Characterization of the
[18.42]0⁺ – X¹Σ⁺ (0,0) Band of Tantalum Nitride, TaN

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Abstract

High resolution laser-induced fluorescence (LIF) spectra of the $[18.42]0^+ - X^1\Sigma^+ (0,0)$ band of tantalum nitride, TaN, near 543 nm, have been recorded and analyzed field-free and in the presence of a static electric field. The nuclear electric quadrupole hyperfine structure due to $^{181}\text{Ta}(I=7/2)$ was resolved and analysis of the field-free spectrum yielded nuclear electric quadrupole coupling constants, eQq_0 , of $-0.24025(75) \text{ cm}^{-1}$ and $-0.05755(76) \text{ cm}^{-1}$ for the $X^1\Sigma^+$ and $[18.42]0^+$ states, respectively. The Stark tuning of the $R(0)$ and $P(1)$ lines was analyzed to determine the magnitude of the molecular frame electric dipole moments, $|\vec{\mu}_{\text{el}}|$, of $3.33(4) \text{ D}$ and $4.48(3) \text{ D}$ for the $X^1\Sigma^+$ and $[18.42]0^+$ states, respectively. The $|\vec{\mu}_{\text{el}}|$ and eQq_0 values are discussed in terms of predicted molecular orbitals for the $X^1\Sigma^+$ and $[18.42]0^+$ states.

1. Introduction

Numerous heavy, polar, paramagnetic diatomic molecules have been used in the search for the permanent electron electric dipole moment (eEDM) because in such molecules the eEDM induced permanent molecular EDM is expected to be orders of magnitude larger than the eEDM itself [1-4]. In the hadron sector, the magnetic quadrupole moment (MQM) of the nucleus can also lead to a permanent atomic or molecular EDM. It was recently pointed out [5] that the experimental advances involving the use of $^3\Delta_1$ states developed to establish the current eEDM limit [6] can also be exploited in attempts to measure MQM-induced EDMs, with ^{181}TaN being identified as the prime candidate. In addition to being a heavy, polar molecule with an accessible paramagnetic $^3\Delta_1$ electronic state, the deformed $^{181}\text{Ta}(I=7/2)$ nucleus is expected to result in a strongly enhanced MQM due to a collective effect [7]. Collectivity is also the cause [8] of the large positive nuclear electric quadrupole moment (EQM) ($=+317 \text{ fm}^2$) of ^{181}Ta . In order to extract the nuclear MQM from the proposed experimental measurements the coupling parameter, W_M , needs to be predicted via a high-level, relativistic, electronic structure calculation. Given that W_M describes the interaction of the nuclear MQM with the gradient of the magnetic field produced by the electrons, the electronic wavefunction in the region of the nucleus must be very accurately predicted. Recently, Skripnikov *et al.* [9] and Fleig *et al.* [10] performed such electronic structure calculations and predicted W_M , and other properties, for the $^3\Delta_1$ electronic state of ^{181}TaN . Fleig *et al.* [10] predicted W_M as an expectation value in a four-component relativistic correlated all electron approach and also used the same computational methodology to predict the molecular frame electric dipole moments, $\vec{\mu}_{\text{el}}$, and magnetic hyperfine parameters for the $^3\Delta_2$, $^3\Delta_3$, $^1\Delta_2$, and $X^1\Sigma^+$ states. The calculations of Skripnikov *et al.* [9] involved a two-step procedure to generate the relativistic four-component electronic structure in the vicinity of

the nucleus. The first step involves using the generalized relativistic effective core potential to produce a very accurate description of the spinors in the valence region. The correct description of the spinors in the core region is then restored in the second step which is based upon the expected proportionality of the valence and virtual spinors. Skripnikov *et al.* [9] used this approach to predict $\bar{\mu}_{\text{el}}$ and magnetic hyperfine parameters for the $^3\Delta_2$, $^3\Delta_3$, and $^1\Delta_2$ states, but not for the $X^1\Sigma^+$ state.

