Controversy on the First Ionization Potential of PuO_2 (Nearly) Settled by New Experimental Evidence

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The first ionization potential of the PuO_2 molecule was for a long time considered to be 4−5 eV higher than that of UO_2. This feature could hardly be explained by the most advanced "ab initio" calculations, which, on the other hand, provide satisfactory results for other actinide oxides. From recent experiments, performed with different techniques, a lower ionization potential of approximately 7 eV was measured, in better agreement with the theoretical predictions. Our recent experiments, where thermally produced ions were measured, make it possible to formulate an accurate relation between the ionization potential of PuO_2 and that of PuO: $I_0(PuO_2) = I_0(PuO) + 0.42 \pm 0.005$ eV. The present uncertainty of I0(PuO) leads to the final assessment, $6.2 \leq I_0(PuO_2) \leq 6.6$ eV, whereby the upper limit is more in line with the aforementioned recent measurements. Considering the still existing uncertainties, one can conclude that these results remove major doubts on the validity of the current theoretical predictions. However, the very small ionization cross section of PuO_2 by low-energy electron collisions, which led to the previous spurious assessment of the ion appearance potential, has still an unexplained cause.

Introduction

Five years ago, we published the results of a series of measurements of the first ionization potential of uranium and plutonium oxides.[1] Our practical objective was to determine the mass spectrometry (MS) signature of actinide-bearing molecules effusing at high temperatures from a Knudsen cell. The appearance potential of ions and ionic molecular fragments was detected by stepwise increasing the ionizing electron energy in the MS source. For all species, for which previous data[2] were available, a good agreement was found with the recommended values. By simple subtraction from the appearance potential thermal excitation effects and achromatism effects in the electron beam, the precision of the deduced ionization potential for the ions U^+, UO^+, UO_2^+, and UO_3^+ was better than 0.5 eV.

The measured first ionization potential of PuO_2(g), however, whose magnitude (10.1 eV) was found to be 4−5 eV above that of UO_2(g), represented a noteworthy result. In the above-mentioned article, we emphasized the similarity of the ionization potential of PuO_2(g) with that of UO_3(g). As for the rest, this trait was not considered as extraordinary and we had no reason to disbelieve its soundness, for the TPIS and TCS tables[3,4] (calculated from the IVTANTHERMO database) reported at that time for PuO_2^+(g) a formation enthalpy at 298 K ranging from 493 to 503 kJ mol^{-1}, which, in connection with the recommended formation enthalpy of PuO_2(g), implies an ionization potential of approximately 9−10 eV. Yet, the experimental data supporting this value consisted of a few measurements carried out at Argonne and shortly published at the end of the 1960s on an ANL annual report.[5] It was, however, Gurvich who, after examining the IR spectra measured by Green and Reedy,[6] provided a consolidation of the thermodynamic data of PuO_2^+ [4] that have never been questioned over the last 2 decades until recently.

In the meantime, an accurate evaluation of the ionization potential of several actinide oxides was carried from a detailed analysis of the energy states predicted by advanced theoretical models.[7,8] While the theoretical results were consistent with the experimental data of most of the examined oxides, it soon appeared that the models would have hardly been able to reproduce an ionization potential of PuO_2(g) exceeding by 4−5 eV that of UO_2(g).[9] By considering the strong disagreement with the experiment, we felt a check of this latter to be necessary.

New experiments were carried out at the Institute Tecnológico e Nucleare, Sacavém (Pt), in cooperation with the Oak Ridge NL,[10] where the ionization energy of PuO_2(g) was measured by electron transfer (dioxide ions were produced by oxidation of laser-desorbed Pu^+(g)). The ionization potential resulted to be 7.03 ± 0.12 eV, a value nearer to that of UO_2 and more in line with the results of the current ab initio calculations.

These data are obviously questioning the validity of the previous experimental measurements. The issue was discussed at the 11th STNM,[11] where we have been asked to consider whether our experimental results could have been spuriously affected by some uncontrolled effect.

