



3 August 2001

**CHEMICAL
PHYSICS
LETTERS**

Chemical Physics Letters 343 (2001) 437–445

www.elsevier.com/locate/cplett

The $X^3\Sigma^-$ ground state of WO

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Received 25 February 2001; in final form 10 May 2001

Abstract

The WO molecule was formed as an impurity during the excitation of a mixture of WCl_6 vapor and He in a microwave discharge lamp. The emission spectra were recorded using a high-resolution Fourier transform spectrometer. A rotational analysis of the strong bands in the 9000–25 000 cm^{-1} interval has been carried out and the bands have been classified into two groups with different lower states. The two lower states have been assigned as the $\Omega = 0^+$ and $\Omega = 1$ spin components of the $X^3\Sigma^-$ ground state. Ab initio calculations have also been performed and they confirm our experimental assignments. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Considerable progress has been made in recent years towards understanding the electronic structure of transition metal-containing molecules [1,2], in spite of the intrinsic complexity of their spectra. The transition metal atoms involved in these molecules typically have open d-shells, which result in many low-lying electronic states with high multiplicities. Strong spin–orbit interactions limit the validity of the usual Hund’s case (a) quantum numbers, and the electronic states have a tendency towards Hund’s case (c) coupling. In such cases the subbands of a given electronic transition can be far apart and this creates a problem in the electronic assignments. WO is a typical example and, until our experiment and theoretical work,

even its ground state was not known with certainty.

The low-resolution arc spectra of WO were first recorded in the 1950s and some bands were tentatively classified into four to six transitions [3–5]. The WO bands were also observed using a shock wave discharge source [6] and some additional bands were found but the spectra remained largely unclassified. The Ne and Ar matrix isolation spectra of WO (and some other tungsten oxides) were observed in 1965 by Weltner and McLeod [7]. The bands were classified into several transitions which were labeled using letters ranging from A to G. The absorption spectra of WO have also been investigated by Samoilova et al. [8] who maintained the letter notation proposed by Weltner and McLeod [7], and also observed some new bands. Samoilova et al. [8] obtained a rotational analysis of a number of bands in the visible and provided the first rotational constants for WO. This work was closely followed by the infrared matrix isolation study of Green and Ervin [9] who measured

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the ground-state vibrational frequency of WO in Ar and Kr matrices. The ground-state vibrational constants obtained in this work were consistent with those obtained by Samoilova et al. [8] in the gas phase. Kuzyakov et al. [10,11] carried out an intracavity electronic absorption study of WO, and more recently laser-induced fluorescence measurements in solid neon were reported by Lorenz et al. [12,13]. Kuzyakov et al. [10,11] obtained a rotational analysis of some additional bands and revised the vibrational assignments in the A–X transition while Lorenz et al. [12,13] extended emission observations into the infrared in a neon matrix. The most recent paper on WO is a rotational analysis of the 0–0 band of the F–X transition by cavity ringdown laser absorption spectroscopy [14]. In spite of these numerous studies, the nature of the ground state of WO is still in question. Weltner and McLeod [7] proposed a $^3\Sigma^-$ ground state while Nelin and Bauschlicher [15] predicted a $^5\Pi$ ground state from SCF and CASSCF calculations.

In the present work we have observed the emission spectra of WO in the 9000–25 000 cm^{-1} interval at high resolution. The observed bands have been classified into two groups with different lower states. The two lower states have been assigned as the $\Omega = 0^+$ and 1 spin components of the $X^3\Sigma^-$ ground state of WO. Ab initio calculations have also been performed on low-lying electronic states of WO. The results are consistent with our $X^3\Sigma^-$ ground-state assignment.

