



Thermochemical studies of the gaseous uranium chlorides

K. H. Lau and D. L. Hildenbrand

Citation: The Journal of Chemical Physics **80**, 1312 (1984); doi: 10.1063/1.446811 View online: http://dx.doi.org/10.1063/1.446811 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/80/3?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

Thermochemical Data for Gaseous Monoxides J. Phys. Chem. Ref. Data **12**, 967 (1983); 10.1063/1.555698

Thermochemical properties of the gaseous lower valent fluorides of uranium J. Chem. Phys. **76**, 2646 (1982); 10.1063/1.443246

Thermochemical properties of the gaseous tantalum fluorides J. Chem. Phys. **71**, 1572 (1979); 10.1063/1.438482

Thermochemical studies of the gaseous lowervalent fluorides of molybdenum J. Chem. Phys. **65**, 614 (1976); 10.1063/1.433119

Mass Spectrometric Study of Gaseous Molybdenum, Tungsten, and Uranium Oxides J. Chem. Phys. **32**, 1373 (1960); 10.1063/1.1730924



Thermochemical studies of the gaseous uranium chlorides^{a)}

K. H. Lau and D. L. Hildenbrand

SRI International, Menlo Park, California 94205 (Received 22 December 1982; accepted 1 June 1983)

The gaseous uranium halides UCl, UCl₂, UCl₃, UCl₄, and UCl₅ were generated under equilibrium conditions using several types of effusive beam sources, and were identified and characterized thermochemically by mass spectrometry. Five independent gaseous equilibria involving these species were studied in sufficient depth so that both reaction enthalpy and entropy changes could be evaluated accurately from second law analysis. The enthalpy data yield the sequence of bond dissociation energies at 298 K in kcal/mol: D° (U-Cl) = 108; D° (ClU-Cl) = 117; D° (Cl₂U-Cl) = 117; D° (Cl₃U-Cl) = 101; and D° (Cl₄U-Cl) = 50, all ± 2 kcal/mol. As expected, the absolute entropies of the gaseous chlorides show that the electronic partition functions of the lighter species are substantial at the experimental temperatures, leading to electronic entropies of 5–7 cal/deg mol at about 2100 K.

INTRODUCTION

The gas phase thermochemistry of the subvalent uranium fluorides has recently been worked out, 1,2 but no such information is available for the U-Cl system or any other actinide halides. There are several technological applications in which this information would be useful, but the experimental difficulties in such determinations are formidable, and theoretical treatments of such large electronic systems have not been fruitful. As part of a continuing program on actinide thermochemistry, we have extended our work to the U-Cl system so as to characterize those molecular species and to examine trends between the fluorides and chlorides.

As before, our approach involves extensive second law studies of gaseous reaction equilibria, with the major objective being the accurate determination of both enthalpy and entropy data. The absolute entropy data are particularly useful, since the electronic energy level structures of these actinide species are expected to be highly complex, and there is little possibility of assigning the levels from spectra in the near future. Therefore, some type of approximate treatment must be used in estimating the levels, and the absolute entropies provide a means of checking the correctness of such estimates. Similarly, the second law enthalpies $\Delta H^{\circ}(II)$ yield individual bond dissociation energies and standard enthalpies of formation without recourse to accurate spectroscopic and molecular constants needed in third law calculations.

A summary of our thermochemical results for the gaseous U-Cl species, obtained from mass spectrometric studies of high temperature reaction equilibria, is presented in this paper.

EXPERIMENTAL

All of the measurements described here were made with the magnetic deflection mass spectrometer and experimental technique described previously.³ As al-

ways, considerable effort was devoted to devising a suitable chemical beam source for generating the molecular species to be studied. It was found that all of the subvalent U-Cl species, UCl₅ through UCl, could be generated by admitting gaseous Cl_2 to the base of a graphite effusion cell containing uranium monocarbide UC. The species distribution was, of course, strongly temperature dependent, with diatomic UCI appearing only at the highest cell temperatures. Some of the equilibrium measurements were made with a UC-Cu mixture in the cell, and also with a tandem cell arrangement in which CaCl₂ from a lower chamber was admitted to the upper chamber containing UC. Identification was based on the mass numbers and threshold appearance potentials (AP) of the ions observed in the mass spectra of the cell beams for various experimental conditions.

