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Absolute intensities of infrared-active fundamentals and combination bands of gaseous PuF_6 and NpF_6

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Results are presented for the absolute integrated molar absorption coefficients of the infrared-active fundamental and binary combination bands of PuF_6 and of NpF_6 between 1400 and 450 cm^{-1}. The low resolution band contours of the combination bands $\nu_1 + \nu_3$, $\nu_2 + \nu_3$, $\nu_3 + \nu_5$, $\nu_2 + \nu_6$, and $\nu_2 + \nu_4$ are discussed. From band center positions, the six harmonic wave numbers were obtained and Coriolis constant ζ_i ($i = 3, 4, 5$, and 6) estimated. For PuF_6, the six normal mode vibrations appear to group into one "local mode" stretching at a mean value of 589 ± 50 cm^{-1} and one local mode bending at 195 ± 5 cm^{-1}. The role of the heavy central atom and the magnitudes of the vibrational force constants are discussed in comparison with UF_6. The measured intensity for ν_3 is discussed in comparison with previously predicted values.

INTRODUCTION

Although the infrared spectra of a number of gaseous hexafluorides have been studied extensively, there is relatively little information available for neptunium and plutonium hexafluorides. The infrared spectra have been reported and assigned previously.[1,2] Here we would like to report a study of the absolute integrated molar absorption coefficients of the infrared-active fundamental and binary combination bands of NpF_6 and PuF_6 in the region from 450 to 1400 cm^{-1}. These spectra provide an interesting comparison with the corresponding spectrum for UF_6, as discussed below. The results provide additional information about vibrational properties and structures of hexafluoride molecules. Finally, these data provide an extension of the tests of the intensity predictions given previously,[3,4] extrapolating now from CH_3F all the way down the Periodic Table to PuF_6.

EXPERIMENTAL PART

PuF_6 studies

The sample of PuF_6 was prepared from reaction of PuF_4 with fluorine. Its isotopic composition was largely $^{239}PuF_6$. The sample was purified by trap to trap distillation. Impurities (HF, CF_4, SiF_4, and probably F_2) could be monitored by their infrared spectra; purification by trap to trap distillation was continued until no further changes occurred in the spectrum. Even so, there is some possibility of contamination of the PuF_6 by noninfrared active impurities such as F_2 or N_2, but since HF concentrations were reduced below 0.1%, we expect very low concentrations of other impurities.

The infrared spectrum was measured with a Nicolet MX-1 Fourier transform infrared (FTIR) spectrometer. These results were analyzed using the QUANTITATION program supplied with this instrument to obtain the integrated intensities reported here. The process was calibrated by measuring the intensities for UF_6 and comparing with previous results[5] (see below). Pressure measurements were made with an MKS Baratron. The gases were handled in a nickel vacuum line that had been preconditioned by overnight exposure to PuF_6 (or UF_6) before measurements were made. The cell was 5.6 cm in length with KCl windows, which did not react with the sample. The cell was contained in a dry box and viewed by the spectrometer through a bubble in the bottom of the dry box. The space between the cell and outer walls (and KCl windows) of the bubble was flushed with dry He gas.

With the evacuated cell in place, the background spectrum was obtained at 1 cm^{-1} resolution by scanning from 4000 to 450 cm^{-1}, where the KCl windows begin to absorb. The cell was then filled with PuF_6 to the desired pressures (from 1 to 3 Torr for the strong ν_3 fundamental up to about 80 Torr for the combination bands) and scanned at 1 cm^{-1} resolution. For use with the QUANTITATION program, another PuF_6 sample at different pressure could be scanned and data stored as the reference spectrum. The QUANTITATION program then integrated the area under a plot of absorbance $[\log_{10}(I_0/I)]$ vs wave number (cm^{-1}) to obtain the integrated area, which could then be compared with the reference spectrum.

The absolute integrated molar absorption coefficient A (or "integrated intensity") of each band was then obtained by

$$A = (2.303/100\,Cl)\int \log_{10}(I_0/I)d\nu. \quad (1)$$

Here A is in units of km mol^{-1}; 2.303 converts from the common to natural logarithm; C is concentration in mol/ℓ $[C = p(\text{atm})/RT(K)]$, where the gas constant, $R = 0.082\,06$ l atm K^{-1} mol^{-1}); l is the path length in cm; and 100 converts A to km mol^{-1}. The temperature T is the temperature of the gas in the cell when the pressure is measured; for these measurements, $T = 296$ K. The absorption for these bands is broad and nearly continuous due to numerous overlapping hot bands, so it is not necessary to pressurize the sample to pressure-broaden rotational fine structure. No inert gas was added to our samples.