Here we report on the high-resolution spectroscopic study of the $[18.42]0^+ - X^1\Sigma^+ (0,0)$ band and the subsequent experimental determination of the magnitude of $\bar{\mu}_{\text{el}}$ and nuclear electric quadrupole coupling constants, eQq_0 , for the $X^1\Sigma^+$ and $[18.42]0^+$ states. A comparison of these readily measurable properties with predicted values is an effective method for assessing the quality of the predicted electronic wavefunctions of the $X^1\Sigma^+$ and $[18.42]0^+$ states, and by implication the ability of those same calculations to predict the EDM/MQM relevant $^3\Delta_1$ electronic wavefunction. A review of the previous experimental studies of TaN can be found in our recent publication describing the medium-resolution, pulsed, laser induced fluorescence (LIF) excitation and dispersed fluorescence (DF) spectroscopic studies [11]. The most relevant of the previous studies is by Ram *et al.* [12] where the high temperature hollow cathode source emission spectrum in the $3000 - 35000 \text{ cm}^{-1}$ region was recorded and analyzed. As part of that study *ab initio* calculations were also performed to predict the term energies (T_e), bond lengths (R_e), and vibrational constants (ω_e) of the valence electronic states having energies less than $25,000 \text{ cm}^{-1}$. Only the scalar-relativistic effects were included using quasi-relativistic pseudo potentials. In our previous study [11], fluorescence branching ratios, transition dipole moments, and vibronic state energies associated with emission from the $[17.58]0^+ (v=0)$, $[18.42]0^+ (v=0)$, $[110.22]1^+ (v=0)$, and $[110.40]1^+ (v=0)$ states were determined. A possible mechanism for

populating the EDM/MQM relevant $a^3\Delta_1$ ($J=1$, $v=0$) state was proposed. At about the same time, Mukund *et al.*[13] reported on measuring and analyzing DF spectra resulting from visible pulsed laser excitation of nine electronic states, including three of the four states of our previous study [11]. This work extended the vibrational analysis up to $v = 10$, 4 and 6 in the $X^1\Sigma^+$, $a^3\Delta_1$ and $a^3\Delta_2$ states, respectively. They also observed the $v = 0$ level of the $A^1\Delta$ state. Fluorescence branching ratios and transition dipole moments were not determined.

2. Experimental

The supersonic expansion production scheme of the internally cold ($T^{\text{rot}} \sim 20$ K) sample was the same as previously reported [11]. Unlike the previous measurements, the resulting free-jet expansion was skimmed to produce a well collimated molecular beam and probed by the output of a single frequency cw-dye laser. The LIF signal resulting from excitation of the $[18.42]0^+ - X^1\Sigma^+ (0,0)$ band was monitored off-resonance through a ± 10 nm band pass filter centered at 640 nm, which corresponds to the $[18.42]0^+ \rightarrow a^3\Delta_1(v=0)$ emission. Spectral line widths of less than 40 MHz FWHM were achieved by a combination of molecular beam collimation and relatively low, unfocused laser intensity. For the Stark measurements, static electric fields were generated by application of a voltage across a pair of highly transmitting, conducting, neutral density filters straddling the region of molecular fluorescence as previously described [14]. The systematic errors due to the electric field strength calibration are estimated to be less than 2%. A polarization rotator was used to align the electric field vector of the linearly polarized laser radiation either parallel "||" or perpendicular " $\perp$ " to that of the applied electric field vector. The absolute wavenumbers were measured by recording the I_2 $B-X$ system at sub-Doppler resolution [15]. Extrapolation between iodine lines was performed by monitoring the transmission of an actively stabilized and calibrated confocal etalon.