Repeated Measurement of the Appearing Potential

We first repeated some of the previous experiments, measuring the ionization curve of PuO_2 of a molecular vapor beam directly effusing into a mass spectrometer from a Knudsen cell heated at approximately 2500 K. Confirming what we observed in the past, we see that the ion current curve vs the electron accelerating potential (Figure 1) in the MS ion source exhibits an atypical trend compared with that of atomic and simple molecular standards, for instance, of nitrogen monoxide (Figure 2). [The following ions were used as standards to check the adequacy of the mass spectrometer setup for IE measurements: Ag^+, Xe^+, H_2O^+, NO^+, Kr^+, Ne^+, Ag^{2+}, Xe^{2+} , Kr^{2+}, $Ne^{+\,+}$, and He^+. In the case of gases, the evaluated absolute ionization cross sections were in agreement with recommended data.] In fact, while in most cases the linear extrapolation of the ionization current to zero can be carried out by fitting the experimental values up to more than one-third of the maximum, that of

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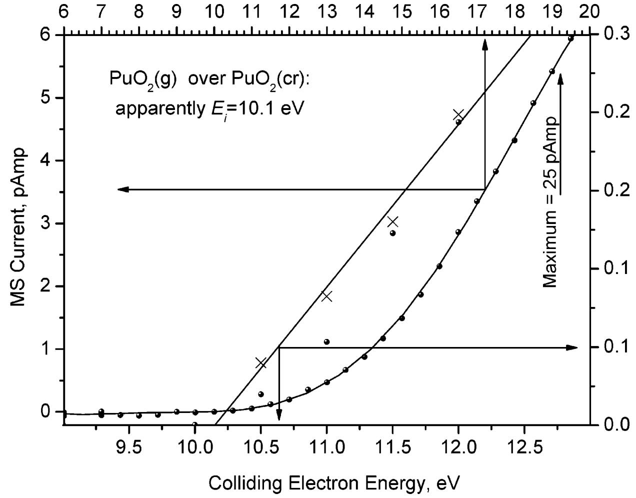

Figure 1. Ionization curve of PuO_2 equilibrium vapor over stoichiometric crystalline plutonium dioxide at 2500 K. The *x*-axis at the top corresponds to the complete curve, and that at the bottom, to the enlarged segment.

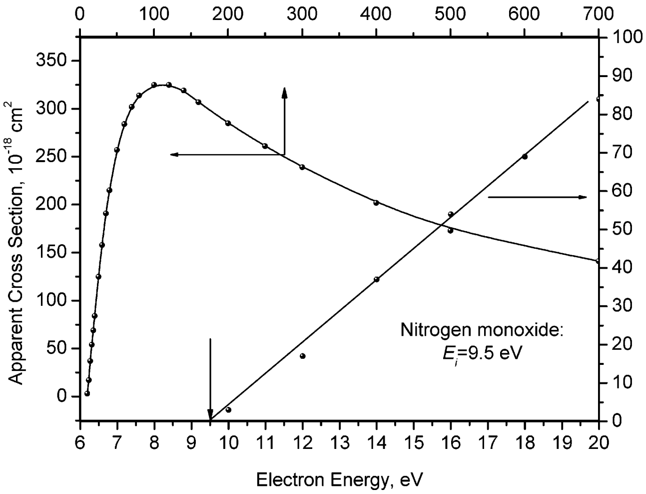

Figure 2. Measured ionization cross section of nitrogen monoxide.

plutonium dioxide shows a continuous decrease in slope down to a full-scale value 3 orders of magnitude lower than the maximum. A reasonable extrapolation of this "tail" (Figure 1) confirms the previously assessed value of 10.1 ± 0.1 eV for the ionization potential of PuO_2.

We have then used different sintered mixed oxides $(U_{1-y}Pu_y)O_2$ to obtain a direct comparison between the ionization of $UO_2(g)$ and $PuO_2(g)$ (at 2500 K the actinide stoichiometry in the equilibrium vapor differs from that of the solid by less than 10%). The result was the same: compared with that of UO_2^+(g), the curve of the PuO_2^+(g) current as a function of the colliding electron energy was apparently shifted of approximately 4−5 eV toward higher energies (Figure 3). In the course of repeated experiments, linear extrapolation of the ion current to 0 over a 300 fA range resulted once more in an appearance potential between 10.0 and 10.4 eV (Figure 3), with a standard deviation of 0.15 eV.

From a phenomenological point of view, however, the observed difference of orders of magnitude in the ion currents of PuO_2^+ and UO_2^+ at low electron collision energies could not be attributed to effective cross sections, as long as these were interpreted as some kind of molecular sizes. [In Born's approximation the ionization cross section is expressed as the product of a function of the colliding electron velocity and the square of a length representing an effective average of the electron/target interaction distance. For mass spectrometry applications such formalism is generally satisfactorily used to calculate the ionization yield of simple species.] The conjecture that PuO_2 has a significantly higher ionization threshold than UO_2 seemed thus corroborated. There was, however, a quality limit in the PuO_2^+ current measurements due to their relatively small dynamic range above the MS noise.