2. Experimental

The emission bands of WO were produced in an electrodeless microwave discharge through the flowing mixture of WCl_6 and He, without adding any O_2 . Presumably, WO formed as an impurity in the plasma from reactions with traces of H_2O and O_2 . The initial aim of this experiment was to search for WCl emission bands, which were not seen. The discharge tube was made of quartz and had an outside diameter of 12 mm. The emission from the lamp was sent directly into the entrance aperture of the 1-m Fourier transform spectrometer associated with the McMath–Pierce telescope

of the National Solar Observatory. The spectrometer was equipped with a UV beam splitter and silicon photodiode detectors. The spectra were recorded in two parts, 9000–19 000 and 17 000–35 000 cm^{-1} . For the 9000–19 000 cm^{-1} region, OG530 red pass filters were used and the spectra were recorded at 0.02 cm^{-1} resolution by coadding six scans in one hour of integration. The 17 000–35 000 cm^{-1} region was recorded using a CuSO_4 filter and coadding six scans at 0.03 cm^{-1} resolution. Attempts were also made to record improved spectra of WN, which was studied earlier by us using a hollow cathode lamp [16]. WN was produced by adding a trace of N_2 to the flow of WCl_6 and He. The WN bands were observed strongly, although some WO bands were also present. This spectrum was very helpful in obtaining the wavenumber calibration for the WO lines by transferring the calibration from WN lines [16], which were calibrated by using the Ne line measurements of Palmer and Engleman [17]. The WO bands were also recorded using the Bruker IFS 120 HR Fourier transform spectrometer at Waterloo, but the present analysis was made using the Kitt Peak data.

The spectral line positions were extracted from the observed spectra using a data reduction program called PC-DECOMP. The peak positions were determined by fitting a Voigt line shape function to each spectral feature. The strongest WO lines have typical signal-to-noise ratios of 30:1. The structure of most bands is complex because of resolved (or partly resolved) structure from the four main isotopomers, ^{182}WO , ^{183}WO , ^{184}WO and ^{186}WO . The uncertainty of measurements is expected to vary from ± 0.002 to ± 0.004 cm^{-1} depending upon the signal-to-noise ratio, extent of blending and line broadening.

3. Observation and analysis

Most of the bands observed by Samoilova et al. [8] in the 16 000–25 000 cm^{-1} interval are also present in our spectra. The higher wavenumber bands ($>25 000$ cm^{-1}) were not observed in our spectra either because of their weaker intensity or because of the cut-off of the filter used in our ex-

periment. The rotational analysis of most of the strong bands has been completed although a few weaker bands still remain to be analyzed. In this Letter we will deal mainly with the analysis of the 0–0 bands of the different transitions, which has allowed us to draw a definite conclusion about the nature of the ground state. Another paper describing a more complete analysis of all the transitions and the results of a more complete set of ab initio calculations will be published elsewhere in the near future.

Our analysis shows that most of the bands can be classified into two groups on the basis of their lower-state rotational constants. A schematic diagram of the observed transitions is provided in Fig. 1. Another group of bands observed in the 9000–10 300 cm^{-1} region have quite different upper- and lower-state constants than the two lower states mentioned previously. These bands probably belong to a quintet–quintet transition and spectra of WO in the 5000–10 000 cm^{-1} region will be recorded in order to complete their analysis.