3. Results

(a) Field Free

The approximate positions of the low- J rotational transitions were calculated using the published rotational constants [12] and the laser was scanned in the predicted regions containing the $R(0) - R(5)$ and $P(1) - P(6)$ lines. The field-free laser excitation spectrum of the $R(2)$ branch feature of the $[18.42]0^+ - X^1\Sigma^+(0,0)$ band is shown in Figure 1. The upper trace is the observed spectrum; the lower trace is a simulated spectrum using the determined constants (see below), $T^{\text{rot}} \sim 20$ K, and a 0.0005cm^{-1} FWHM Lorentzian line shape. All the rotational lines showed clearly resolved $^{181}\text{Ta}(I=7/2)$ hyperfine structure and no evidence of $^{14}\text{N}(I=1)$ splitting. The higher J ($J > 3$) levels were quite complex with rotational lines consisting of up to 22 hyperfine components with normal electric dipole allowed selection rules $\Delta F = 0, \pm 1$. Although the hyperfine structure in the $R(0)$ and $P(1)$ lines, which are entirely due to the $J = 1$ levels of the upper and ground states, respectively, could be readily assigned, the hyperfine patterns for the higher J ($J > 3$) levels were complex enough that assignment could not be done purely on visual inspection. In the end 132 lines were precisely measured and assigned and are presented in Supplemental Table 1 along with the difference between the measured transition wavenumber and those predicted using the optimized parameters (see below).

The field-free energies of the $[18.42]0^+$ and $X^1\Sigma^+$ states were modelled by including solely the rotational and nuclear electric quadrupole terms in the effective Hamiltonian [16] :

$$\hat{H}^{\text{eff}} = B_0 \hat{\mathbf{J}}^2 - D_0 \hat{\mathbf{J}}^4 + eQq_0 \frac{(3\hat{I}_z - \hat{\mathbf{I}}^2)}{4I(2I-1)}, \quad (1)$$

where $\hat{I}$ and $\hat{I}_z$ are the nuclear spin angular momentum operators and $\hat{J}$ is the molecular rotational angular momentum operator. Initial estimates of eQq_0 were obtained by fitting the splitting of the $R(0)$ and $P(1)$ lines to the expression [16] for the Hund's case ($a_{\beta J}$) basis expectation value of $\hat{H}^{eff}$:

$$\langle Case(a_{\beta J}) | \hat{H}^{eff} | Case(a_{\beta J}) \rangle = B_0 J(J+1) - D_0 J^2(J+1)^2 + eQq_0 \left[-\frac{[0.75C(C+1) - I(I+1)J(J+1)]}{2I(2I-1)(2J-1)(2J+3)} \right], \quad (2)$$

where $C = [F(F+1) - J(J+1) - I(I+1)]$. Calculated spectra using these eQq_0 constants and the published rotational constants [12] reproduced the observed hyperfine structure well enough to enable assignment of the remaining spectral components. Fitting all 132 observed and assigned lines to the analytical expression revealed a slight systematic residual for the lowest rotational level branch features. In the final fit both the diagonal (Eq.2) and $\Delta J = \pm 2$ off-diagonal matrix elements associated with the nuclear quadrupole hyperfine interaction were required. Because only transitions up to $J = 6$ were recorded, the rotational distortion constants, D , were fixed at the values determined by Ram *et al.* [12] who observed transitions up to $J = 61$. The final optimized parameters and associated error are shown in Table 1. The standard deviation of the fit is 0.00034 cm^{-1} , which is commensurate with the estimated measurement uncertainty.

(b) Stark Spectra

The $R(0)$ and $P(1)$ rotational lines were selected for optical Stark measurements because of their limited hyperfine structure. Figure 2 shows (bottom to top) the recorded spectra of the $7/2-5/2$ ($F'-F''$), $7/2-10/2$ and $7/2-7/2$ hyperfine components of the $P(1)$ line (a) field free, (b) in the presence of an applied 2186 V/cm electric field perpendicular, (c) parallel to the electric field of the laser radiation, and (d) the recorded sub-Doppler iodine spectrum in the region.

Supplemental Table 2 lists the 46 measured Stark shifts (MHz) along with quantum number assignments, and the observed minus calculated shifts obtained using the optimized values of $|\vec{\mu}_{el}|$ (see below).