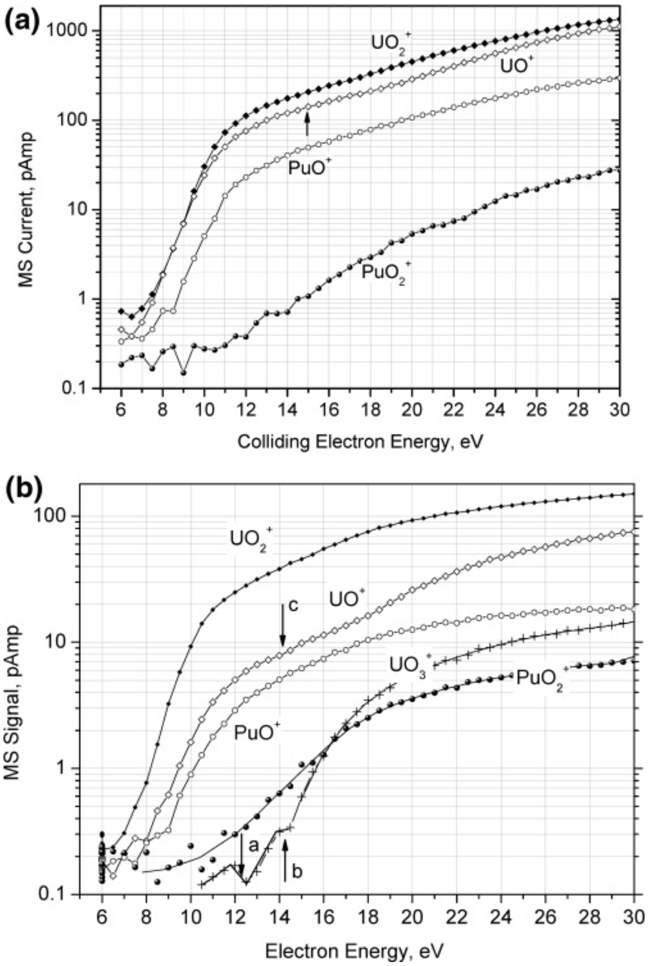

Figure 3. (a) Ionization curves of UO_2 and PuO_2 over a stoichiometric mixed oxide of composition $(U_{0.8},Pu_{0.2})O_2$. It can be seen that above 14 eV the ion current of UO^+ increases in slope due to a substantial contribution from a fragmentation reaction of UO_2 (see Table 3); this effect is much weaker for PuO^+ (see Figure 5a), whose parent PuO_2 preferentially dissociates in neutral fragments. The situations change at higher energies where the curve of PuO_2 maintains a slightly larger slope and eventually crosses that of PuO at approximately 90 eV. (b) Ionization curve of a mixture of slightly hyperstoichiometric UO_2 and PuO_2. Here the curve of UO_3 is also plotted. Arrows a−c indicate the position of three dissociation thresholds, respectively for $UO_3 \rightarrow UO_2^+ + O + e$, $UO_3 \rightarrow UO^+ + O_2 + e$, and $UO_2 \rightarrow UO^+ + O + e$.

New Type of Experiment and Discussion

We then raised the Knudsen-cell temperature up to near the melting point of pure stoichiometric PuO_2 to obtain a denser effusion beam. At these temperatures, however, we observed a considerable increase of the offset signals of the PuO^+ and PuO_2^+ masses. By switching off the MS ion-source electron beam, we eventually realized that signals were still detected, which were apparently due to ions produced thermally in the cell (Figure 4). At 2600 K, we measured in the vapor $[PuO^+]/[PuO_2^+] = 3 \pm 0.5$. At 2670 K, this ratio decreases to the more accurate value of 2.1 ± 0.03, as obtained from higher, more precise MS signals.