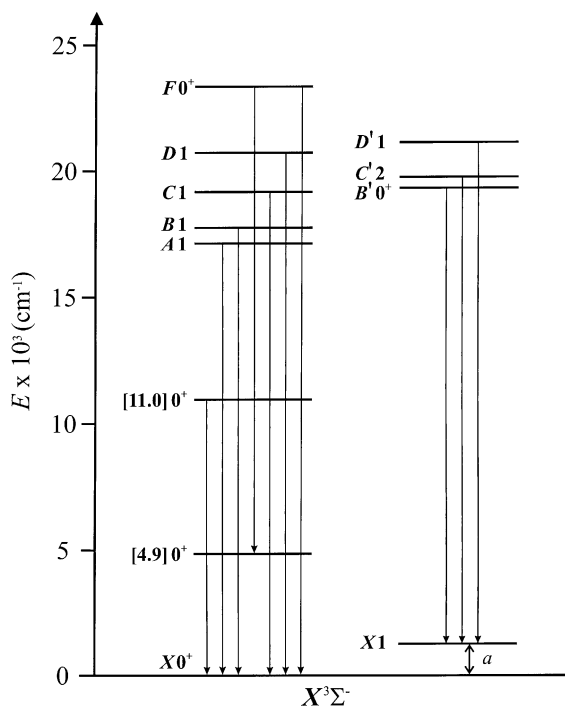


Fig. 1. An schematic energy level diagram of the observed transitions of WO.

The first group consists of seven transitions out of which six have a common lower state. The lines in these bands show no doubling and the common lower state behaves like a $^1\Sigma^+$ or a $\Omega = 0^+$ state. We have labeled this state as $X0^+$ state. The transitions with this common lower state have their band origins near 10 965 cm^{-1} ($[11.0]0^+ - X0^+$), 17 165 cm^{-1} ($A1 - X0^+$), 17 241 cm^{-1} ($B1 - X0^+$), 19 182 cm^{-1} ($C1 - X0^+$), 20 793 cm^{-1} ($D1 - X0^+$) and 23 401 cm^{-1} ($F0^+ - X0^+$). These transitions were observed by the relaxed laser-induced fluorescence measurements of Lorenz et al. [12,13] and the matrix isolation absorption experiment of Weltner and McLeod [7] except the transition at 10 965 cm^{-1} , which was not observed by Weltner and McLeod [7]. This suggests that the common lower state of these transitions is certainly the ground state of WO.

The W atom has four main isotopes ^{182}W (26.3%), ^{183}W (14.3%), ^{184}W (30.7%) and ^{186}W (28.6%) and we have concentrated only on the analysis of the most abundant ^{184}WO isotopomer. The rotational assignment in these bands was straight forward using combination differences for the common electronic states. The rotational constants were determined by fitting simultaneously the lines in each group of bands to the customary energy level expressions:

$$F_v(J) = T_v + B_v J(J+1) - D_v [J(J+1)]^2 + H_v [J(J+1)]^3, \quad (1)$$

$$F_v(J) = T_v + B_v J(J+1) - D_v [J(J+1)]^2 + H_v [J(J+1)]^3 + L_v [J(J+1)]^4 \pm 1/2 \{ qJ(J+1) + q_D [J(J+1)]^2 + q_H [J(J+1)]^3 + q_L [J(J+1)]^4 \} \quad (2)$$

for $\Omega = 0$ states (Eq. (1)) and $\Omega = 1$ states (Eq. (2)).

The constants obtained for ^{184}WO are summarized in Table 1. The common lower state of the transitions in the first group has a rotational constant of $B''_0 = 0.4155285(73) \text{ cm}^{-1}$ and has been assigned as the $\Omega = 0^+$ state ($X0^+$). Another transition near 18 490 cm^{-1} with $\Delta\Omega = 0$ has its upper state in common with the $F0^+ - X0^+$ transition. This places the lower $\Omega = 0^+$ state of this

