740         2295.1766           68         2612.5327         2488.8300         2367.4064           70         2760.5173         2635.6416         2512.9509      <				
54         1693.4552         1577.3335         1464.1737           55         1752.2913         1635.6681         1521.9572           56         1812.1792         1695.0479         1580.7794           57         1873.1182         1755.4723         1640.6397           58         1935.1071         1816.9404         1701.5374           59         1998.1452         1879.4513         1763.4718           60         2062.2314         1943.0042         1826.4422           61         2127.3647         2007.5981         1890.4478           62         2293.5442         2073.2323         1855.4878           63         2260.7688         2139.9057         2021.5614           64         2329.0376         2207.6176         2088.6800           65         2398.3494         2276.3669         2156.8066           66         2468.7032         2346.1527         2225.9764           67         2540.0980         2416.9740         2296.1766           68         2612.5327         2488.8300         2367.4064           69         2686.0062         2561.7195         2439.6648           70         2760.5173         2635.6416         2512.9509	52	1578.9425	1463.8035	1351.7259
55         1752.2913         1635.6681         1521.9572           56         1812.1792         1695.0479         1580.7794           57         1873.1182         1755.4723         1640.6397           58         1935.1071         1816.9404         1701.5374           59         1998.1452         1879.4513         1763.4718           60         2062.2314         1943.0042         1826.4422           61         2127.3647         2007.5918         1899.4478           62         2193.5442         2073.2323         1955.4878           63         2260.7688         2139.9057         2021.5614           64         2239.0376         2207.6176         2088.6680           65         2398.3494         2276.3669         2156.8066           66         2468.7032         2346.1527         2225.9764           67         2540.0980         2416.9740         2296.1766           68         2612.5327         2488.8300         2677.4066           72         2636.051         2710.5953         2587.2640           72         2912.6483         2786.5795         2626.6030           71         2836.0551         2710.5953         2587.2640      <			1520.0451	1407.4298
56         1812.1792         1695.0479         1580.7794           57         1873.1182         1755.4723         1640.6397           58         1935.1071         1816.9404         1701.5374           59         1998.1452         1879.4513         1673.4718           60         2062.2314         1943.0042         1826.4422           61         2127.3647         2007.5981         1899.4478           62         2193.5442         2073.2323         1955.4878           63         2260.7688         2139.9057         2021.5614           64         2329.0376         2207.6176         2008.6680           65         2398.3494         2276.3669         2156.8066           66         2468.7032         2346.1527         2225.9764           67         2540.0980         2416.9740         2296.1766           68         2612.5327         2488.8300         2367.4064           69         2686.0062         2561.7195         2439.6648           70         2760.5173         2635.6416         2512.9509           71         2836.0651         2710.5953         2587.2640           72         2912.6483         2786.5795         2662.6030				
58         1995.1071         1816.9404         1701.5374           59         1998.1452         1879.4513         1763.4718           60         2062.2314         1943.0042         1826.4422           61         2127.3647         2007.5981         1890.4478           62         2193.5442         2073.2323         1995.4878           63         2260.7688         2139.9057         2021.5614           64         2329.0376         2207.6176         2088.6680           65         2398.3494         2276.3669         2156.8066           66         2468.7032         2346.1527         2225.9764           67         2540.0980         2416.9740         2296.1766           68         2612.5327         2488.8300         2367.4064           69         2686.0062         2561.7195         2439.6648           70         2760.5173         2635.6416         2512.9509           71         2816.0651         2710.5953         2587.2640           72         2912.6483         2786.5795         2662.6030           73         2990.2658         2863.5932         2738.9670           74         3068.9164         2941.6353         2816.5355	56	1812.1792	1695.0479	1580.7794
59         1998.1452         1879.4513         1763.4718           60         2062.2314         1943.0042         1826.4422           61         2127.3647         2007.5981         1890.4478           62         2193.5442         2073.2323         1855.4878           63         2260.7688         2139.9057         2021.5614           64         2329.0376         2207.6176         2088.6680           65         2398.3494         2276.3669         2156.8066           66         2468.7032         2346.1527         2225.9764           67         2540.0980         2416.9740         2296.1766           68         2612.5327         2488.8300         2367.4064           69         2686.0062         2561.7195         2439.6648           70         2760.5173         2635.6416         2512.9509           71         2836.0651         2710.5953         2887.2640           72         2912.6483         2786.5795         2662.6030           73         2990.2658         2863.5992         2738.9676           73         2299.1664         2941.6353         2816.3551           75         3148.5990         3020.7048         2894.7663				
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99 5367.2896 5223.5406 5080.7748		5160.1626	5017.8037	4876.5006

$$\langle \delta^2 {}^1\Sigma^+|H_{so}|B {}^3\Pi_{0e}\rangle = 2\hat{a}_{\delta},$$

where it is supposed that the  $\delta$  electron is a pure Ti 3d (with l=2).