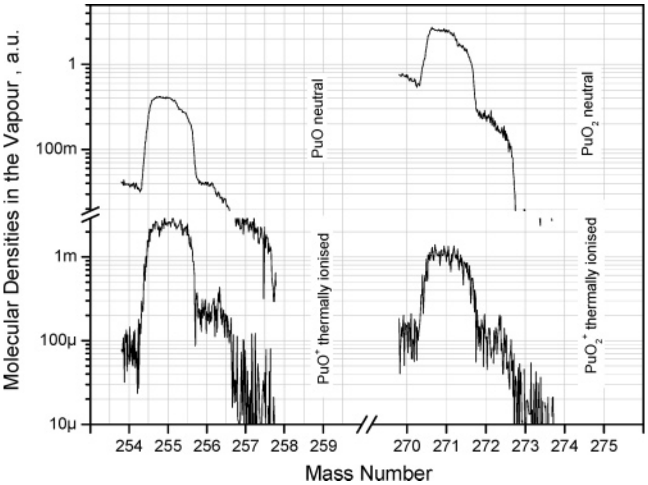

Figure 4. MS spectrometric signals of PuO^+ and PuO_2^+ measured over PuO_2(cr) at 2670 K. The abscissa represents the mass number. At the bottom are plotted the signals of the thermally produced ions, and at the top, those of the ions produced by electron collisions at 70 eV.

Since these ions were produced in the Knudsen cell, their concentration in the vapor was established by the thermodynamic equilibrium at the given temperature. We then fitted the enthalpy of formation of PuO_2^+(g) at 0 K to obtain the observed ratio of the equilibrium concentrations of PuO_2^+(g) and PuO^+(g) at 2670 K. To this purpose, we assumed two cases:

(A) The thermodynamic data of PuO(g), PuO^+(g) and PuO_2(g) were taken as reported in the TPIS and TCS tables, where an enthalpy $\Delta H(0) = 5.8$ eV is assigned to the reaction $PuO(g) \rightarrow PuO^+(g) + e^-$.

(B) The first ionization potential of PuO(g) was taken equal to 6.1 ± 0.2 eV, as found in refs 7 and 12, a value in agreement with that (6.6 eV) measured at 2500 K in ref 1 if the thermal excitation correction is applied. [In the collision ionization process the neutral molecules are expected to have the excitation state corresponding to the source temperature (2500 K in ref 1). The produced ions, however, may be found starting from the ground state. This incertitude is one of the sources of error in the evaluation of I_0.]

The expressions of $C_p = C_p(T)$ for all species involved were maintained in both cases as reported in the TPIS-TCS tables.

The relevant data of the equilibrium vapor calculations are listed in Tables 1 and 2.

As a first conclusion, there is no doubt that the thermal ionization measurements are fully incompatible with the hypothesis that the magnitude of the first ionization energy of PuO_2 be of 4−5 eV higher than that of PuO, the calculated ratio $[PuO^+]/[PuO_2^+]$ differing in this case by 6 orders of magnitude from the experimental value.

The results concerning cases A and B indicate the effect of the uncertainty in the first ionization potential of PuO on that of PuO_2.

For case (A), the corresponding value of the enthalpy of the reaction $PuO_2(g) \rightarrow PuO_2^+(g)+e^-$, at 0 K results to be 6.2 eV (6.7 eV at 2600 K).

For case B, the enthalpy values are somewhat higher: 6.5 eV at 0 K and 7.0 eV at 2600 K.

One might argue that the ionization potential of PuO of case B should bee the correct one since it is confirmed by two different experiments. Yet, at least for the datum of ref 1, the value of 6.6 eV was obtained with the same method as that producing a spurious result for PuO_2. Therefore, it remains the suspect that some error in excess might also have affected the PuO^+ appearance potential. This doubt is supported by some considerations on the thermodynamic properties of PuO. In fact, one can see that in case B the enthalpy of the dissociation reaction $PuO(g) \rightarrow PuO(g) + O$ is very near to that of the ionization $PuO(g) \rightarrow PuO^+(g) + e^-$ (see Table 3). This would entail, in collisions with electrons, a significant dissociation probability and a consequent lower ionization efficiency of PuO compared, for instance, with UO. This is, however, not the case, as one can see from the ionization curves of Figure 3.

Furthermore, we tried to detect the threshold for the reaction $PuO_2(g) \rightarrow PuO^+(g) + O + e^-$ occurring at collision energies at which sufficiently high and precise MS signals are produced. The ionization curve (Figure 5a) indicates a threshold just above 12 eV, in better agreement with the lower value of $I_0(PuO) = 5.8$ eV. Other dissociation thresholds have been measured (Figure 5b,c) confirming the consistency of the thermodynamic data of PuO(g) and PuO_2(g) (see also Table 3).