Table 1
Spectroscopic constants (in cm^{-1}) for the observed states of WO

State	T_0	B_0	$10^6 \times D_0$	$10^{10} \times H_0$	$10^{15} \times L_0$	$10^3 \times q_0$	$10^6 \times q_{D0}$	$10^{10} \times q_{F0}$	$10^{15} \times q_{I0}$
<i>Group I</i>									
F0 ⁺	23401.0960(33)	0.383870(16)	0.418(14)	0.514(34)	—	—	—	—	—
D1	20793.8669(10)	0.3888987(77)	0.2394(23)	-0.0140(17)	—	-0.2464(23)	-0.0207(16)	0.0272(26)	—
C1	19182.4711(20)	0.391369(11)	0.189(11)	-0.409(50)	2.48(81)	-0.0841(56)	-0.0670(74)	0.405(23)	—
B1	17242.0042(12)	0.3923904(92)	-1.6628(78)	-1.568(29)	—	4.1916(71)	-1.343(13)	1.560(54)	—
A1	17164.9702(12)	0.3913207(86)	2.1233(59)	1.834(23)	-5.94(32)	3.4282(56)	1.1307(84)	-1.819(39)	8.54(58)
[11.0] ⁺	10965.4480(13)	0.4151406(79)	0.2704(23)	—	—	—	—	—	—
[4.90] ⁺	4910.6361(44)	0.403457(18)	0.428(16)	0.402(40)	—	—	—	—	—
X0 ⁺	0.0	0.4155285(73)	0.2534(19)	—	—	—	—	—	—
<i>Group II</i>									
D'1	a + 21222.3042(16)	0.384929(19)	0.3219(58)	—	—	1.5225(62)	-0.0339(72)	0.141(21)	—
C'1	a + 19782.8005(16)	0.387975(19)	0.3058(58)	—	—	—	—	—	—
B'0 ⁺	a + 19439.6302(17)	0.385489(19)	0.3078(60)	—	—	—	—	—	—
X1	a	0.416247(19)	2.902(60)	—	—	1.6697(92)	—	—	—

Numbers in parentheses are one standard deviation in the last digits and 'a' refers to the undetermined location of the $\Omega = 1$ spin component of the $X^3\Sigma^-$ state.

transition at 4910.6 cm⁻¹. This 18 490 cm⁻¹ transition has not been seen in the matrix spectra. The newly observed states at 4910.6 and 10 965.4 cm⁻¹ have been labeled as [4.9]0⁺ and [11.0]0⁺ in Table 1.

The rotational analysis of bands in the second group shows that the three transitions have a common lower state with $B''_0 = 0.416247(19)$ cm⁻¹ and significant Ω -doubling, consistent with an $\Omega'' = 1$ assignment. The 0–0 bands of these transitions have their origins near 19 440 (B'0⁺–X1), 19 783 (C'1–X1) and 21 222 (D'1–X1) cm⁻¹, none of which were observed in the laser-induced fluorescence experiments of Lorenz et al. [12,13] and the matrix isolation experiment of Weltner and McLeod [7]. The transition with its 0–0 band near 19 440 cm⁻¹ has been observed for the first time. This transition has been labeled by us as B'0⁺ state in Table 1. The fact that none of the bands in the second group were observed in a matrix absorption experiment [7] suggests that the lower state is well above the ground $\Omega = 0^+$ state. It may be noted that the rotational constants of the lowest $\Omega = 0^+$ and 1 states are similar in magnitude suggesting that they are the spin components of the same Hund's case (a) state which we identify as the X³Σ⁻ state. This assignment is confirmed by our ab initio calculations described below.

4. Ab initio calculations

We have performed ab initio calculations on the low-lying electronic states of WO in the triplet, quintet and septet manifold in order to determine the ground-state symmetry. Singlet transitions were found to lie higher in energy and are not discussed in this Letter. The potential energy curves and the spectroscopic properties of these states have been calculated with the program MOLPRO [18] at the contracted multireference configuration interaction (CMCRI) level of theory [19] with explicit correlation of all valence electrons. The molecular orbitals used in these calculations are first optimized by state-averaged full-valence complete active space self-consistent field (CASSCF) calculations [20] and Davidson's correction [21] is taken into account in the

CMRCI energies. Basis sets and quasi-relativistic electron core potentials from the Stuttgart library [22,23] are used, with an extra polarization orbital on each atom (*f*-type Gaussian with an exponent of 0.8 on W and *d*-type Gaussian with an exponent of 0.8 on O). The valence orbital space is defined by the four σ , two π and one δ molecular orbitals arising from the 5d and 6s orbitals of W and the 2s and 2p orbitals of O. The same computational procedure was used successfully in our previous work on transition metal nitrides [24–26] and chlorides [27,28].