The cells were heated by radiation from a noninductively wound tantalum spiral heating element; these Ta elements, wound from 0.318 cm diam wire, are relatively easy to fabricate and in recent years have proved to be more durable for high temperature use than the tungsten elements employed earlier. Cell temperatures were measured by optical pyrometry, sighting on a black-body cavity in the cell lid; the pyrometer calibration is checked periodically against a standard ribbonfilament lamp. As usual, ion signals at each data point were given the neutral beam defining slit test to check for any extraneous background contributions. All other features of the experimental technique, including data interpretation and analysis, are as described in previous publications.^{3,4}

All samples were reagent grade materials used without any further purification.

Our assessment of the effects of experimental errors on the accuracy of derived thermochemical quantities is based on the following considerations. The accuracies of second law (slope) enthalpies, the primary quantities of interest here, are determined almost entirely by systematic errors that are usually difficult to uncover. Statistical standard deviations or other precision indices tend to indicate much smaller uncertainties, but

²⁾ This research was supported by the Office of Basic Energy Sciences, U.S. Department of Energy.

TABLE I. Threshold appearance potentials of ions observed in U–Cl reaction studies.

Ion	AP (eV)ª	Cell temperature	Neutral precursor	Literature
UCI	10.2	600	UC l ₅	
UCI	10.0	600	UC14	9.97(v) ^b
UCI	12.0	600	UC14	
-	8.5	1400	UC13	
UC1 [*]	11.5	1400	UC1 ₃	
-	6.8	1950	UCl ₂	
UC1 ⁺	11.0	1950	UCI ₂	
	6.3	2200	UCI	
U*	6.2	2200	U	6.194°
Ca ⁺	6.1	1800	Ca	6.11 ^d
CaC1 ⁺	6.0	1800	CaCl	6.01 [•]
Cu ⁺	8.0	1350	Cu	7.73 ^d
CuCl ⁺	10.5	1350	CuC1	10.7 ^f
C1 ⁺ 2	11.6	600	Cl ₂	11.48 ^d
^a All ±0	.3 eV.	^d Refe *Pofe	rence 17.	
Refere	nce 16	fRefe	rence 3	

give no real information about absolute accuracy; these are generally reported solely to indicate the level of precision. We believe that the most reliable indication of the accuracy of a second law slope enthalpy comes from two factors: (1) The degree to which established slope values can be reproduced by the experimental technique, and (2) the degree to which a given slope value can be routinely reproduced in replicate determinations. Based on our frequent checks with vapor pressure standards such as gold and tin, and the reproducibilities observed, we estimate the second law enthalpy changes determined in this work to have an accuracy of ± 1.5 kcal/mol. When individual standard enthalpies of formation are derived from these values and then used successively in the analysis of other reactions, we assume (in accordance with error theory) that for additive processes the errors propagate as the square root of the sum of the squares. In deriving reaction entropies, equilibrium constants estimated to be accurate within a factor of 2 are combined with the enthalpy changes, leading to uncertainties in the ΔS° values of about 2 cal/moldeg.