In case A, the resulting value of $I_0(PuO_2)$ is approximately 0.7 eV below that obtained in refs 7 and 11. The disagreement is not entirely due to the incertitude of I_0(PuO) since the difference $I_0(PuO_2) - I_0(PuO)$ can be evaluated from the MS measurements of the thermal ion emission with a greater precision. In fact, with a generous estimate of the error, it results

TABLE 1: Thermodynamic Data[a] for Thermally Ionized Vapor over PuO_2 Input and Output (Italic) of the Equilibrium Calculations

			equilib temp (K) for PuO(g)		equilib temp (K) for PuO_2(g)	
param	type	case	0	2670	0	2670
ΔH_f (kJ mol^{-1})	molecule		−60	−96	−411	−440
	positive ion	case A	500	511	*189*	*209*
		case B	528	542	*218*	*235*
ionization energy (eV)		case A	5.82[b]	6.31[b]	*6.24*	*6.75*
		case B	6.11[c]	6.5,[d,e] 6.6[e]	*6.53*	*7.01*

[a] The thermodynamic data for the two molecules have an accuracy of class F; i.e., the error of $\Delta H_f(0)$ is less than 30 kJ mole^{-1}. [b] NTIS-TPS (IVTANTHERMO) database. [c] Experimental value from refs 7 and 11. [d] Neutral molecule at 2670 K and ion at 0 K. [e] Experimental value from ref 1.

TABLE 2: Equilibrium Partial Pressures of Neutral Molecules and Ions over PuO_2: Case A

	vapor phase equilib over PuO_2 at 2670 K for ion species			
param	PuO	PuO^+	PuO_2	PuO_2^+ [a]
equilib pressure (Pa)	13.7	2.01×10^{-2}	86.7	9.83×10^{-3} (3.20×10^{-9})
$p(PuO^+)/p(PuO_2^+)$(calcd)			2.04 (1.49×10^6)	
$p(PuO^+)/p(PuO_2^+)$(expt)			2.10 ± 0.03	

[a] The figures in parentheses correspond to an assumed PuO_2 ionization energy of 10 eV.