5. Ab initio results

Full-valence CASSCF calculations show that the low-lying states in the triplet manifold arise from the following valence electron configurations, with the corresponding states in parentheses:

- (A) $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2 1\delta^2$ (³Σ⁻),
- (B) $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1 1\delta^3$ (³Δ),
- (C) $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2 1\delta^1 2\pi^1$ (³Φ, ³Π).

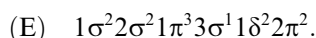
At this level of theory, the ³Σ⁻ state is predicted to be the lowest triplet, with an equilibrium internuclear distance of 1.67 Å. The term energies are calculated to be 8200, 20 600 and 21 200 cm⁻¹ for the ³Δ, ³Φ and ³Π states, respectively. This ordering suggests that configuration (A) is the lowest configuration, and that $3\sigma \rightarrow 1\delta$ and $1\delta \rightarrow 2\pi$ single-electron promotions lead to the excited (B) and (C) configurations, respectively. Electrostatic splitting within configuration (A) obeys Hund's rule, with the ¹Γ and ¹Σ⁺ states located, at the CASSCF level, at 6100 and 9400 cm⁻¹ above the ³Σ⁻ state. The $3\sigma \rightarrow 4\sigma$ excitation, leading to configuration $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1 1\delta^2 4\sigma^1$, gives one ³Σ⁺ and two ³Σ⁻ states, but these states are found to be more than 30 000 cm⁻¹ above the lowest ³Σ⁻ state, given the pronounced antibonding character of the 4σ orbital.

A similar CASSCF investigation of the quintet manifold reveals a single low-lying state, of ⁵Π symmetry, arising from configuration:

- (D) $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1 1\delta^2 2\pi^1$.

It corresponds to a $3\sigma \rightarrow 2\pi$ excitation with respect to configuration (A). Notice that configuration (D) also contributes, together with configuration (C) to the lowest ${}^3\Phi$ and ${}^3\Pi$ states (see Table 2). The ${}^5\Pi$ state is located at 11 500 cm^{-1} above the lowest ${}^3\Sigma^-$ state. Other possible quintet states are found at higher energies, such as ${}^1\Sigma^+$ (from $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^1 1\delta^1 2\pi^2$), the ${}^1\Sigma^+$ and ${}^1\Sigma^-$ states (from $1\sigma^2 2\sigma^2 1\pi^3 3\sigma^2 1\delta^2 2\pi^1$) and the ${}^1\Phi$ (from $1\sigma^2 2\sigma^2 1\pi^3 3\sigma^2 1\delta^1 2\pi^2$), lying at about 15 000, 20 000, 20 200 and 28 000 cm^{-1} above the ${}^5\Pi$ state, respectively. A single test calculation at the CMRCI level confirms the above CASSCF energy for the ${}^5\Pi$ - ${}^5\Delta$ adiabatic separation, which is calculated to be 16 000 cm^{-1} .

A ${}^7\Pi$ low-lying state was also calculated in the septet manifold. This state arise from the configuration:



Given the $1\pi 3\sigma \rightarrow 2\pi^2$ excitation, it lies at high energies (about 29 000 cm^{-1} at CASSCF level) above the ${}^1\Sigma^-$ state. It is also characterized by a bond significantly larger (2.01 Å) than the other low-lying states of WO (1.67–1.71 Å).

The conclusion of this preliminary CASSCF investigation is thus that the ground state of WO should be of ${}^3\Sigma^-$ symmetry, and not of ${}^5\Pi$ symmetry, as predicted by the previous ab initio work of Nelin and Bauschlicher [15]. Nelin and Bauschlicher [15] did not consider the possibility of a triplet ground state in their calculations, based on the periodic trend established by CrO and MoO.

