VIBRATIONAL ANALYSIS OF THE URANIUM HEXACHLORIDE SPECIES
IN OXIDATION STATES OF IV, V AND VI

by

Jacob Shamir, Atara Silberstein,
John R. Ferraro, and Monica Choca

MASTER

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

For Presentation At:

Vibrational Spectroscopy Symposium,
Argonne National Laboratory, Argonne, Illinois,
May 17, 1974

U of C-AUA USAEC

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

THIS IS UNCLASSIFIED

je

Vibrational Analysis of the Uranium Hexachloride Species in
Oxidation States of IV, V and VI^{*}

Jacob Shamir,

Department of Inorganic and Analytical Chemistry

The Hebrew University

Jerusalem, Israel

Atara Silberstein,

Department of Inorganic and Physical Chemistry

Soreq Nuclear Research Center

Yavne, Israel

John R. Ferraro,[†] and Monica Choca[§]

Chemistry Division

Argonne National Laboratory

Argonne, Illinois 60439

^{*}Work performed under the auspices of the U. S. Atomic Energy Commission.

[†]To whom correspondence should be addressed.

[§]Present address: Nalco Chemical Co., Chicago, Illinois 60629.

Abstract- The infrared and Raman data for the uranium hexachlorides (UCl_6 , UCl_6^{1-} , and UCl_6^{2-}) are reported. The vibrational frequencies are assigned on the basis of an O_h point group symmetry, and using the Modified Urey-Bradley Force Field (MUBFF) and the Molecular Orbital Valence Force Field (MOVFF), a Normal Coordinate Treatment (NCT) was made. The trend of frequencies with oxidation state and counter ion, and the primary stretching force constant (K) variation with oxidation state and non-bonding valence electrons is discussed.

INTRODUCTION

Various hexahalides of the type MX_6^n (where $n = 0, -1, -2$) are expected to exist in an octahedral symmetry (O_h). In such a centrosymmetric structure the rule of mutual exclusion is operable. Three Raman-active fundamental modes and two infrared-active fundamentals are predicted by selection rules. Many of these compounds are solids at room temperature, and are highly colored. Raman studies of these molecules have been lacking, since spectra of highly colored materials have been difficult to obtain by conventional Raman spectroscopy. Recently, Raman spectra of UCl_6 as well as those of the lower oxidation studies - UCl_6^{1-} and UCl_6^{2-} were obtained.¹

This paper presents the low frequency infrared spectra of UCl_6 and UCl_6^{2-} . Heretofore, these data were incomplete or unavailable. These results when combined with the recently obtained Raman results¹ support an octahedral geometry for the UCl_6^n species. The data for UCl_6^{2-} are in good agreement with the frequencies

obtained from vibronic spectra. Based on an O_h symmetry a Normal Coordinate Treatment (NCT) was attempted. Force constants were calculated for all three uranium hexachloride species. The trend of frequencies with oxidation state and counter ion, and the primary stretching force constant (K) variation with oxidation state and non-bonding valence electron is discussed.

EXPERIMENTAL SECTION

Preparation of Compounds

The UCl_6 and the UCl_6^{1-} and UCl_6^{2-} compounds were prepared according to procedures described in the literature.¹⁻⁵

Infrared Spectra

The UCl_6 and the Cs_2UCl_6 compounds were studied in the far-infrared region. The UCl_6 samples were loaded in a glove box flushed with an inert gas. The diamond-anvil cell technique was used together with a 6X beam condenser and the Perkin-Elmer Model #301 spectrophotometer. Details of the technique have been previously reported.⁶ The Cs_2UCl_6 sample was examined in a Nujol mull.

Computer and Force Constant Calculations

Computer calculations made in this study were obtained using an IBM 360-195 or a Sigma V. The details and the programs used have been discussed in previously published publications.⁷⁻⁹

RESULTS AND DISCUSSION

A. NCT of UCl_6^n Species

Table I summarizes the observed vibrational frequencies and assignments of the various uranium hexachloride species in the IV, V, and VI oxidation states. Although some of the data have been deduced from vibronic data,¹⁰⁻¹¹ sufficient vibrational information is now available to obtain a NCT for these molecules. The ν_6 vibration is calculated from the relationship $\nu_6 = \nu_5/\sqrt{2}$.

The Modified Urey-Bradley Force Field (MUBFF) and the Molecular Orbital Valence Force Field (MOVFF) were used in performing the NCT. These force fields and the force constants involved have been previously described.⁷ The MUBFF has five independently variable force constants. Three of these are the standard UBFF constants K, H, and F. Two other General Valence Force Field (GVFF)-type interaction constants are included. These are the constants h and k, where h is the interaction constant between two angles sharing a common bond and at right angles to each other, and k is the interaction constant for two bonds trans to each other. The MOVFF has five force constants. Four are basic Orbital Valence Force Field (OVFF) Constants (i.e., K, D, F and F') and the fifth is the GVFF-type interaction, k, as defined for the MUBFF above. F' is allowed to equal $-1/10$ F.