RESULTS

A summary of the U-Cl ion threshold AP's observed for various cell temperatures with the UC + Cl₂ beam source is given in Table I. Thresholds were evaluated by the vanishing current method. These same threshold energies were observed with the other reactive beam sources that yielded, in addition, the AP values for the reaction partner species shown in Table I. As in the U-F system, the lowest threshold AP's of the U-Cl species decreased progressively from the pentahalide, where the halogen character of the ionizing orbital predominates, to the monohalide with an AP close to that of atomic uranium. This is precisely the expected behavior of the molecular ionization potentials as successive halogen ligands are removed from the central uranium atom. Thus, the AP data provide direct identification of the series of U-Cl species, as well as the temperature ranges in which they are present in detectable amounts. Note that the fragment contributions to UCl^{*}, UCl^{*}₂, and UCl^{*}₃ set in at 11-12 eV, so that it is necessary to avoid this fatal complication by making all abundance measurements on the subchloride parent ions within a few eV of the lowest ionization thresholds. For UCl^{*}₄, the observed AP of 10.0±0.3 eV is close to the vertical ionization potential of UCl₄ deduced from photoelectron spectroscopy⁵ 9.97 eV, while the values for U^{*} and the other reaction partners agree with previous values on the corresponding neutrals.

Equilibrium measurements

With species identities established and conditions for their observation defined, several gaseous equilibria were investigated to determine the reaction thermodynamics. In all cases, reaction equilibrium constants Kwere evaluated from parent ion intensities measured at ionizing electron energies 3 eV above threshold so as to eliminate fragmentation contributions. Corrections were also applied for isotopic distributions, and for parent ion fragmentation as determined experimentally. These two corrections have no effect on second law enthalpy determination, but need to be included in evaluating absolute equilibrium constants for entropy calculations or for third law analysis. Each reaction system was checked for attainment of chemical equilibrium, either by noting the response of derived K values to changes in Cl₂ gas flow rate and species partial pressures, or by adjusting the CaCl₂ sample level to modify the relative partial pressures. In all cases, the values of K were found to be unchanged within experimental error, satisfying the mass action criterion for equilibrium behavior.

Initially, the reaction

$$UCl_4(g) + 1/2 Cl_2(g) = UCl_5(g)$$
 (1)

was studied over the range 613 to 920 K with the $UC + Cl_2$ source. A summary of the experimental results on reaction (1) is given in Table II; absolute equilibrium constants K were evaluated from the intensity ratios by applying an additional correction derived from the instru-

TABLE II. Equilibrium constants for the gaseous reaction $UCl_4(g) + 1/2 Cl_2(g) = UCl_5(g)$.

T/K	K ₁	T/K	K ₁
613.1	160	717.1	11.8
613.1	169	742.3	8.34
613.1	160	769.9	5.76
654.9	56.4	769.9	5.78
682.6	23.7	824.5	2.47
682.8	24.3	858.4	1.18
706.0	17.7	881.5	1.07
706.0	17.5	918.5	0.596
706.0	17.5	920.4	0.574
717.1	11.9		

TABLE III. Equilibrium constants for the gaseous reaction $UCl_3(g) + CuCl(g) = UCl_4(g) + Cu(g)$.

T/K	K ₂	T/K	K ₂
1337	0.391	1444	0.312
1348	0.388	1489	0.300
1348	0.419	1507	0.270
1372	0.386	1507	0.288
1372	0.388	1507	0.283
1385	0.362	1559	0.255
1385	0.378	1559	0.247
1411	0.337	1601	0.228
1444	0.325	1601	0.237
$\log K_2 =$	(-1.886 ± 0)	.048) + (2008	$3 \pm 70)/T$

mental sensitivity constant and estimated ionization cross section ratios.

The reaction

$$UCl_3(g) + CuCl(g) = UCl_4(g) + Cu(g)$$
⁽²⁾

was investigated with the $(UC-Cu)+Cl_2$ source in the range 1337 to 1601 K, with the results summarized in Table III. With the UC+CaCl₂ beam source, it was possible to study the two reactions

$$UCl_2(g) + CaCl(g) = UCl_3(g) + Ca(g)$$
(3)

and

$$UCl(g) + CaCl(g) = UCl_2(g) + Ca(g)$$
(4)

over the ranges 1967 to 2181 and 2038 to 2217 K. Values of K derived from the measurements are listed in Table IV. At still higher temperatures in the range 2162 to 2436, the reaction

$$U(g) + UCl_2(g) = 2 UCl(g)$$
(5)

was studied with the $UC + Cl_2$ effusion beam source, with the results shown in Table V.