The interaction with the static electric field was modeled using the conventional Stark Hamiltonian:

$$\hat{H}^{Stark} = -\vec{\mu}_{el} \cdot \vec{E} \quad (3)$$

where $\vec{E}$ is the static electric field and $\vec{\mu}_{el}$ is the permanent electric dipole moment operator of the molecule. The Stark energies for the $X^1\Sigma^+$ ($v=0$) and $[18.42]0^+$ states were determined by diagonalizing a matrix representations of $\hat{H}^{Stark}$ constructed in $F = 0.5$ to 5.5 Hund's case ($a_{\beta J}$) basis sets. The matrix elements are given by [17]:

$$\langle Case(a_{\beta J}) | \hat{H}^{eff} | Case'(a_{\beta J}) \rangle = -E\mu_{el} (-1)^{F-M_F+F'+1+I} [(2F+1)(2F'+1)]^{1/2} [(2J+1)(2J'+1)]^{1/2} \begin{pmatrix} F & 1 & F' \\ -M_F & 0 & M'_F \end{pmatrix} \begin{Bmatrix} J' & F' & I \\ F & J & 1 \end{Bmatrix} \begin{pmatrix} J & 1 & J' \\ 0 & 0 & 0 \end{pmatrix}. \quad (4)$$

The 46 measured Stark shifts were used as input into a non-linear least squares fitting program which optimized $|\vec{\mu}_{el}|$ for the $X^1\Sigma^+$ ($v=0$) and $[18.42]0^+$ states. The optimized values for $|\vec{\mu}_{el}|$ ($X^1\Sigma^+$ ($v=0$)) and $|\vec{\mu}_{el}|$ ($[18.42]0^+$) are 3.33 ± 0.04 D and 4.48 ± 0.03 D, respectively. The standard deviation of the fit is 12.4 MHz, which is commensurate with the measurement uncertainties. In Figure 3 the Stark tuning of the hyperfine levels associated with the $P(1)$ transition obtained using optimized field-free parameters and $|\vec{\mu}_{el}|$ values is illustrated.

4. Discussion

The band origin, T_{00} , and rotational constants, B , are compared in Table 1 with those obtained by Ram *et al.* [12]. There are small differences between the two sets of values due mainly to the lack of low J ($J < 17$) data in the previous work. The newly determined eQq_0 parameters are very large and negative, with that for the $X^1\Sigma^+$ state being about 4.2 times greater than that for the $[18.42]0^+$ state. The $X^1\Sigma^+$ state is predicted [12] to have a dominant $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2$ configuration. It is reasonable to assume that the observed $[18.42]0^+$ state is a component of the predicted [12] $1^3\Pi_r$ ($T_e=18732 \text{ cm}^{-1}$) state, which has a dominant $1\sigma^2 2\sigma^2 1\pi^3 3\sigma^2 1\delta^1$ configuration. According to the scalar-relativistic orbital picture of this calculation, in these configurations the 1σ is primarily the N($2s$), the 2σ and 1π orbitals are bonding orbitals formed between the N($2p$) orbital and the Ta($5d$) orbitals, the 1δ is essentially a pure Ta($5d_{+2}$) orbital, and the 3σ orbital is a $5d_0/6s$ hybrid orbital polarized away from the electrophilic N-center. The predicted orbital contours [12] indicate that $2\sigma \approx 60\% \text{ N}(2p_0) + 40\% \text{ Ta}(5d_0)$, $1\pi \approx 50\% \text{ N}(2p_{\pm 1}) + 50\% \text{ Ta}(5d_{\pm 1})$, $3\sigma \approx 50\% \text{ Ta}(6s) + 50\% \text{ Ta}(5d_0)$. The eQq_0 constant is given by [16]:

$$eQq_0(\text{MHz}) = Q \left[\frac{e \times 10^{-6}}{4\pi\epsilon_0 h} \right] \langle \Lambda | \sum_i \frac{(3\cos^2 \theta_i - 1)}{r_i^{-3}} | \Lambda \rangle = -234.96 \times Q \langle \Lambda | \sum_i \frac{(3\cos^2 \theta_i - 1)}{r_i^{-3}} | \Lambda \rangle. \quad (5)$$