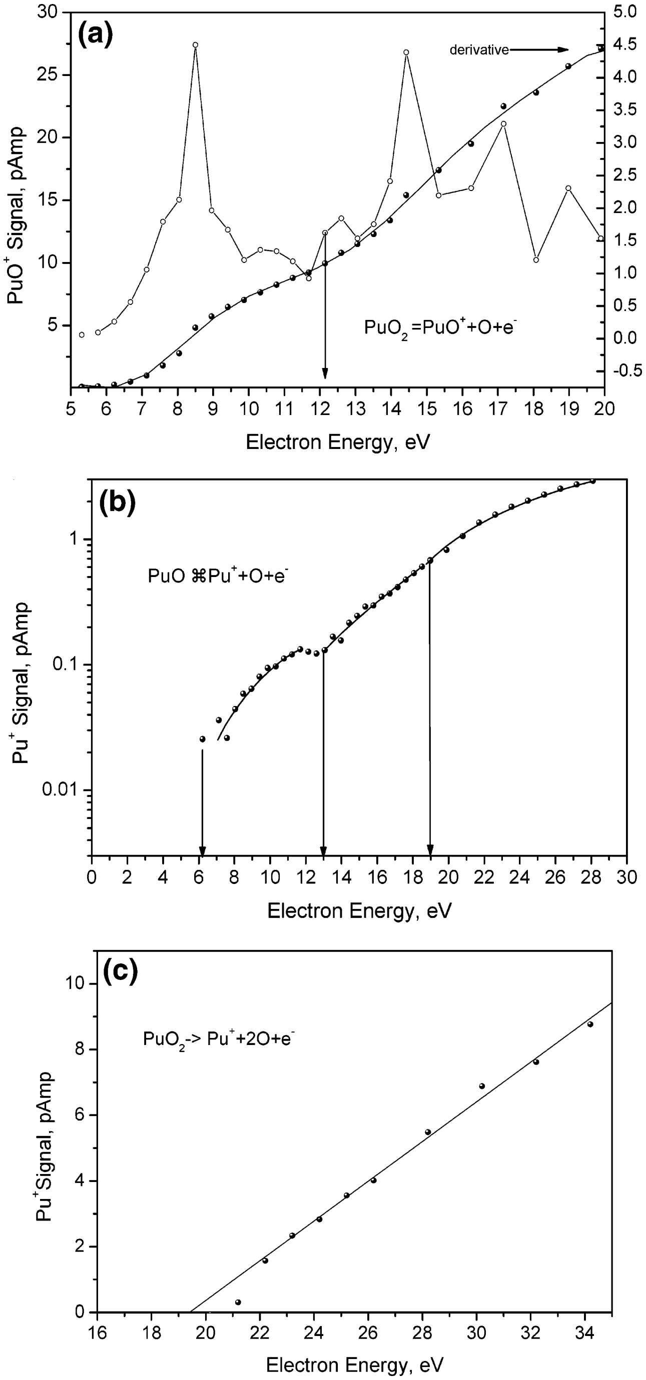

Figure 5. (a) Ion current of PuO$^+$ as a function of the colliding electron energy. A contribution from the dissociation reaction of PuO_2 is appearing just above 12 eV. The segmented line represents the derivative of the ionization curve. (b) Ion current of Pu$^+$ as a function of the colliding electron energy, showing the contribution from the dissociation reaction of PuO above 13 eV. (c) Ion current of Pu$^+$ as a function of the colliding electron energy, showing the contribution from the dissociation reaction of PuO_2 above 19.2 eV. The curve was obtained by subtracting from the total ionization curve those due to direct ionization of Pu and to the dissociation of PuO.

that

$$I_0(PuO_2) = I_0(PuO) + 0.42 \pm 0.005 \text{ eV}$$

Conversely, if the difference in the two ionization energies were 0.9 eV, as reported in refs 7 and 11, the equilibrium ratio of $[PuO^+]/[PuO_2^+]$ would be at least five times larger than that measured, irrespective of the value of I_0(PuO) within an uncertainty range of the order of 1 eV.

TABLE 3: Enthalpy (eV) of the Dissociation and Ionization Reactions of Gaseous Uranium and Plutonium Oxides at 298 K

$UO_3 \rightarrow UO_2 + O$			5.93
$UO_2 \rightarrow UO_2^+ + e^-$			5.9−6.1
$UO \rightarrow UO^+ + e^-$			6.0−6.1
	$PuO \rightarrow PuO^+ + e^-$	case A	5.9
		case B	6.2
	$PuO_2 \rightarrow PuO + O$		6.23
	$PuO_2 \rightarrow PuO_2^+ + e^-$	case A	6.3
		case B	6.6
	$PuO \rightarrow Pu + O$		6.8
$UO \rightarrow U + O$			7.83
$UO_2 \rightarrow UO + O$			7.87
	$PuO_2 \rightarrow Pu + O_2$		7.9
$UO_3 \rightarrow UO + O_2$			8.62
$UO_3 \rightarrow UO_3^+ + e^-$			10.1
$UO_2 \rightarrow U + O_2$			10.52
	$PuO_2 \rightarrow PuO^+ + O + e^-$	case A	12.1
		case B	12.4
	$PuO \rightarrow Pu^+ + O + e^-$		13.0
$UO_2 \rightarrow UO^+ + O + e^-$			14.0
	$PuO_2 \rightarrow Pu^+ + 2O + e^-$		19.2

In this context, the accuracy of $I_0(PuO_2)$ depends on two quantities: the error of I_0(PuO) directly affecting eq 1 and the enthalpy change, $\Delta H_r(0)$, of the reaction PuO(g) → Pu(g) + O(g) on the value of which a preference for case A is justified. In the TPIS tables, to the former is given the accuracy class VI-G and to the latter class VI-F. This means that the accuracy of I_0(PuO) is worse than 0.3 eV while the enthalpy of the dissociation reaction of PuO has an error of less than 0.3 eV. Only supposing a possibly higher I_0(PuO), one might reproduce the value of $I_0(PuO_2)$ of refs 7 and 11. However, to not to incur a fortiori in the arguments in favor of case A, also the dissociation energy of PuO should be assumed to lie at the top of its uncertainty interval (±0.3 eV). We might then arrive to the best agreement with the data of refs 7 and 11 by assuming

$$\Delta H_r(0)[PuO(g) \rightarrow Pu(g) + O(g)] = 7.1 \text{ eV}$$

$$I_0(PuO) = 6.2 \text{ and } I_0(PuO_2) = 6.6 \text{ eV}$$

Notes on the Ionization Cross Section of U and Pu Oxides

While the ionization potential of PuO_2 was definitively found to be close to that of UO_2, in conformity with theoretical predictions, we are still confronted with the cause of its relatively low ionization cross section in the upper vicinity of the ionization potential. Comparison of the ionization curves of UO_2 and PuO_2 excludes simple phenomenological explanations, since at sufficiently high collision energies (>80 eV) the ionization curve of PuO_2 in Figure 3 reaches and slightly overtakes that of PuO.