TABLE IV. Equilibrium constants for the gaseous reactions $UCl_2(g) + CaCl(g)$ = $UCl_3(g) + Ca(g)$ and UCl(g) + CaCl(g)= $UCl_2(g) + Ca(g)$.

T/K	K ₃	K ₄	T/K	K ₃	K ₄
1967	2.41	•••	2115	1.75	6.28
1970	2.67	• • •	2115	1.78	6.48
1972	2.44	•••	2118	1.74	•••
1972	2.37	• • •	2118	1.79	•••
2008	2.19		2142	•••	6.24
2037	2.20		2142	•••	6.16
2038	2.08	8.25	2149	1.67	•••
2038	2.25	7.95	2149	1.64	• • •
2041	2.10	• • •	2174	1.59	5.87
2041	2.13	• • •	2174	•••	5.83
2067	1.99	•••	2181	1.57	•••
2082	1.93	• • •	2181	1.51	•••
2091	• • •	7.28	2217	•••	5.41
2091	• • •	6.89	2217	•••	5.33
$\log K_3$	= (- 1.7	16±0.0	81) + (41	.61 ± 166	S)/T
$\log K_4$	= (-1.2	93±0.1	11) + (44	71 ± 238)/T

TABLE V. Equilibrium constants for the gaseous reaction $U(g) + UCl_2(g)$ = 2 UCl(g).

Т /К	K_5	T/K	K_5
2162	0.969	2232	1.11
2162	0.945	2232	1.15
2188	0.975	2272	1.09
2213	1.03	2334	1.05
2213	0.975	2334	1.06
2213	1.02	2375	1.12
2213	0.896	2375	1.15
2227	0.980	2436	1.18
2232	1.02		

A few measurements on the reaction

$$U(g) + CaCl(g) = UCl(g) + Ca(g)$$
(6)

were also made with the UC + CaCl₂ source at 2250 to 2300 K, but these were not sufficiently extensive for second law analysis. The results did establish, however, that $K_8 = 10.0$ at 2300 K.

Enthalpy data

The equilibrium constant data for reactions (1)-(5)were fitted by least squares analysis to yield the equations given in the various tables. From the coefficients of the 1/T term, the reaction enthalpies at the average experimental temperature $\Delta H^{\circ}(II)$ were evaluated. These values were corrected to the reference temperature 298 K using thermodynamic functions for the U-Cl species calculated from estimated molecular constants described in the Appendix; functions for the auxiliary species were taken from the JANAF tables.⁶ Electronic state contributions to the functions of the U-Cl species were omitted for this purpose, since these contributions are unknown and difficult to estimate with certainty. Although these electronic terms are sure to be significant, it is assumed that their contributions to the heat capacities and enthalpy increments of adjacent U-Cl species will cancel to a first approximation so that only the rotational and vibrational contributions are needed. The entropy data discussed below provide some corroboration for the above assumption. Reaction enthalpy data obtained in this fashion are summarized in Table VI; the stated uncertainties are standard deviations from the least squares fitting. The absolute accuracies of these quantities are estimated to be ± 1.5 kcal/mol, as noted earlier.

Since Eqs. (1)-(5) represent five independent thermochemical determinations with only the standard enthalpies of formation of the five U-Cl species as unknowns, the latter were evaluated by combining the values of $\Delta H^{\circ}_{296}(II)$ from Table VI with the thermochemical properties of the Ca, Cu, and Cl species, ⁶ plus that of U(g).⁷ The standard enthalpies of formation and corresponding bond dissociation energies (BDE) of the U-Cl molecular species derived in this manner are given in Table VII. As a check on the internal consistency of the results, the sum of the first four BDE values is $443 \pm 5 \text{ kcal/mol}$,