In plotting out the resulting spectra, the wave number

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scale and the absorbance scales can be expanded as desired for optimum integration. In our case, we expanded until the noise, or steps in data, limited the result. The intensity of the ν_3 fundamental is so large compared to that of the combination bands that a survey spectrum (Fig. 1) shows only the fundamental absorption with very weak bands elsewhere. Hence in Fig. 2 we show expanded-scale plots of each individual band or region where absorption is observed at pressures of PuF_6 up to 80 Torr in the 5.6 cm cell.

NpF_6 studies

After completion of the PuF_6 work, it became possible also to repeat these same measurements for NpF_6. The experimental procedure was the same as described above for PuF_6, except that the measurements were made using a Nicolet SX-20 spectrometer and analyzed with the appropriate software for that spectrometer. A survey spectrum of the overtone region of the spectrum (600–1500 cm^{-1}) for NpF_6 is nearly identical with that for PuF_6. The similarity is striking, indeed.

RESULTS

Because of the similarity in the spectra for NpF_6 and PuF_6 shown in Fig. 2, we shall discuss first the detailed comparison between PuF_6 and UF_6, and then consider the results for NpF_6. In all cases, we find that the latter are intermediate between the results for UF_6 and those for PuF_6, as might perhaps have been expected.

The frequencies and band shapes of the infrared bands of PuF_6 in Fig. 2 are very similar to the corresponding band shapes in UF_6, as can be seen by comparison with McDowell, Asprey, and Paine (Fig. 1 in Ref. 6). The corresponding spectrum for NpF_6 is nearly identical to that for PuF_6 except for small changes in wave number and intensity. The assignment of these absorption bands by comparison with UF_6 is straightforward, and the previous assignments[1,2] are confirmed here. The assignments, wave numbers, and band shapes are summarized in Table I. This table also summarizes the corresponding wave numbers for UF_6 for comparison. It should be noted that the $\nu_1 + \nu_3$ and $\nu_2 + \nu_3$ combination bands at 1250 and 1140 cm^{-1} for PuF_6 (and 1274 and 1154 cm^{-1} for NpF_6) have the shape characteristic for "normal" hexafluorides, with no indication of Jahn–Teller distortion[2] for all three molecules.

For the bands with *PQR* structure, the band origins of the fundamental $v = 0 \rightarrow 1$ transition are estimated by comparison with UF_6. Because of the similarity in band shapes for PuF_6 and NpF_6 with UF_6, we can expect similar values for the Coriolis constants for the three molecules. Estimating these from the *PR* separation (maxima) using the approximate equation

$$\Delta\nu_{PR} \cong -4B(1-\zeta)\left(\frac{kT}{Bhc}\right)^{1/2}, \qquad (2)$$

we find for the ν_3 fundamental transition of PuF_6 with $\Delta\nu_{PR} = 11.25\ cm^{-1}$ that $\zeta_3 = 0.18$, in very good agreement with the value for UF_6. We may assume that the Coriolis constants for PuF_6 and NpF_6 are the same (within our rather large error) as those for UF_6. The estimated *PR* separations are listed in Table I, compared with the observed values. For bands with only doublet structure we have assumed the interpretation indicated in Table I; i.e., the doublet is observed because one of the branches is missing, as indicated. Of course the precise interpretation of the band shape requires more detailed knowledge of the Coriolis constants than is presently known.

The vibrational constants for PuF_6 are summarized in Table II. Obviously this table cannot be as complete as was the corresponding table given for UF_6 by McDowell, Asprey, and Paine[6]; no Raman study has been made for gaseous NpF_6 or PuF_6. (According to Malm, Weinstock, and Claas-

