

Ab Initio Calculations of the Geometry and Vibrational Frequencies of the Triplet State of Tungsten Pentacarbonyl Amine: A Model for the Unification of the Preresonance Raman and the Time-Resolved Infrared Experiments

Snežana Zarić,[†] Marc Couty,[‡] and Michael B. Hall*

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

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Abstract: Ab initio calculations of the vibrational frequencies of $W(CO)_5NH_3$ in its ground electronic 1A_1 ($b_2^2e^4$) and lowest excited state 3E ($b_2^2e^3a_1^1$) have been performed at the HF level. The calculated frequencies of the $\nu(CO)$ bands are in agreement with observed data on experimentally studied $W(CO)_5(\text{amine})$ molecules. The optimized geometries of the ground and the excited states show that the $W-N$, $W-C_{eq}$, $W-C_{ax}$, $C-O_{eq}$ bonds lengthen and the $C-O_{ax}$ bond shortens on excitation. Our results resolve an apparent disagreement between the fast time-resolved infrared (TRIR) spectroscopy and the preresonance Raman (PRR) spectroscopy. The unexpected simultaneous lengthening of both $W-C_{eq}$ and $C-O_{eq}$ is due to $C-O_{eq}$ antibonding character in the a_1 orbital which more than offsets its loss from the e . In addition a new band, predicted but as yet unresolved in the TRIR, accounts for the $C-O_{ax}$ shortening as expected from the PRR $W-C_{ax}$ lengthening.

Introduction

There has been considerable study of the photochemical properties of $W(CO)_5\text{pyr}$ and $W(CO)_5\text{pip}$.¹ A knowledge of the geometry of the excited state is important for a thorough understanding of the photochemistry; in principle the bonding changes in excited electronic states should correlate with ligand photolabilization.^{1e,2-5} Information on the structures of excited states of $W(CO)_5\text{pyr}$ and $W(CO)_5\text{pip}$ has been obtained experimentally by ground-state preresonance Raman (PRR)⁴ and fast time-resolved infrared (TRIR) spectroscopy.⁵ Using a time-dependent formalism, Zink and co-workers analyzed their PRR spectra and concluded that in the lowest excited state (3E) the $W-N$, $W-C_{ax}$, and $W-C_{eq}$ bonds are longer than in the ground state. They suggested that it is reasonable to assume^{4a} that if the $W-C$ bonds lengthen then the corresponding $C-O$ bonds will shorten. However, Turner and co-workers⁵ interpreted the $\nu(CO)$ TRIR spectra, using a relationship between $C-O$ bond length and $C-O$ force constants,⁶ as showing that all the $C-O$ bonds are longer in the excited state. Then, the implication is that all the $W-C$ bond lengths are shorter in this excited state.⁵

[†] Permanent address: Faculty of Chemistry, University of Belgrade, Studentski trg 16, 11001 Beograd, Yugoslavia.

[‡] Current address: Université de Marne-la Vallée, M2, bois de l'étang, rue galilée, 77420 Champs sur Marne, France.

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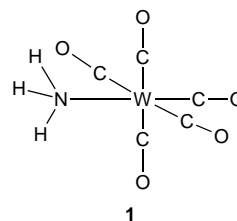
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Ab initio calculations for excited states can contribute to understanding photochemical reaction mechanisms.⁷ In order to elucidate the apparently differing experimental results, we have performed calculations on $W(CO)_5NH_3$ (**1**) as a model compound. We report vibrational frequencies and optimized geometries for $W(CO)_5NH_3$ in its ground and first excited states obtained from ab initio calculation, and compare the frequencies and differences in bond lengths with experimental data.

Theoretical Details

The geometries of $W(CO)_5NH_3$ were optimized at the restricted Hartree-Fock (RHF) level for the ground electronic state 1A_1 ($b_2^2e^4$). For the excited state 3E ($b_2^2e^3a_1^1$) geometries were optimized at the unrestricted Hartree-Fock (UHF) level, both with and without a geometric J-T distortion. During the geometry optimization $W-C-O$ and $C_{ax}-W-N$ bond angles were fixed at 180° , $C_{eq}-W-C_{eq}$ was 90° , and NH_3 had local C_3 symmetry. In the geometry exhibiting Jahn-Teller distortion $W-C_{eq}$ and $C_{eq}-O$ bond lengths were different in the x and y directions; otherwise they were equivalent.

Numerical frequencies were calculated at the optimized geometries.