If spin-spin interactions are neglected (see their magnitude on Table I), the observed level structure is obtained by diagonalizing the following  $3\times3$  matrix

$$\begin{pmatrix} |^1\Sigma^+\rangle^0 & |^3\Sigma^-_0\rangle^0 & |^3\Pi_{0e}\rangle^0 \\ E^0(^1\Sigma^+) & 2\hat{a}_\delta & -\hat{a}_\delta \\ & E^0(^3\Sigma^-_0) & \hat{a}_\delta \\ \text{Symmetrical} & T-A+2/3\lambda+(o+p+q) \end{pmatrix},$$

where the superscript 0 indicates a nonperturbed quantity. The diagonalization gives the calculated values

$$\begin{vmatrix} |1\Sigma^{+}\rangle & |3\Sigma^{-}_{0}\rangle & |3\Pi_{0e}\rangle \\ E(1\Sigma^{+}) & 0 & 0 \\ E(3\Sigma^{-}_{0}) & 0 \\ Symmetrical & T-A+2/3\lambda-(o+p+q) \end{vmatrix}$$

Unfortunately, the positions of the  $^1\Sigma^+$  and  $^3\Sigma^-$  states of TiO have not been determined but only roughly evaluated in Ref. 13 as  $E(^1\Sigma^+)=14\,000\,\,\mathrm{cm}^{-1}$  and  $E(^3\Sigma^-_{~0})=5000\,\,\mathrm{cm}^{-1}$ . The diagonalization is possible only if the matrix element  $\langle \delta^2,\ ^1\Sigma^+|H_{so}|\delta^2,^3\Sigma^-\rangle$  is different from the two matrix elements involving  $\langle \delta^{1,3}\Sigma|H_{so}|\delta^2$   $B^3\Pi\rangle$ . Keeping  $\langle \delta^2,\ ^1\Sigma^+|H_{so}|\delta^2,\ ^3\Sigma^-\rangle=2\hat{a}_\delta=202.6\,\,\mathrm{cm}^{-1}$  and taking the integrals involving the  $B^3\Pi_{0e}$  level in terms of a new variable parameter  $\hat{a}'_{~\delta}$ , one obtains an iterative solution correctly reproducing the  $^3\Pi_0$  positions if

$$\hat{a}'_{\delta} = 53.8 \text{ cm}^{-1}$$
.

This value is about half the expected one, i.e.,  $101.3 \text{ cm}^{-1}$ . This effect, much weaker than in VN, <sup>15</sup> is ascribed to the fact that the  $4\pi$  m.o. is a mixture of Ti  $(3d\pi)$  and O  $(2p\pi)$ . Balfour *et al.* <sup>15</sup> have shown, by analogy with the NbN molecule, that the configuration mixing would put some  $\sigma^2$  <sup>1</sup> $\Sigma^+$  character into the  $\delta^2$  <sup>1</sup> $\Sigma^+$  state, leading to a reduction of  $\hat{a}_{\delta}$ , but this parameter remains much greater than  $\hat{a}'_{\delta}$ .

Obviously the  $\Lambda$  doubling interpretation in the TiO  $B^3\Pi$  state needs more reliable *ab initio* calculations and also experimental observation of the  $^1\Sigma^+$ ,  $^3\Sigma^-$  electronic states and of the  $^1\Pi$  state arising from the  $(1\,\delta^2)$  and from the  $(1\,\delta)^1$   $(1\pi)^1$  configurations respectively.

#### VII. CONCLUSION

Owing to the high resolution and to the high signal to noise obtained in the experiment, it has been possible to achieve a detailed analysis of the rotational structure of the B  ${}^3\Pi - X$   ${}^3\Delta$  (1,0) band of TiO. A set of 24 molecular parameters has been derived. The first-order spin-orbit constants have been interpreted in terms of the electron configurations giving rise to these electronic states.

The  $X^3\Delta$  state is well represented by the ... $(8\sigma)^2 (3\pi)^4 (9\sigma)^1 (1\delta)^1$  electron configuration in which the  $9\sigma^1$  m.o. is mainly Ti 4s and the  $1\delta^1$  is a pure Ti 3d orbital.

The  $B^3\Pi$  state is partly ... $(8\sigma)^2 (3\pi)^4 (1\delta)^1 (4\pi)^1$ , where the antibonding  $4\pi$  orbital is mainly Ti 3d. The isoconfigurational spin-orbit interaction, partly reproduces the position of the  $a^1\Delta$  state but fails totally for the  $^1\Pi$  companions of  $B^3\Pi$ . Moreover the  $\Lambda$  doubling in the  $B^3\Pi$  component is not at all explained by the spin-orbit interactions with the states arising from the  $\delta^2$  configuration. Clearly, new *ab initio* calculations are necessary to reproduce the observed the TiO spectrum.

#### **ACKNOWLEDGMENT**

C.A. is grateful to Professor Anthony J. Merer (University of British Columbia, Canada) for a fruitful correspondence about matrix elements in triplet states and TiO problems.

## APPENDIX A: RELATIVE TERM VALUES (IN cm<sup>-1</sup>) FOR THE TIO $B^{3}\Pi$ (v=1) LEVEL (TABLE II)

F1 is written for  $\Omega$ =0, F2 for  $\Omega$ =1, and F3 for  $\Omega$ =2 spin-orbit sublevels.

# APPENDIX B: RELATIVE TERM VALUES (IN cm<sup>-1</sup>) FOR THE TIO $X^3\Delta$ (v=0) LEVEL (TABLE III)

F1 is written for  $\Omega$ =1, F2 for  $\Omega$ =2, and F3 for  $\Omega$ =3 spin-orbit sublevels. See the text for the origin of energies.

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