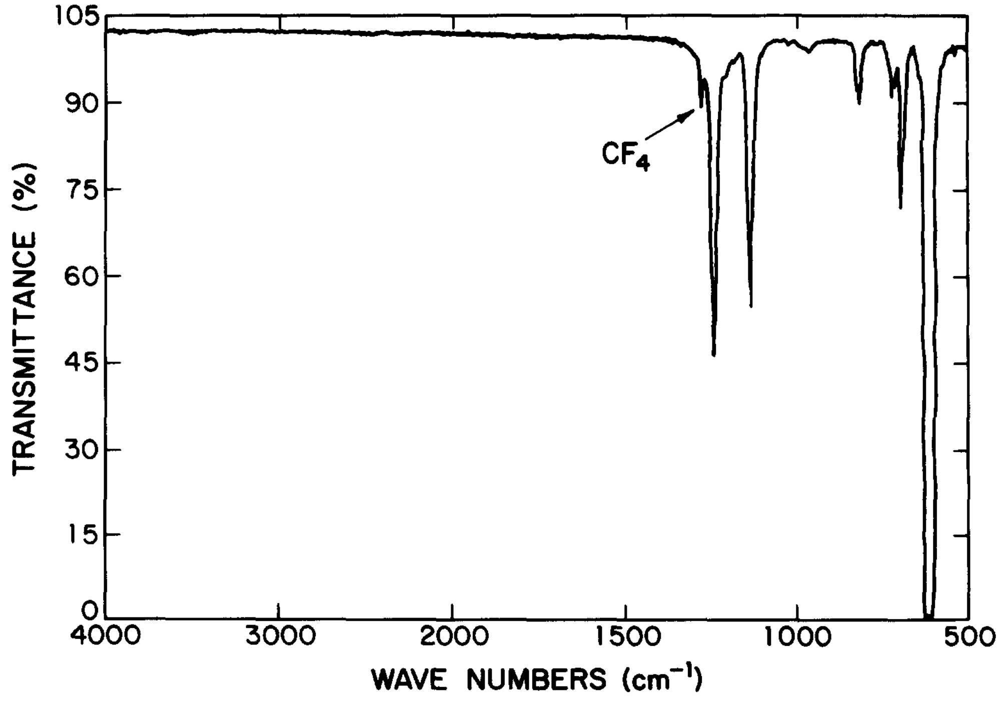

FIG. 1. Survey spectrum of a sample of PuF_6 (78 Torr in 5.6 cm cell), taken at 1 cm^{-1} resolution with Nicolet MX-1 FTIR spectrometer showing about 1% CF_4 impurity.

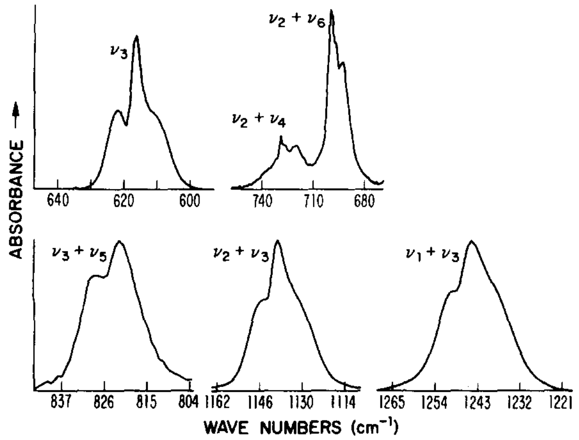

FIG. 2. The stronger infrared bands of PuF_6 at 296 K, as recorded at 1 cm^{-1} resolution with the Nicolet MX-1 FTIR spectrometer, 5.6 cm cell. All are measured with 7.8 Torr, except for ν_3, which was with 3.07 Torr.

sen,[1(b)] the colored PuF_6 suffered photochemical decomposition when the Raman study was attempted.) Hence, we have not attempted to include anharmonic constants in this table. The similarity between PuF_6 and UF_6 in Table I, however, suggests that the anharmonic constants are probably not drastically different for these two compounds, so that the harmonic frequencies for PuF_6 have been estimated accordingly.

In comparing the observed wave numbers for PuF_6 with those for UF_6, we are struck by the similarity. For PuF_6, the vibrations appear to be slightly more decoupled, with a local mode PuF stretch at a mean value of 589 ± 50 cm^{-1} and a local mode FPuF bend at 195 ± 15 cm^{-1}. (These values compare with 602 ± 55 and 176 ± 30 cm^{-1} for the corresponding UF_6 modes and with 597 ± 50 and 188 ± 18 cm^{-1} for NpF_6.) The PuF_6 stretching vibration is thus about 2% lower than for the UF stretch, indicating a slightly weaker PuF bond, and the bending mode is about 11% higher. Such decoupling can be expected to some extent for molecules with heavy central atoms, particularly between ν_3 and ν_4, but the near degeneracy of all three stretching and of all three bending modes implies also interesting relations between the force constants, as well.

Using the observed frequencies, we have calculated the symmetry force constants for PuF_6 by comparison with the treatment for UF_6. We have assumed that the very small interaction F_{34} is the same ($F_{34} = -0.05$ mdyn Å^{-1}) for both molecules. The results are summarized in Table III, which also lists for comparison the values for the valence force constants derived with a slightly different assumption by Weinstock and Goodman.[2] The changes in force constants when harmonic frequencies are used for PuF_6 are expected to be similar to those found for UF_6.[6] Clearly the force constants for NpF_6 will be intermediate between those for PuF_6 and UF_6.