J. Chem. Phys., Vol. 80, No. 3, 1 February 1984

Gaseous reaction	Range (K)	$\Delta S_{T}^{*}(II)^{a}$ (cal/mol K)	$\Delta H_{T}^{*}(\mathrm{II})^{\mathbf{b}}$ (kcal/mol)	$\Delta H_{298}^{\circ}(II)^{b}$ (kcal/mol)
(1) $UCl_4 + 1/2 Cl_2 = UCl_5$	613-920	-23.1 ± 0.3	-20.3 ± 0.3	- 20,9
(2) $UCl_3 + CuCl = UCl_4 + Cu$	1337-1601	-8.6 ± 0.2	-9.2 ± 0.3	-11.2
$(3) UCl_2 + CaCl = UCl_3 + Ca$	1967 - 2181	-7.8 ± 0.4	-19.0 ± 0.8	- 22.4
(4) $UCl + CaCl = UCl_2 + Ca$	2038 - 2217	-5.9 ± 0.5	-20.5 ± 1.1	-22.1
(5) $U + UCl_2 = 2 UCl^2$	2162 - 2436	3.4 ± 0.7	7.5 ± 1.6	9.6

TABLE VI. Summary of reaction thermochemistry.

^aAbsolute accuracy 2 cal/mol K.

^bAbsolute accuracy 1.5 kcal/mol.

while the heat of atomization of $UCl_4(g)$ evaluated from calorimetric and sublimation equilibrium data is 437.5 kcal/mol, with a stated uncertainty of 1 kcal/mol. This latter value follows from the standard enthalpy of formation of $UCl_4(s)^{10}$ and our enthalpy of sublimation⁹ which gives the corresponding value $\Delta Hf_{298}^{\circ}(UCl_4, g)$ = -243.5 + 49.0 = -194.5 kcal/mol; for the atomization process UCl₄ = U + 4Cl one then derives $\Delta H_{298}^{\circ} = 127.0$ +4(29.0) - (-194.5) = 437.5 kcal/mol. The accord between these two independent results seems reasonable, thereby corroborating the equilibrium data presented here. It has been reported recently⁸ that the standard enthalpy of formation of $UCl_4(s)$ may be 3 kcal/mol more negative than the accepted values, in which event the BDE sum and the ΔH_{298}° (atom, UCl₄) would be brought into closer agreement.

The equilibrium data for reaction (6) provide another check on the consistency of the results. Although only a third law calculation is possible for the single data point, previous results for the U-F system,² as well as the U-Cl entropy data discussed below indicate that the electronic partition functions of the gaseous monohalides UF and UCl are very similar to that of U(g). Therefore, the change in Gibbs energy function $-(G^{\circ})$ $-H_{298}^{\circ})/T$ for reaction (6) can be evaluated, to a reasonably accurate first approximation, solely from the translational, rotational, and vibrational contributions. One calculates then for reaction (6) at 2300 $K \Delta G^{\circ}/T = -4.58$ cal/mol K and $-\Delta(G^{\circ} - H_{298}^{\circ})/T = -1.5$ cal/mol K, yielding $\Delta H^{\circ}_{298}(6) = -14.0$ kcal/mol. When combined with thermochemical data for the reaction partners, ^{6,7} this leads to $\Delta Hf_{298}^{\circ}(UCl, g) = 47.0 \pm 2 \text{ kcal/mol and } D_{298}^{\circ}(U-Cl)$ = $109.0 \pm 2 \text{ kcal/mol}$, in good agreement with values in Table VII derived from second law studies of other reactions.

Entropy data

As noted above, we have attempted to include all pertinent corrections to the experimental ion intensity ratios so that absolute reaction equilibrium constants and, therefore, reaction entropy changes can be evaluated. These values of ΔS_T° are estimated to be accurate to within about ± 2 cal/mol K as described earlier, considering the various sources of error, and are listed in Table VI; the statistical errors shown there are considerably smaller. It is then possible to combine these values with the known entropies of the reaction partner species to evaluate the absolute entropies of the U-C1 molecular species. Values derived in this way are shown in Table VIII. For gaseous UCl₄, we prefer the more accurate entropy value at 650 K obtained from our recent sublimation studies.⁹