B. Frequency Trends

1. Oxidation State

It may be observed from Table I that the stretching frequencies ν_1, ν_2, ν_3 vary as a function of the oxidation state, decreasing in

the order $VI > V > IV$. Within an oxidation state, the Raman absorptions change in frequency in the order $\nu_1 > \nu_2 > \nu_5$, while the infrared absorptions vary in the order $\nu_3 > \nu_4$. For all oxidation states the five frequencies vary in the order

$$\nu_1 > \nu_3 > \nu_2 > \nu_5 > \nu_4$$

These trends are consistent with previous results obtained for hexavalent chlorides.^{7,9,14,15}

2. Counter-ion Effect

For the oxidation states IV and V the counter ion appears to play a role in determining the location of the frequency positions of ν_1 , ν_2 and ν_5 . In general, these frequencies are found at higher energy for the Cs compound as opposed to R_3N compound. The bulkier R_3N^+ cations tend to decrease the frequency positions of these vibrations. Similar behavior was noted for the LnX_6^{3-} complexes,⁹ and for the transition series $MoCl_6^{2-}$ complexes.^{15,16}

C. Force Constant Trends

1. Oxidation State

Table II summarizes the NCT data. The table includes the values of the observed frequencies and those calculated using the MUBFF and the MOVFF. The percentage deviation of the calculated values from the observed values are included for the average of the three stretching vibrations (ν_1 , ν_2 , ν_3), and for the three bending vibrations (ν_4 , ν_5 , ν_6). The final set of converged force constants are also included.

The variation of the stretching force constant K with the oxidation state follows the expected order $VI > V > IV$. These results parallel the ν_1 , ν_2 , ν_3 frequency trends previously mentioned, and are indicative of stronger uranium-chlorine bonding in UCl_6 as compared to UCl_6^- and UCl_6^{2-} . Similar trends have been observed for other hexahalide molecules.^{7,9,14,15}

2. Dependence of K on Non-bonding Valence Electrons (n)

The dependence of K from the MUBFF or the MOVFF on the number of non-bonding valence electrons (n) of the uranium atom is plotted in Fig. 1. A decrease in K is noted as the number of non-bonding valence electrons increases. The results are parallel to those obtained for actinide hexafluorides (UF_6 , NpF_6 , PuF_6) for a similar plot, but are reversed from those obtained for the transition series hexahalide complexes and for the lanthanide series hexahalides.^{7,9} For the transition element hexafluorides an increase in K was observed as the number of valence non-bonding electron increases, with a maximum value occurring at $n = 2$. In the lanthanide series a constant increase is noted with an increase in n .

D. Comparison of Force Fields

The percentage deviations of the calculated values from the observed values are larger for the three stretching vibrations than for the three bending modes insofar as the MOVFF is concerned, while the reverse is true for the MUBFF. It appears that a better fit for the bending modes is provided by the MOVFF, and a better fit for the stretching modes by the MUBFF.

It is interesting to note that when F' is allowed to vary independently of F in the MOVFF, it refines near $-1/10F$. This reinforces the use of the $F' = -1/10F$ for MOVFF and verifies that the interaction between non-bonded atoms behave according to Van der Waal interactions.

E. Potential Energy Distribution (PED)

The calculated PED for the MUBFF and MOVFF indicate that ν_1 is $\sim 2/3$ due to K and $\sim 1/3$ F . The ν_2 and ν_3 vibrations are predominantly K . Thus, it is very apparent that ν_1 , ν_2 , and ν_3 relate to stretching modes. The ν_4 vibration is mostly F but mixed with K , $D(H)$, $F'(h)$, while the ν_5 vibration is mostly due to F . It may be observed that for the ν_1 vibration the F (repulsion force constant) participation increases with a lowering of oxidation for both the MUBFF and the MOVFF, indicating a weaker uranium-halogen bonding from $U(VI) \rightarrow U(V) \rightarrow U(IV)$. The results are parallel to the trends reported for the stretching force constant K , where the same trend is observed.

Table I. Vibrational Frequencies (cm^{-1}) and Assignments of Various UCl_6 Species.