The CASSCF results are confirmed by our extensive CMRCI calculations performed on the ${}^3\Sigma^-$, ${}^3\Delta$, ${}^3\Phi$, ${}^3\Pi$, ${}^5\Pi$ and ${}^7\Pi$ states. The calculated potential energy curves are presented in Fig. 2 and the corresponding calculated spectroscopic properties are reported in Table 2. The calculated properties are the equilibrium values of the internuclear distances r_e , the harmonic frequencies ω_e , the electric dipole moments μ_e , and the term energies T_0 , which have been corrected for the zero point energy contribution calculated within the harmonic approximation. Also reported are the weights of the dominant configurations contributing to the CMRCI wavefunctions and some data from the Mulliken population analysis.

Table 2
Spectroscopic properties of some low-lying electronic states of WO from CMRCI calculations

State	T_0 (cm^{-1})	r_e (Å)	ω_e (cm^{-1})	μ_e (D)	Main configuration weights ^a	Atomic fractional charge q^b	s-type population on $W m^b$	d-type population on $W m^b$
$X^3\Sigma^-$	0	1.672	1050	1.72	83% (A)	0.42	1.7	3.7
${}^1\Sigma^+$	9548	1.716	[1065.6231(52)] ^c	3.44	84% (D)	0.44	0.1	5.3
${}^3\Delta$	12231	1.679	1022	3.43	85% (B)	0.47	0.9	4.5
${}^3\Pi$	14964	1.710	972	2.73	75% (C) + 6% (D)	0.51	1.3	4
${}^3\Phi$	15067	1.713	964	2.83	58% (C) + 21% (D)	0.52	1.5	3.8
${}^7\Pi$	33777	2.022	584	3.19	92% (E)	0.46	0.9	4.4

^aWeights (in percent) are obtained from the square of the corresponding configuration interaction coefficients; see text for the configuration labeling, A to E.

^bIn electrons, from CASSCF calculations.

^cExperimental values for the XO^+ spin component.

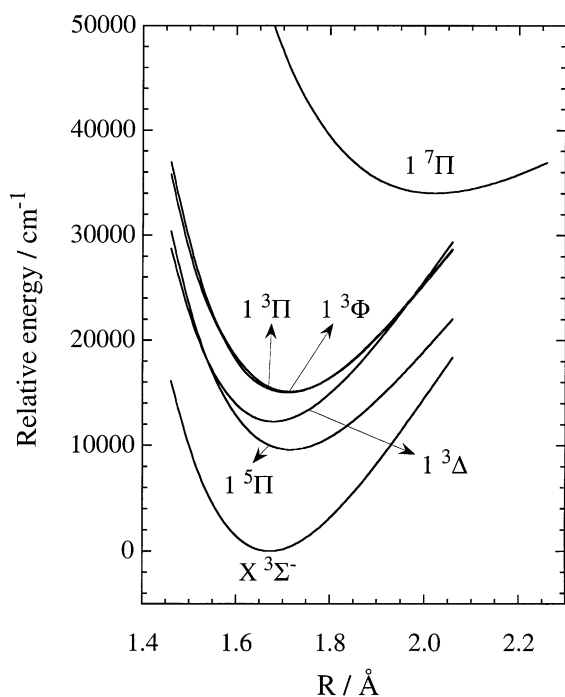


Fig. 2. The low-lying potential-energy curves of WO in the triplet, quintet and septet manifolds, from CMRCI calculations.