The comparison of symmetry force constants in Table III is not very informative, except that those involving the PuF stretching modes are all somewhat lower, and those involving the FPuF bend all somewhat higher, than the corresponding UF_6 constants, as expected from the frequencies. On examining the valence force constants, we see that these changes appear as small changes in most of the force constants, but the significant changes appear to be the decrease in the stretching constants f_r and f_{rr} and the increase in the bending constant ($f_\alpha - f_{\alpha\alpha}$). In general, though, the bonding in PuF_6 and NpF_6, as measured by the vibrational properties, appears remarkably similar to that in UF_6.

VIBRATIONAL INTENSITIES IN PuF_6

We are particularly interested in measuring the absolute intensities of the PuF_6 and NpF_6 bands for comparison with UF_6. The values we have measured are presented in Table IV, where they are compared with the corresponding values we have measured in this experiment for UF_6. First of all, we note that the intensity measured here for ν_3 of UF_6 is in excellent agreement with the value previously reported.[5]

TABLE I. Infrared spectrum of PuF_6 from 450 to 1300 cm^{-1}.

Assignment[a]	PuF_6 $\nu(cm^{-1})$	NpF_6 $\nu(cm^{-1})$	Structure	Calculated[c] $\Delta\nu_{PR}(cm^{-1})$	Observed $\Delta\nu_{PR}(cm^{-1})$	$\nu(cm^{-1})UF_6$
$\nu_1 + \nu_3$	1248	1274	*PQR*	11.2	11.0	1294
$\nu_2 + \nu_3$	1143	1154	*PQR*	11.2	13.7	1160
$\nu_1 + \nu_4$	(830?)[b]	(845)[b]	(?)	9.5	···	853
$\nu_3 + \nu_5$	825	829	Doublet (*P* missing)	11.5	6.2 (*RQ*)	823
$\nu_2 + \nu_4$	725	725	Doublet (*Q* missing)	9.5	9.0	715
$\nu_2 + \nu_6$	702	699	Doublet (*R* missing)	20.5	7 (*PQ*)	677
ν_3	619	624	*PQR*	11.2	11.2	628

[a] This list includes all possible allowed binary combinations or difference bands in this region. A number of bands are expected from 300 to 425 cm^{-1}, plus the ν_4 fundamental at 201 cm^{-1}. A number of weaker ternary combinations and difference bands were observed in UF_6 at long path lengths (Ref. 6) and corresponding bands can be expected in PuF_6. However, this list includes *all* absorption bands observed for PuF_6 at 80 Torr in 5.6 cm cell.

[b] This band is not observed in PuF_6 or in NpF_6 and is presumably very weak or else overlapped by the stronger $\nu_3 + \nu_5$ absorption at 825 cm^{-1} (829 cm^{-1} for NpF_6).

[c] Calculated using Eq. (2), with $\zeta_1 = \zeta_2 = 0$, $\zeta_3 = 0.18$, $\zeta_4 = 0.30$, $\zeta_5 = 0.50$, and $\zeta_6 = -0.50$, as for UF_6.

TABLE II. Vibrational parameters for PuF_6.[a]

PuF_6	$i = 1$	2	3	4	5	6
i	A_{1g}	E_g	F_{1u}	F_{1u}	F_{2g}	F_{2u}
ν_i	627	524	619	201	206	178
ω_i	632 ± 6	530 ± 6	627 ± 6	201 ± 6	206 ± 6	178 ± 6
ζ_i	0	0	0.18	0.30	−0.50	−0.50
NpF_6						
ν_i	650	530	624	195	205	165
ω_i	655 ± 6	536 ± 6	632 ± 6	195 ± 6	205 ± 6	178 ± 6
ζ_i	0	0	0.18	0.30	−0.50	−0.50
$\nu_i(UF_6{}^b)$	667	534	626	186	200	143

[a] Units are cm^{-1}, except for the dimensionless ζ_i values. Uncertainties in ν_i estimated to be about $\pm 1\ cm^{-1}$ and about ± 10% in ζ_3 and ζ_4. The harmonic wave numbers ω_i are estimated by comparing the observed values (ν_i) with the values for UF_6 given in Ref. 6.

[b] For comparison, values for UF_6 from Ref. 6 are listed here.

Hence, we believe our experimental procedure is correctly calibrated.