Effective core potentials were used for all atoms except hydrogen. For W a relativistic ECP was used,^{8b} the 5s, 6s, 5p, 6p, and 5d orbitals and their electrons were taken as active, and the basis set was the recently proposed 541/651/211 contraction.⁸ For C, N, and O the

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double- ζ basis set and effective core potentials of Stevens et al.^{9a} were used. For hydrogen a double- ζ basis set was used.^{9b}

Optimized geometries and frequencies were also calculated at the Møller–Plesset second-order perturbation (MP2) level. Earlier theoretical results for $W(CO)_6$ have shown that the CO bond distances are in better agreement with experimental data at the HF level than at the MP2 level (although W–C bond distances are in better agreement with experimental data at the MP2 level).¹⁰ At the HF level the CO bond distance is shorter than the experimental value by about 0.01 Å, and at the MP2 level it is longer by about 0.04 Å. Our calculated frequencies at the HF level are about 100 cm^{-1} higher than experimental values, while at the MP2 level they are about 200 cm^{-1} lower than experimental values. Even the order of the calculated frequencies at the MP2 level is in disagreement with experimental data: A and E frequencies are switched. Thus, the HF level is more appropriate for this problem and in this paper we present results at that level. Future calculations with higher-order methods are anticipated.

Ab initio calculations were performed with GAMESS-UK^{11a} and GAUSSIAN 92^{11b} software packages on a Cray SMP-22 at the Chemistry Department, on the IBM-SP2 at the Cornell Theory Center, and on SGI Iris Indigo and Power Indigo2 workstations in our laboratory.

Results and Discussion

There is good agreement about the position and assignment of $\nu(CO)$ frequencies for ground state $W(CO)_5pyr$ and $W(CO)_5pip$.^{1ab,5,12} Experimental data for ground and excited states⁵ and average values in nonpolar solvents are shown in Table 1.

To simplify the calculations $W(CO)_5NH_3$ was used as a model compound. For $W(CO)_5NH_3$, $W(CO)_5pyr$, and $W(CO)_5pip$ the lowest excited state is 3E , although there are some $W(CO)_5$ complexes with substituted pyridines where 3E is not the lowest excited state.^{1a} It was suggested⁵ that the π interactions with the N-donors are not very significant since IR spectra of $W(CO)_5pyr$ and $W(CO)_5pip$ in both ground and excited states are so similar (Table 1). Although we would not expect exact agreement for the NH_3 model, the pattern of frequencies should be well reproduced. Because a J–T distortion is expected in the 3E excited state, calculations have been performed with and without J–T distortion.

Frequencies. The calculated CO stretching frequencies and intensities are shown in Table 2. The assignment of the calculated frequencies in the ground state is based on the degeneracy and intensity. In the excited state the bands are mixed because of the lower electronic symmetry and the J–T geometric distortion. In addition, the C–O modes are weakly coupled to the N–H modes. Thus, the absolute intensities are not accurate, but relative magnitudes are. The assignment of the calculated frequencies in the excited state is made from the normal coordinates and intensities in the ground and excited states.

The high-frequency a_1 vibration moves to slightly lower frequency in the excited state and gains some intensity. The

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Table 1. The Experimental Frequencies (cm^{-1}) of the $\nu(CO)$ Bands of $W(CO)_5L$ in the Ground and in the Excited State

solvent	bands				ref
	$A_1^{(1)}$	$A_1^{(2)}$	E	B_1	
L = Pyridine					
ground state					
cyclohexane	2072	1919	1932		1b
isooctane	2071	1918	1930		1a
cyclohexane	2073	1921	1935		12b
<i>n</i> -heptane	2080	1920	1933		12c
$CHCl_3$	2076	1895	1933	1980	12d
isooctane	2072	1920	1933		1e
methylcyclohexane/isopentane	2071	1903	1927		5
excited state					
methylcyclohexane/isopentane	1942	1860	1809		5
L = Piperidine					
ground state					
cyclohexane	2065	1917	1926		1b
isooctane	2070	1915	1926		1a
2,2,4-trimethylpentane	2072.5	1919	1930		12a
<i>n</i> -hexane	2073.5	1918	1928.5		12c
methylcyclohexane/isopentane	2069	1898	1920		5
excited state					
methylcyclohexane/isopentane	1942	1855	1788		5
av ^a ground state	2071.7	1915.2	1929.1		
av excited state	1942	1857.5	1798.5		

^a Average for nonpolar solvents.