In Eq. 5 the summation runs over all electrons, θ_i are the azimuthal angles for those electrons, and the conversion factor assumes that Q is in Barnes and $\langle r^{-3} \rangle$ is in a_0^{-3} . Using the SCF-Hartree-Fock-Slater predicted value [17] of $6.103 a_0^{-3}$ for $\langle r^{-3} \rangle_{5d}$, estimated eQq_0 values of -7021 MHz and -3880 MHz for the $X^1\Sigma^+$ and $[18.42]0^+$ states, respectively, are obtained. Given the

qualitative nature of the assumptions used for this prediction, the estimated $X^1\Sigma^+$ value (-7021 MHz) is in reasonable agreement with the measured values of -7202 ± 22 MHz. It is noteworthy that the four-component relativistic correlated all electron approach used by Fleig *et al.* [10] predicts that the $\sigma_{6s}(\text{Ta})$ spinor displays a 71% $6s(\text{Ta})$, 8% $6p_z(\text{Ta})$, and 10% $5d_{x^2-y^2, z^2}(\text{Ta})$ leading atomic contribution, which is considerably different from the scalar-relativistic orbital picture of Ref. 12. Therefore, the relatively good agreement may be fortuitous. The relatively poor agreement between the estimated value for the $[18.42]0^+$ state (-3880 MHz) with the observed value of -1725 ± 22 MHz would improve if this state had a sizable contribution from the $1\sigma^2 2\sigma^2 1\pi^3 3\sigma^1 1\delta^2$ configuration because $\langle \delta | (3\cos\theta - 1) | \delta \rangle = -4/7$. The prediction of Ram *et al.* [12] estimated that this configuration makes only a 4% contribution to the $1^3\Pi_r(T_e=18732 \text{ cm}^{-1})$ state.

The experiment determines only the magnitude of the dipole moment, $\bar{\mu}_{el}$, but it is reasonable to assume that the charge distribution is $\text{Ta}^{+\delta}\text{N}^{-\delta}$ for the $X^1\Sigma^+$ and $[18.42]0^+$ states. The experimentally determined value for $|\bar{\mu}_{el}|$ ($X^1\Sigma^+$ ($v=0$)) of 3.33 ± 0.04 D is smaller than but close to that calculated by Fleig *et al.* [10] of 3.515 D at an $R_e = 1.683 \text{ \AA}$, which is close the experimental $R_0 = 1.685 \text{ \AA}$. The bond length gives a reduced dipole moment, $\mu_e/R_0 = 1.108 \text{ D/\AA}$, which represents an effective nuclear charge of 0.41e, i.e. $\delta = 0.41$. The Mulliken atomic population analysis of the CASSCF wavefunctions [12] predicts a value of $\delta = 0.25$ for the $X^1\Sigma^+$ state.

Excitation to the $[18.42]0^+$ state increases the bond length from $1.685 \text{ \AA}$ to $1.736 \text{ \AA}$ and the electric dipole moment from 3.33D to 4.48D. The 35% increase in $|\bar{\mu}_{el}|$ cannot be attributed

solely to the increase in bond length (3%). The reduced dipole moment, μ_e/R_0 , in the excited state is 2.58 D/Å and $\delta = 0.54$. Assuming that the observed $[18.42]0^+$ state is a component of the predicted $[12] 1^3\Pi_r (T_e=18732 \text{ cm}^{-1})$ state, then to a first approximation the $X^1\Sigma^+ \rightarrow [18.42]0^+$ excitation is associated with the a promotion of an electron from the bonding 1π ($\approx 50\% \text{ N}(2p_{\pm 1}) + 50\% \text{ Ta}(5d_{\pm 1})$) orbital to the non-bonding 1δ ($\approx \text{Ta}(5d_{\pm 2})$) orbital, which is consistent with the observed increase in R_0 . Unfortunately, this promotion is inconsistent with observed 35% increase in $|\vec{\mu}_{\text{el}}|$ because it represents a transfer of charge in the bonding orbital to a Ta-center, which would result in a decrease in $|\vec{\mu}_{\text{el}}|$. An excitation from the back-polarized 3σ ($\approx 50\% \text{ Ta}(6s) + 50\% \text{ Ta}(5d_0)$) orbital to the 1δ ($\approx \text{Ta}(5d_{\pm 2})$) orbital would be consistent with a large increase in $|\vec{\mu}_{\text{el}}|$.