Actually, inelastic collisions of electrons with molecules compared with collisions with atoms manifest in a much greater variety of events, ranging from complex energetic relations in dissociative transitions to negative ion formation by electron capture. Furthermore, the increasing sensitivity of advanced ion-detecting methods entails in some sense an intrinsic indefiniteness in molecular ionization potentials. In this context, the relationship between the appearance potential and the ionization potential (defined here as the difference between the energy of the ground state of the molecule and molecular ion) is not as simple as in atomic scattering models.

Actually, in the context of the available ionization curves of molecules, the behavior of PuO_2 is not exceptional. For instance, the comparative trend of the ionization curves of UO_3 and UO_2 displays a close analogy with that of PuO and PuO_2, whereby in the former case predominant fragmentation of UO_3 is clearly detected at collision energies just above the UO_3^+ appearing potential.[1] [This feature deserves further investigation and might lead to a possible revision of the UO_3 ionization potential.] Some light on the inelastic collision processes in the examined molecules is cast by scrutiny of their thermochemical properties reported in Table 3, where the first ionization energy and the dissociation-reaction enthalpy at 298 K of UO_x(g) and PuO_x(g) are listed in ascending order. One can see that PuO_2 and UO_3 have dissociation reactions whose enthalpy is near or below the ionization energy. Therefore, one can understand that in collisions with relatively slow electrons the probability of forming an ion is small, as ionization takes place only for a restricted range of impact parameters for which an external electron is given a favorable momentum to be ejected far from the target molecule.

On the other hand, for low collision energies, cross sections for dissociative attachment can vary from orders of magnitude larger than cross sections for positive ion formation (for molecules of high electron affinity) to values that are several orders of magnitude lower (for molecules of low electron affinity). To the former class of molecules most likely belongs UO_3 while for PuO_2 a similar property can be only conjectured. Both theory and experimental methods are not yet sufficiently developed for a quantitative study of these kinds of inelastic collisions;[13] however, a comparison of the electron affinity of these two molecules would be in this respect instructive.

The electron affinity of PuO_2 is so far estimated to be equal to that of UO_2 (-0.94 eV).[3] Direct experimental data are, however, not available. If one considers, on the other hand, that UO_3, whose electron affinity estimate is around -2 eV, has also a very low ionization cross section, one can infer that PuO_2 should lie with its electron affinity nearer to UO_3 than to UO_2. This would imply that deduction of the ionization threshold of UO_3 from the appearance potential of its positive ion might also require a revision. [The UO_3 electron affinity was also calculated by Gurvich.[3] As for the electron affinity of UO_2, he deduced his estimate from corresponding electron affinities of different tetra- and hexafluorides. It is, however, worthwhile noting that in a previous edition of his tables he gave $A_0(UO_3) = 5.2$ eV.]

In conclusion, independently of the value of its ionization potential, the ionization cross section of PuO_2 is posing once more the question of the different features of the 5f electrons in the molecular bonding of actinide oxides. Measurements of negative ion formation in the equilibrium vapor may provide useful evidence on the type of bonding. Such measurements have been especially recommended in the context of phase diagram and equation of state models: this issue might give one more reason to undertake appropriate experiments in this direction.

Conclusions

New experiments have shown that the ionization energy, I_0, of PuO_2(g) is substantially lower than that previously deduced from the appearance potential of PuO_2^+ in mass spectrometric measurements. The ionization energy was eventually found to be only 0.42 eV higher than that of PuO(g). By assuming the current thermochemical properties of PuO(g) of the IVTAN-THERMO database, the value of I_0(PuO) more consistent with other available data is 6.2 eV, and hence $I_0(PuO_2)$ results to be 6.6 eV. This latter is 0.4 eV lower than that recently found by other authors.

The measured ionization cross section of PuO_2(g) is much lower than that of UO_2(g). This is due to alternative channels in the energy exchanges during collisions, which cause molecule dissociation and diminish the sharpness or even remove the discontinuity across the ionization threshold. Despite the high sensitivity of the methods adopted to detect ion formation, a great uncertainty in the experimental evaluation of the ion appearance potential is still faced.

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