Assignments	U(VI)	U(V)			U(IV)	
	UCl_6	CsUCl_6	$(\text{CH}_3)_4\text{NUCl}_6$	$(\text{C}_3\text{H}_7)_4\text{NUCl}_6$	Cs_2UCl_6	$[(\text{CH}_3)_4\text{N}]_2\text{UCl}_6$
$\nu_1(\text{A}_{1g})$	367	348	345	340	308	296
$\nu_2(\text{E}_g)$	321	288	278	278	230	230
$\nu_3(\text{F}_{1u})$	343^+		310^{11}	310^{13}	267^+	259^{12}
$\nu_4(\text{F}_{1u})$	101^+		122^{11}	121	116^+	114^{10}
$\nu_5(\text{F}_{2g})$	133	136	134	129	126	124
$\nu_6^*(\text{F}_{2u})$	94	96	95	91	89	88

$^*\nu_6 = \nu_5/\sqrt{2}$

$^+$ IR frequencies from this work.

Table II. Observed and Calculated Frequencies and Force Constants for Several Uranium Hexachlorides.

Oxidation State	Compound	Frequencies (cm ⁻¹)						Force Constants (mdyn/Å)					Average % Deviation		
		ν ₁ (A _{1g})	ν ₂ (E _g)	ν ₃ (F _{1u})	ν ₄ (F _{1u})	ν ₅ (F _{2g})	ν ₆ (F _{2u})	MUBFF	(K)	(F)	(H)	(h)	(k)	(ν ₁ , ν ₂ , ν ₃)	(ν ₄ , ν ₅ , ν ₆)
								MOVFF	K	F	D	F'	k		
U(IV)	Cs ₂ UCl ₆	obs.	308	230	267	116	126	89							
		MOVFF	285	239	267	115	130	88	1.01	.15	.02	-.01	.06	3.5	1.6
		MUBFF	293	236	269	112	133	86	.97	.19	-.01	-.002	.06	2.7	3.9
	(CH ₃) ₄ N ₂ UCl ₆	obs.	296	230	259	114	124	88							
		MOVFF	281	237	259	113	127	86	.98	.15	.02	-.01	.08	2.8	1.2
		MUBFF	286	236	260	111	130	85	.95	.17	-.004	-.002	.09	1.9	3.3
U(V)	(CH ₃) ₄ NUCl ₆	obs.	345	278	310	122	134	95							
		MOVFF	329	286	310	122	137	95	1.45	.17	.03	-.01	.12	2.6	0.9
		MUBFF	335	283	311	119	140	93	1.42	.20	-.01	-.004	.11	1.7	2.9
	(C ₃ H ₇) ₄ NUCl ₆	obs.	340	278	310	121	129	91							
		MOVFF	325	286	310	121	131	91	1.48	.15	.03	-.01	.12	2.9	0.9
		MUBFF	330	283	311	118	135	90	1.44	.18	-.003	-.002	.11	1.8	3.3
U(VI)	UCl ₆	obs.	367	321	343	101	133	94							
		MOVFF	364	323	343	101	133	94	1.80	.20	-.01	-.002	.18	0.6	0.2
		MUBFF	369	319	343	101	132	94	1.80	.22	-.03	-.01	.18	0.4	0.6

References

1. J. Shamir and A. Silberstein, J. Inorg. Nucl. Chem.
accepted for publication.
2. T. A. O'Donnel, D. F. Steward and P. Wilson, Inorg. Chem.
5, 1438 (1966).
3. J. Selbin, J. D. Ortego and G. Gritzner, Inorg. Chem.
7, 976 (1969).
4. J. Ferraro, J. Inorg. Nucl. Chem. 4, 283 (1957).
5. G. A. Candela, C. A. Hutchinson, Jr., and W. B. Lewis,
J. Chem. Phys. 30, 246 (1959).
6. J. R. Ferraro, S. S. Mitra and C. Postmus, Inorg. Nucl. Chem.
Letts. 2, 269 (1966).
7. P. LaBonville, J. R. Ferraro, M. C. Wall and L. J. Basile,
Coord. Chem. Revs. 7, 257 (1972).
8. L. J. Basile, J. R. Ferraro, P. LaBonville and M. C. Wall,
Coord. Chem. Revs. 11, 21 (1973).
9. M. Choca, J. R. Ferraro and K. Nakamoto, Coord. Chem. Revs.
12, 295 (1974).
10. S. A. Pollack and R. A. Satten, J. Chem. Phys. 36, 804 (1962).
11. J. L. Ryan, J. Inorg. Nucl. Chem. 33, 153 (1971).
12. D. Brown, J. Chem. Soc. A, 766 (1966).
13. K. W. Bagnall, D. Brown and J. G. H. du Fres, J. Chem. Soc.
2603 (1964).
14. D. M. Adams, "Metal-Ligand and Related Vibrations", E. Arnold,
London (1967).

15. J. R. Ferraro, "Low-Frequency Vibrations of Inorganic and Coordination Compounds", Plenum Press, N. Y. (1971).
16. D. M. Adams, H. A. Gebbie and R. D. Peacock, Nature 199, 278 (1963).

Fig. 1. Plot of K stretching force constant in MOVFF vs. number of non-bonding valence electrons.