In Table VIII, the experimental absolute entropies are compared with the corresponding values calculated from estimated spectroscopic constants excluding the unknown electronic contributions. These comparisons should be quite meaningful for the smaller U–Cl molecular species, since the rotational and vibrational contributions can be estimated with reasonably good accuracy, leading to total entropies (excluding electronic) that are accurate to about 1 cal/mol K. As seen in Table VIII, the comparison shows that except for UCl₅, the experimental entropies are in each case substantially larger than the calculated translation + rotation + vibration (trv) values, with the differences ranging from 5–7 cal/mol K. This shows clearly that the missing electronic level contributions are indeed substantial.

TABLE VIII. Comparison of experimental and calculated entropies.

TABLE	E VII.	Standard e	enthalpies	s of	formation a	and
bond di	ssocia	tion energ	ies of U-	C1 s	species.	

Gaseous Molecule	$\Delta H f_{238}^{\circ}$ (kcal/mol)	Bond	D ₂₉₈ (kcal/mol)
UCI	48.4 ± 2.0	UCl	108 ± 2
UC12	-39.7 ± 2.5	C1U_C1	117
UCI3	-128.1 ± 3.0	Cl ₂ U-Cl	117
UC14	-200.3 ± 3.5	$Cl_3U - Cl$	101
UC15	-221.2 ± 4.0	Cl ₄ U–Cl	50

		$S_{T}^{*}(cal/$	'mol K)
Molecule	T (K)	Expt.	Calc. (trv)
UC1	2100	85.7±2.0	78.8
UCl ₂	2100	108.2 ± 2.5	103.2
UCL	2100	128.8 ± 3.0	123.8
UCI	650	117.8 ± 0.5^{a}	110.2
-	2100	145.4 ± 3.5	140.4
	740	128.5 ± 2.5	129.3

^aFrom UCl₄ sublimation data (Ref. 9).

J. Chem. Phys., Vol. 80, No. 3, 1 February 1984

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 137 189 170 231 Op: Sat 20 Dec 2014 15:22:48



FIG. 1. Trends in individual bond dissociation energies of the uranium halides.

DISCUSSION

There are no previous thermochemical measurements on the lower-valent uranium chlorides or indications as to expected bond energy patterns. In Fig. 1 the observed trends in BDE values as halogen ligands are added to the central uranium atom are shown for the U-F and U-Cl systems; the former are from our earlier studies,² while the latter are from the present work. Also shown are some preliminary BDE values on the U-Br system, also obtained in this laboratory. The differences in the U-F and U-Cl BDE patterns up through UX₄ are very striking, with no similarity whatever. However, both systems show the sharp decrease in bond strength with addition of the fifth halogen atom, evidence for the appreciable drop in the thermodynamic stability in passing from the tetravalent state to the higher valence states of uranium.

Although we have not determined $D(Cl_5U-Cl)$ in the present work, our results for $UCl_5(g)$ can be combined with a critically reviewed value for $UCl_6(g)^{10}$ to give for the reaction

$$UCl_{6}(g) = UCl_{5}(g) + Cl(g) .$$
⁽⁷⁾

 $\Delta H^{2}_{298} = D^{\circ}_{298}(\mathrm{Cl}_{5}\mathrm{U}-\mathrm{Cl}) = -221.2 + 29.0 - (-242.2) = 50.0$ kcal/mol. This value seems unreasonably high, since it shows $D(\mathrm{Cl}_{5}\mathrm{U}-\mathrm{Cl}) \sim D(\mathrm{Cl}_{4}\mathrm{U}-\mathrm{Cl})$. From the U-F system behavior, one would expect $D(\mathrm{Cl}_{5}\mathrm{U}-\mathrm{Cl}) \sim 20$ to 30 kcal/mol. Although the tabulated enthalpy of formation of UCl_6(g) has a stated uncertainty of 3.4 kcal/mol, the value is based on several discordant determinations for UCl_6(s) and on uncertain sublimation data. Therefore, the above discrepancy probably should not be taken too seriously at this point. We are considering the feasibility of electron impact measurements of the processes UCl_6 + $e \rightarrow \mathrm{UCl}_5^+ + \mathrm{Cl} + 2e$ and UCl_5 + $e \rightarrow \mathrm{UCl}_5^+ + 2e$ to resolve the discrepancy.