A first comment on these results is that the energy ordering of the calculated states is qualitatively the same as at the CASSCF level except for a permutation of the ordering of the $^3\Delta$ and $^5\Pi$ states. The CMRCI term energy values are, however, significantly shifted with respect to the preliminary CASSCF values, with ΔT_e (CMRCI–CASSCF) values of 4000, -5500 , -6200 , -1900 and 5000 cm^{-1} for the $^3\Sigma^-$, $^3\Delta$, $^3\Phi$, $^3\Pi$, $^5\Pi$ and $^7\Pi$ states, respectively. This demonstrates the importance of electron correlation effects in such systems, in which a multireference treatment involving all valence electrons is absolutely required for getting a balanced description of the different states. In comparison with the work of Nelin and Bauschlicher [15], we used a better basis set, a larger active space in the CASSCF expansions (7 CSF [15] to be compared to 2000 in the present work) and a better treatment of electron correlation. The $^5\Pi$ state was predicted [15] to be the ground state, with a longer bond ($r_e = 1.99$ Å and $\omega_e = 580$ cm^{-1}) than from our CMRCI cal-

culations ($r_e = 1.72$ Å and $\omega_e = 936$ cm^{-1}). Moreover, the $^7\Pi$ state was calculated [15] at SDCl level to be 8400 cm^{-1} above the $^5\Pi$ state, while our corresponding CMRCI value is 24200 cm^{-1} . We suspect that this discrepancy is due to the small active space used to describe the $^5\Pi$ state, which resulted in too much antibonding character. The $^7\Pi$ state is probably better described, thanks to its single reference nature (see the configuration weights in Table 2).

6. Discussion

Among the first group of transitions, the C1– $X0^+$ transition has an extensive vibrational structure in the ground state. In this transition the 0–0, 0–1, 1–2, 2–3, 0–2, 1–3 and 2–4 bands were observed. A rotational analysis of these bands provides the equilibrium constants of $\omega_e'' = 1065.6231(52)$ cm^{-1} , $\omega_e x_e'' = 4.0271(22)$ cm^{-1} , $B_e'' = 0.416694(23)$ cm^{-1} , $\alpha_e'' = 0.002032(45)$ cm^{-1} and $r_e'' = 1.658074(63)$ Å for the $X0^+$ state. In most of the other transitions only one or two vibrational levels were observed in the ground and excited states. Our analysis indicated that the $v'' = 2$ vibrational level of the ground $X0^+$ state is locally perturbed near $J'' = 26$.

It has also been observed that most of the transitions have anomalous isotope effects. This effect is most noticeable in the A– $X0^+$ and B– $X0^+$ transitions. For example, in the 0–1, 0–0 and 1–0 bands of the A– $X0^+$ transition, the ^{184}WO – ^{186}WO isotope shifts of 0.40, 0.66 and 0.80 cm^{-1} have been observed, compared to the calculated values of -0.48 , -0.03 and $+0.36$ cm^{-1} , respectively. The 0–1 and 0–0 bands of this transition were earlier assigned [8] as the 3–1 and 3–0 bands on the basis of the anomalous isotope effects. An inspection of our spectra indicates that these assignments [8] are incorrect because other expected vibrational bands were not present at their predicted positions. In fact Kuzykov et al. [10,11] were also misled by the anomalous vibrational isotope shifts and incorrectly reassigned the A–X bands. Their revised assignment leads to an excited-state vibrational interval of 1057.41 cm^{-1} , which exactly matches the known ground-state vibrational interval and is

therefore also incorrect. This anomalous isotope effect is the result of strong interactions in the excited state which shifts the different isotopomers by different amounts [14]. The excited states of WO are extensively perturbed through interaction with other states and the strength of the perturbations depend on the isotopomer. Higher-order effective molecular constants for the A1, B1, C1 and D1 states (Table 1) are needed as a result of these interactions. In the second group, only the $v'' = 0$ and 1 vibrational levels were observed in the lower state. The analysis of bands in group II provides $\Delta''G(1/2) = 1059.9309(12) \text{ cm}^{-1}$, $B''_e = 0.417253(15) \text{ cm}^{-1}$, $\alpha''_e = 0.002019(17) \text{ cm}^{-1}$ and $r''_e = 1.656963(30) \text{ \AA}$ for the $X^3\Sigma^-, \Omega = 1$ state.