5. Conclusion

The first high resolution molecular beam study of the electronic spectra of TaN has been performed. The lowest J lines of the $[18.42]0^+ - X^1\Sigma^+ (0,0)$ band were precisely measured and analysis showed that the $eQq_0(X^1\Sigma^+)$ is a large negative value, which is qualitatively consistent with the predicted orbital nature. The approximate 4.2 times smaller value of $eQq_0([18.42]0^+)$ is not readily explained. At present there are no published *ab initio* predictions of these eQq_0 constants. The recent high-level calculation [10] using an all electron configuration interaction theory in the framework of the Dirac-Coulomb Hamiltonian did predict a $|\vec{\mu}_{\text{el}}|$ for the $X^1\Sigma^+$ state which is approximately 5% larger than the observed value. The observed large increase in $|\vec{\mu}_{\text{el}}|$ upon excitation to the $[18.42]0^+$ state suggest that the transition is associated with excitation out of the back-polarized $\text{Ta}(6s/5d_0)$ hybrid orbital.

There is a clear need for a high-level *ab initio* prediction of eQq_0 , which represent the interaction of the nuclear EQM and the electric field gradient (EFG) at the position of the same nucleus. The EFG operator samples the wavefunction in the vicinity of the nucleus where accounting for relativistic effects is challenging [18], and at the same time needs to be accurately modelled for the proposed nuclear-MQM induced EDM experiments. Experiments are presently underway in our laboratory to experimentally determine the magnetic and quadrupole hyperfine structure, optical Stark effect, and optical Zeeman effect for transitions involving the $a^3\Delta_1$ state, which has been the primary focus of theoretical calculations [9, 10].

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Figure Captions:

Figure 1. The recorded high resolution spectrum of the $R(2)$ line of the $[18.42]0^+ - X^1\Sigma^+ (0,0)$ band of TaN. The upper trace is the observed spectrum; the lower trace is a simulated spectrum using the determined constants in Table 1, $T^{\text{rot}} = 20\text{K}$, and a 0.0005 cm^{-1} Lorentzian linewidth. The associated energy level pattern is shown above the spectrum with lines identifying the individual components.

Figure 2. (*Bottom - top*) The recorded Stark spectrum of the $7/2-5/2$ ($F'-F''$), $7/2-10/2$ and $7/2-7/2$ hyperfine components of the $P(1)$ line (a) field free, (b) in the presence of an applied 2186V/cm electric field perpendicular or (c) parallel to the electric field of the laser radiation, and (d) the recorded sub-Doppler iodine spectrum in the region.

Figure 3. The calculated Stark shifts with respect to electric field strength of the associated energy levels for the $P(1)$ hyperfine components.

Figure 1

Figure 2

Figure 3

Table 1. Field-free parameters (in cm^{-1}) for the $[18.42]0^+ - X^1\Sigma^+ (0,0)$ band system of TaN.

Parameter	$X^1\Sigma^+$		$[18.42]0^+$	
	Present work	Ref. [12]	Present work	Ref. [12]
T_{00}			18422.45617(14) ^a	18422.4321(26)
B	0.456752(16)	0.4567341(34)	0.430236 (18)	0.430293(44)
$D (\times 10^7)$	3.351 ^b	3.351(63)	11.166 ^b	11.166(20)
eqQ_0	-0.24025(75)		-0.05755(76)	
RMS	0.00034			

^a Associated 1σ error in brackets.

^b Distortion constants fixed at values in ref. [12]