Table 2. Calculated C–O Frequencies^a and Intensities of $W(CO)_5NH_3$

	ground state		excited state					
			UHF wo/J-T		UHF w/JT			
	freq	inten	freq	inten	freq	inten		
A_1	2207.2	19.13	A_1	2163.1	283	A_1	2184.6	117
B_1	2099.5	0.06	A_1	2052.7	796	A_1	2078.9	935
E	2050.1	3865.2	E	2009.0	3222	E	2075.7	3219
E	2050.0	3864.6	E	1900.0	8922	B_1	1871.2	23
A_1	2012.8	1718.8	B_1	1840.9	20	E	1741.3	11795

^a Calculated numerical frequencies using Gaussian 92. Geometrical data for optimized geometries are given in Table 4.

very weak b_1 vibration shifts to much lower frequency and gains some intensity, but remains very weak. The low-frequency, strong a_1 vibration moves to higher frequency and loses intensity. The calculated frequencies for the E vibrational band in the ground state split into two frequencies in the excited state. This can be explained by the differences in the geometry and the electronic structure between the ground and the excited states. Although the geometry of the excited state without J–T distortion has the same geometric symmetry as the ground state, with different bond lengths and angles (Table 4), the excited state electronic structure has lower symmetry. The electronic configuration for the ground state (1A_1) is $b_2^2e^4$, and that for the excited state (3E) is $b_2^2e^3a_1^1$. In calculating one component of 3E , for example the $d_{xz}^2d_{yz}^1$, the electronic wave function is already distorted, with different electronic distribution along the x and y directions. This electronic distortion is, in some sense, the origin of the geometric J–T distortion.

As is well-known, HF frequencies for covalent bonds are usually higher (Table 2) than the experimental values (Table 1) because the HF wave function does not dissociate properly. The errors are systematic, and they are amenable to scaling techniques.¹³ An excellent correlation exists between the calculated and experimental frequencies (Figure 1), where the

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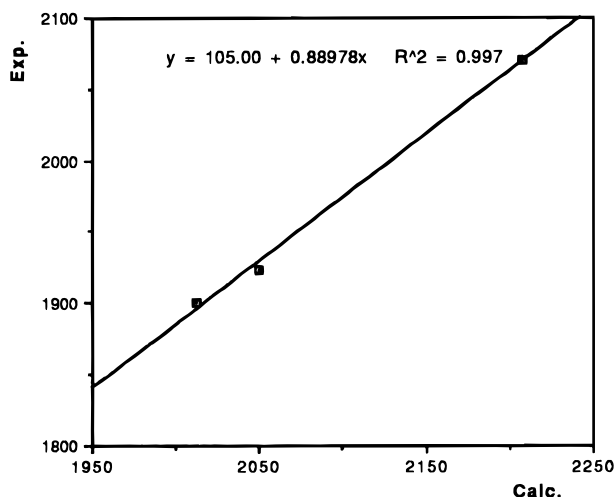


Figure 1. Relationship between experimental and computed frequencies for $W(CO)_5L$ ($L = NH_3$ for computed data; $L = pyr, pip$ for experimental data) in the ground state.

Table 3. Experimental^a and Predicted^b C–O Frequencies of $W(CO)_5L^c$ in the Ground and Excited States

ground state		excited state		
exp	pred	exp	pred	
			UHF wo/J-T	UHF w/J-T
		A_1	2029.7	2048.8
A_1	2071.7	A_1	1942	1954.8
E	1929.1	A_1	1857.5	1951.9
A_1	1915.2	E	1798.5	1654.3
		E	1795.5	1654.3

^a Average data from Table 1. ^b Data have been obtained from Table 2 (omitting B frequencies) using correlation from Figure 1. Geometrical data are given in Table 4. ^c $L =$ pyridine, piperidine for experimental data; $L = NH_3$ for predicted data.

average values of experimental frequencies of the $\nu(CO)$ bands of $W(CO)_5L$ ($L =$ pyridine, piperidine) in the ground state⁵ were used to make the plot. When an average value of all experimental data in nonpolar solvent was used to make the plot, predicted frequencies were very similar. The least-squares correlation from the ground state was used to correct the calculated frequencies for both the ground and the excited states. The experimental and the predicted (calculated and scaled) frequencies are given in Table 3.