In a $^3\Sigma$ state where the two spin components are well separated, the spin-spin constant λ can be estimated using the following formula [32]:

$$q = \frac{(\gamma - 2B)^2}{2\lambda + \gamma - 2B},$$

where q is the effective lambda-doubling constant in the $^3\Sigma_1$ spin component. Using the positive value of q for the X1 state, a value of $\lambda = 514 \text{ cm}^{-1}$ has been estimated for the $X^3\Sigma^-$ ground state of WO. This spin-splitting places the $^3\Sigma_1$ spin components at $\sim 1028 \text{ cm}^{-1}$ (2λ) above the lowest $^3\Sigma_0$ spin component. Such a ground-state spin-splitting places the C'2, D1 and B'0⁺ states close together in energy. The C'2 (20810 cm^{-1}), D1 (20794 cm^{-1}) and B'0⁺ (20467 cm^{-1}) states thus form a cluster of states that could originate from a $^3\Pi_r$ state. The $1^3\Pi_r$ state from configuration C is calculated to lie at $\sim 15000 \text{ cm}^{-1}$ (Table 2), but a more complete set of calculations are needed to confirm that the C'2, D1 and B'0⁺ states arise from this $^3\Pi_r$ state.

The electronic structure of WO is expected to be very similar to that of the isoelectronic ReN which has been studied in detail recently [29–31]. The ground state of ReN has been established as $X^3\Sigma^-, \Omega = 0^+$ from the analysis of dispersed laser-induced fluorescence. Several excited states of ReN are involved in extensive interactions and a deperturbation analysis has resulted in the identification of several high Ω states of ReN [31]. Similar interactions with the unobserved higher Ω states are probably responsible for the abnormal isotope

effects in WO. In a recent Letter Kraus et al. [14] have discussed similar abnormal isotopic effects in the $F0^+-X0^+$ transition of WO. WO does not follow the periodic trend established by CrO and MoO which have $^5\Pi$ ground states.

The experimental values of the ground-state constants have also been compared with the theoretical values in Table 2. The experimental vibrational frequency of $\omega_e = 1065.6231(52) \text{ cm}^{-1}$ and bond length of $r_e = 1.658074(63) \text{ \AA}$ are in good agreement with the calculated values of 1.672 \AA and 1050 cm^{-1} , respectively. Other interesting data in Table 2 are provided by the Mulliken atomic population analysis performed on the CASSCF wavefunctions: the atomic fractional charge (q) and the s-type (n) and d-type (m) populations on W. The ionicity of the system is given by the q value describing the system as $W^{+q}O^{-q}$. One sees that these values range between 0.42 and 0.52, but do not clearly explain the large differences found in the dipole moment values, in particular the low value of the dipole moment in the ground state. More spectacular are the n and m changes. These numbers give an idea of the relative atomic contributions ($6s^n5d^m$) on the W atom within the molecule. Note that $6 - (n + m)$ is not exactly equal to q , due to small p-type contributions (about 0.2) not reported here. Also notice that all states exhibit about the same ($2s^{1.9}2p^{4.5}$) atomic occupation on oxygen. The $^5\Pi$ state is thus characterized by an almost pure ($5d^5$) W^+ structure in contrast to the $^3\Sigma^-$ state which has a mixed ($6s^25d^3$)/($6s^15d^4$) character, while the other states are intermediate cases. It seems that the high values of the dipole moment correspond to a high population in the 5d orbital.

Acknowledgements

We thank C. Plymate, M. Dulick and D. Branston of the National Solar Observatory for assistance in obtaining the spectra. The National Solar Observatory is operated by the Association of Universities for Research in Astronomy, Inc., under contract with the National Science Foundation. We thank C. Bauschlicher for his comments. The research described here was supported

by funding from NASA laboratory astrophysics program. Some support was also provided by the Natural Sciences and Engineering Research Council of Canada. J.L. thanks the Fonds National de la Recherche Scientifique de Belgique for financial support.

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