Even more striking is the closely parallel behavior of the U-Cl and U-Br BDE patterns; the U-Br data are from preliminary analysis of measurements made in this laboratory with the same experimental techniques used in this work. It may be that the distinctly different BDE pattern in the U-F system can be accounted for on the basis of a significantly higher degree of ionic character in the fluorides. Although the experimental dissociation energy, D_0° of UF appears consistent with an electrostatic bonding model,² use of the dipole polarizability of U⁺ inferred from the UF calculation yields an electrostatic model value of $D_0^{\circ}(\text{UCl})$ that is too low by about 12 kcal/mol. This is further evidence for a difference in bond type. These are, of course, very qualitative arguments, and one needs to probe the charge distribution within these species to obtain a more satisfactory explanation for the BDE patterns.

The entropy correlations in Table VIII are helpful in estimating the size of the missing electronic contributions to the calculated functions. Interestingly enough, the experimental data indicate the electronic entropy of diatomic UCl at 2100 K to be about 6.9 cal/mol K, compared to a corresponding value of 7.8 cal/molK for atomic uranium at the same temperature. This is a reasonable result, consistent with the idea that the electronic level structure of atomic U is not appreciably split or altered by approach of the first chlorine ligand forming UC1. By comparison, the difference between experimental and calculated (trv) entropies for diatomic UF indicated an electronic entropy of about 6.8 cal/mol K at 2300 K, in close accord with that found for UC1. The entropy deficits of 5 cal/mol K for both UCl_2 and UCl₃ at 2100 K are also reasonable electronic entropies for these species, and should be very useful in refining models for estimating the electronic level structures of the U-Cl and other uranium halide species.

For UCl₄, the more accurate entropy value obtained from the sublimation studies is preferred, although both experimental values are higher than the calculated (trv) results based on a regular tetrahedral geometry. It appears that a substantial portion of the discrepancy (3.56 cal/mol K) can be accounted for by assigning UCl₄ the less-symmetrical C_{2v} structure suggested by electron diffraction studies.¹¹ The sequence of electronic levels inferred from the optical spectrum of UCl₄ vapor¹⁴ yields electronic entropies of 2.9 and 4.0 cal/mol K at 650 and 2100 K, respectively. A detailed discussion of the vapor thermodynamics and the implications regarding spectroscopic and molecular constants will be given in a separate publication on the UCl₄ sublimation studies. For UCl₅, the experimental value indicates at most a relatively small electronic entropy, in approximate agreement with expected trends in the electronic level structures that yield a maximum entropy contribution for the monohalide and a minimum for the valence-saturated hexahalide.

APPENDIX

The thermodynamic functions of the U–Cl molecular species were needed in correcting reaction enthalpies to standard reference temperature and for certain en-

TABLE IX. Estimated spectroscopic constants.

Molecule	$I \times 10^{39} (g \mathrm{~cm}^2)$	σ	$\omega_i(\text{cm}^{-1})$
UCI	20.0	1	900
001	32.0	1	300
UC1 ₂	23.4	2	310, 300, 80
	43.2		
	66.6		
UC13	57.4	3	300, 250(2), 130,
	57.4		100(2)
	98.8		
UC14	100.5	12	330(4), 110(5)
	100.5		
	100.5		
UC 15	110.4	4	390, 350(2), 340,
	110.4		330, 120(3), 110(2),
······	147.2		100, 80

tropy comparisons. Functions were also needed for third law calculations involving UC1. The spectroscopic and molecular constants used in calculating these functions were selected or estimated as described below. No attempt was made to estimate the missing electronic levels, since these contributions are assumed to cancel, in first approximation, in the enthalpy calculations, as noted in the text. All species other than UC1₄ were assumed to have a common U-Cl distance of 2.50 Å, close to that observed in the tetrachloride (2.53 Å).¹¹ The resulting moments of inertia (*I*), rotational symmetry numbers (σ), and vibrational frequencies (ω) are summarized in Table IX.