Comparing the experimental and predicted frequencies in the excited state shows that the highest frequency at 2029–2050 cm^{-1} appears to be missing from the experimental assignments. This frequency would be difficult or impossible to observe in TRIR spectroscopy¹⁴ because the sample is a mixture of molecules in the ground and the excited states. This band (2029–2050 cm^{-1}) of the excited state is very weak and very close to the corresponding band (2072 or 2069 cm^{-1}) of the ground state. Therefore, this excited state band might be lost in the background or edge of the stronger ground state band.¹⁵ For other frequencies, the positions and relative intensities are in excellent agreement with experimental data (Table 3). However, our assignment of the frequencies differs from TRIR assignments⁵ (Table 3).

There is much better agreement between the experimental frequencies and those calculated without J–T distortion (Table 3). This result suggests that our calculation is overestimating

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Table 4. Geometrical Data^a in Ground and Excited States of $W(CO)_5NH_3$

geometric parameter	ground state ^b	excited state	
		UHF wo/J-T ^c	UHF w/J-T ^d
W–C _{ax}	1.996	2.050	2.054
C–O _{ax}	1.167	1.152	1.152
W–C _{eq}	2.069	2.078	x axis 2.064 y axis 2.090
C–O _{eq}	1.157	1.164	x axis 1.155 y axis 1.174
W–N	2.397	2.516	2.515
N–H	1.018	1.020	1.020
C _{ax} –W–C _{eq}	90.78	93.88	x axis 92.60 y axis 96.27
W–N–H	110.62	109.63	109.64

^a All distances in Å and angles in deg. ^b $E_{HF} = -184.154868$ au. ^c $E_{UHF} = -184.081607$ au. ^d $E_{UHF} = -184.083026$ au.

the degree of distortion. Although one expects some distortion, it may be much smaller than we calculated on a free static molecule for at least three reasons. Firstly, the molecules may be only weakly distorted because the sample is in the solid state. When molecules were promoted from the ground state to the excited state, the solid matrix could provide the energy to prevent the appearance of the full J–T distortion. Secondly, the energetic difference (including zero-point energy) between the geometries with and without J–T distortion is only 0.77 kcal/mol. Thus, the first vibrational level of the disorder structure is only 0.77 kcal/mol below the transition state. Because of the anharmonicity of the potential energy curve for the distortion, the true vibrationally averaged structure will have a smaller distortion than that calculated for the static molecule. Thirdly, the degree of distortion may be overestimated by the UHF method since it depends on the correct description of a configuration with one doubly occupied orbital and one singly occupied orbital ($e_x^2 e_y^1$). Without explicit electron correlation the description of the doubly occupied orbital will be less accurate than that of the singly occupied orbital.

The calculated W–C stretching frequencies in the ground state are in the 400–500- cm^{-1} region, as observed experimentally.^{4a} In the excited state these frequencies move lower and correlate with the change in bond distances, as discussed below. The calculated W–N stretching frequency also moves to lower energy in the excited state.

Geometries. Geometric data for the optimized geometries of $W(CO)_5NH_3$ in ground and excited states are given in Table 4. In the ground state, the axial W–C bond is shorter than the equatorial bonds and the axial C–O bond is longer than the equatorial bonds. This is in agreement with the experimental X-ray structure of $W(CO)_5pyr$,^{4a} and with the calculated structure for the $W(CO)_5$ fragment.¹⁰ Differences in W–C and W–O bond distances between calculated $W(CO)_5NH_3$ structure and X-ray $W(CO)_5pyr$ structure are less than 0.04 Å.

The J–T distorted geometry of the 3E state has a b_1 distortion (Table 4), in which a pair of *trans* W–C–O linkages differ from the other pair. A J–T distorted geometry of 3E with b_2 distortion, where the C_{eq} –W– C_{eq} angles would be alternately greater than and less than 90°, has not been found. The only geometries corresponding to a b_2 distortion were for other electronic states. It is interesting to compare the geometries of the ground and the excited states, especially bond lengths, as they have been determined from experimental results. The W–N, W–C_{ax}, W–C_{eq}, and C–O_{eq} bonds are all longer, and only the C–O_{ax} bond is shorter in the excited state. The C_{ax} –W– C_{eq} bond angle is increased in the excited state (Table 5). These geometrical changes are in substantial agreement with experimental results. Longer W–C bonds in the 3E excited state