UCI

The vibrational frequency was estimated from the stretching frequencies in UCl_2^{12} and UCl_4^{14} .

UCI₂

A nonlinear structure with 100° apex angle was assumed, as suggested from matrix IR studies.¹² The stretching frequencies were taken from the matrix work, while the bending frequency was estimated from the assigned value in $PbCl_2$.¹²

UCI₃

A pyramidal geometry predicted from semiempirical correlations¹³ was adopted, with assumed Cl-U-Cl angle of 110°. The vibrational frequencies were estimated to be close to those of pyramidal $BiCl_3$.¹⁸

UCI₄

A tetrahedral geometry was assumed for simplicity, although there is mixed evidence for both T_d and C_{2v} symmetries. The difference has only a minor effect on the enthalpy corrections. However, the sublimation entropy data⁹ to be published later clearly favor the C_{2v} structure. The frequency assignment was estimated from two observed IR bands¹⁴ and from the assigned values in PbCl₄.¹⁹

UCI₅

Both the square pyramidal geometry and the estimated frequency assignment were based on the predicted molecular constants of UF_5 .¹⁵

- ¹D. L. Hildenbrand, J. Chem. Phys. 66, 4788 (1977).
- ²K. H. Lau and D. L. Hildenbrand, J. Chem. Phys. 76, 2646 (1982).
- ³D. L. Hildenbrand, J. Chem. Phys. 48, 3657 (1968); 52, 5751 (1970).
- ⁴D. L. Hildenbrand, Int. J. Mass Spectrom. Ion Phys. 4, 75 (1970); 7, 255 (1971).
- ⁵J. M. Dyke, N. K. Fayad, A. Morris, I. R. Trickle, and G. C. Allen, J. Chem. Phys. 72, 3822 (1980).
- ⁶JANAF Thermochemical Tables, Natl. Stand. Ref. Ser., Natl. Bur. Stand. 37 (U.S. GPO, Washington, D.C., 1971).
- ⁷F. L. Oetting, M. H. Rand, and R. J. Ackermann, *The Chemical Thermodynamics of the Actinide Elements and Compounds, Part* 1, The Actinide Elements, International Atomic Energy Agency, Vienna, 1976.
- ⁸P. A. G. O'Hare, Argonne Natl. Lab. (private communication).
- ⁹R. D. Brittain and D. L. Hildenbrand (unpublished data).
- ¹⁰V. B. Parker, Natl. Bur. Stand. Rep. NBSIR 80-209, July, 1980.
- ¹¹Y. S. Ezhov, P. A. Akishin, and N. G. Rambidi, Zh. Strukt. Khim. 10, 571 (1969).
- ¹²J. W. Hastie, R. H. Hauge, and J. L. Margrave, High Temp. Sci. 3, 56 (1971).
- ¹³M. C. Drake and G. M. Rosenblatt, J. Electrochem. Soc. **126**, 1387 (1979).
- ¹⁴J. B. Gruber and H. G. Hecht, J. Chem. Phys. 59, 1713 (1973).
- ¹⁵B. J. Krohn, W. B. Person, and J. Overend, J. Chem. Phys. 65, 969 (1976).
- ¹⁶R. W. Solarz, C. A. May, L. R. Carlson, E. F. Worden, S. A. Johnson, J. A. Paisner, and L. J. Radziemski, Jr., Phys. Rev. A 14, 1129 (1976).
- ¹⁷H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, J. Phys. Chem. Ref. Data 6, Suppl. No. 1 (1977).
- ¹⁸S. Bhagavantam, Indian J. Phys. 5, 66, 86 (1930).
- ¹⁹R. J. H. Clark and B. K. Hunter, J. Mol. Struct. 9, 354 (1971).