Table 5. Experimental and Calculated Changes of Geometrical Data^a in Ground and Excited States of W(CO)₅L

geometric parameter	experimental		calculated, L = NH ₃	
	L = pyr	L = pip	UHF wo/J-T	UHF w/J-T ^d
W-C _{ax}	+0.12 ^b	+0.25 ^b	+0.054	+0.058
C-O _{ax}	+0.006 ^c	+0.005 ^c	-0.015	-0.015
W-C _{eq}	+0.04 ^b	+0.05 ^b	+0.011	x axis -0.005 y axis +0.021
C-O _{eq}	+0.024 ^c	+0.026 ^c	+0.007	x axis -0.002 y axis +0.017
W-N	+0.18 ^b	<+0.3 ^b	+0.119	+0.118
C _{ax} -W-C _{eq}			+3.10	x axis +1.82 y axis +5.48

^a All distances in Å and angles in deg. ^b From ref 4a. ^c From ref 5.

have been found by PRR spectroscopy,⁴ longer C-O bonds have been found by TRIR spectroscopy,⁵ and both methods indicate an increase in the C_{ax}-W-C_{eq} bond angle and an increase in the W-N bond length.^{4,5}

A longer W-N bond in the excited state (by about 0.1 Å) is expected from the photochemical behavior exhibited by W(CO)₅pyr and W(CO)₅pip;^{1a,16,17} the quantum yield for loss of pyridine or piperidine from these compounds is very high, and this is in agreement with previous results.^{4,5} The change in the W-N bond length is nearly twice as large as the change in any of the other bond lengths. The W-C_{ax} bond lengthens more than the W-C_{eq} (0.06 Å vs 0.01 Å) bond, and this is in agreement with Zink's results.^{4a} The C-O_{ax} bond is shortened (about 0.015 Å), but the C-O_{eq} bonds are lengthened (about 0.007 Å). This latter result is unusual because it is unexpected that both W-C_{eq} and C-O_{eq} bonds would lengthen.^{1b,4a,16} In the simple molecular orbital picture, when the W-C bond lengthens, because of depopulation of the π bonding orbital (d_{yz}) and population of the σ antibonding orbital (d_z^2), it reduces back-bonding to C, thus strengthening the C-O bond and decreasing the C-O bond length. But our results show that in the excited state the newly populated a_1 orbital has substantial CO_{eq} π^* character (Figure 2). This orbital is weakly W-C bonding and strongly C-O antibonding. Therefore, depopulation of the d_{yz} orbital decreases the W-C π bonding and increases the C-O bonding, and populating the a_1 orbital decreases the C-O bonding. Since the latter more than offsets the former, both the W-C_{eq} and C-O_{eq} bonds are longer in the excited state. A similar description of the nature of this excited state orbital has been made on the basis of extended Hückel calculation.⁵ In the axial direction, lengthening of the W-C bond reduces back-bonding from W to C, strengthening the C-O bond and

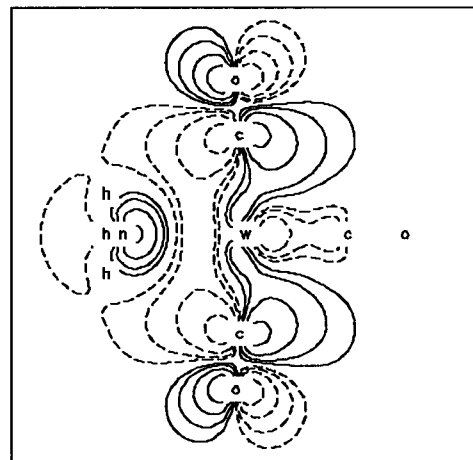


Figure 2. Contour plots of the a_1 molecular orbital. The values of the contour lines are ± 0.015 , ± 0.031 , ± 0.0625 , and ± 0.1250 au.

decreasing the C-O bond length. In our results C-O_{ax} is shorter as expected because the a_1 orbital has little axial C-O component.

Conclusion

Ab initio calculations of the vibrational frequencies for the W(CO)₅NH₃ molecule in the ground state and in the ³E excited state are in good agreement with the experimental frequencies for W(CO)₅L (L = pyridine, piperidine) as measured by TRIR. Comparing of optimized geometries in the ground and in the excited states shows that both W-C_{eq} and C-O_{eq} bonds lengthen in the excited state, an unexpected result, which is in agreement with experimental data from both PRR⁴ and TRIR⁵ spectroscopy, respectively. The C-O antibonding character of the excited state's a_1 orbital accounts for this result. A missing C-O band in the TRIR data accounts for the remaining discrepancy, i.e. the W-C_{ax} bond lengthening and the C-O_{ax} bond shortening in the experimental data. Thus, our work unites two seemingly disparate experimental studies.^{4,5}

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