Next, we note that the absolute intensities measured for the combination bands in UF_6 are not always the same as might be estimated using the relative peak height intensities given by McDowell, Asprey, and Paine.[6] We believe this result is to be expected, since the band widths for different bands are not necessarily the same.

We note that the integrated intensity of ν_3 in PuF_6 is about 0.70 that of ν_3 of UF_6. The intensities of combination bands in PuF_6 are comparable to those for the corresponding bands in UF_6 except for $\nu_1 + \nu_3$, which is almost twice as intense for PuF_6 as for UF_6, and for $\nu_2 + \nu_6$, which is more than twice as intense for UF_6 as for PuF_6. The latter result is almost certainly due to some Fermi resonance with ν_3, which will be much stronger in UF_6 than in PuF_6 because of the proximity of $\nu_2 + \nu_6$ ($677\ cm^{-1}$) to ν_3 ($628\ cm^{-1}$) in UF_6 compared to PuF_6 (702 to $619\ cm^{-1}$).

The most likely cause of the greater intensity of $\nu_1 + \nu_3$ in PuF_6 compared to that for UF_6 may be a larger value for the principal mechanical anharmonicity constant k_{133} contributing to the intensity [see Eq. (15) of Ref. 3]. This constant does not contribute to the intensities of other combination bands in Table IV, so they may not be expected to differ so much from the UF_6 values. This constant will affect the anharmonicity constant (particularly X_{13}), but probably would not change it much.

It is useful to express the intensity results in other units. For example, the intensity for ν_3 of PuF_6, $524\ km\ mol^{-1}$ $(RT \times 10^{-5}) = 127\ cm^{-2}\ atm^{-1}$ at $296\ K = 524\ (10^5/N_A)$ $= 8.70 \times 10^{-17}\ cm\ mol^{-1}$. Or we can calculate the Einstein A coefficient:

$$A_E = [A(\mathrm{km\ mol^{-1}})][\nu_0(\mathrm{cm^{-1}})]^2 \times (g_0/g_1)(8000\,\pi c/N_0)100 = 8.38\ \mathrm{s^{-1}}, \quad (3)$$

or the transition moment[4]

$$\mu_{01} = 0.3646[A(\mathrm{km\ mol^{-1}})/\nu_0(\mathrm{cm^{-1}})]^{1/2} = 0.335\ D = 0.0699\ \mathrm{eA}. \quad (4)$$

Finally, it is useful to give the apparent peak optical cross section. The apparent optical cross section σ_A for the Q-branch peak of ν_3 of PuF_6 at $616\ cm^{-1}$ is

$$\sigma_A = (1/Cl)\ln(I_0/I)_{\max} = 0.107\ \mathrm{Torr^{-1}\ cm^{-1}}$$

at $296\ K = 3.27 \times 10^{-18}\ cm^2\ molecule^{-1}$.

The intensities of NpF_6 in Table IV are either the same as or they fall in between the values for PuF_6 and UF_6. The value for the integrated intensity of ν_3 appears to vary smoothly from PuF_6 to NpF_6 to UF_6, with the value for NpF_6 closer to that for UF_6, just as was found for the wave number of ν_3. The interpretation of the change in intensity for $\nu_3 + \nu_6$ as due to Fermi resonance with ν_3 appears to be supported by the result for NpF_6.

DISCUSSION

The infrared spectra of gaseous PuF_6 and NpF_6 are remarkably similar to that for UF_6. Nevertheless, there are some differences. The frequencies are slightly different, indi-

TABLE III. Force constants (in mdyn $Å^{-1}$) for PuF_6, compared to those for UF_6 (using observed frequencies, ν_i).

Symmetry force constants[a]	PuF_6		UF_6[a]
$F_{11} = f_r + 4f_{rr} + f'_{rr}$	4.41		4.98
$F_{22} = f_r - 2f_{rr} + f'_{rr}$	3.08		3.19
$F_{33} = f_r - f'_{rr}$	3.62		3.74
$F_{34} = 2(f_{r\alpha} - f''_{r\alpha})$	(−0.05)		−0.05
$F_{44} = f_\alpha + 2f_{\alpha\alpha} - 2f''_{\alpha\alpha} - f'''_{\alpha\alpha}$	0.182		0.154
$F_{55} = f_\alpha - 2f_{\alpha\alpha} + f'''_{\alpha\alpha}$	0.119		0.112
$F_{66} = f_\alpha - 2f_{\alpha\alpha} + 2f''_{\alpha\alpha} - f'''_{\alpha\alpha}$	0.174		0.114
	PuF_6		
Valence force constants[a]	This work	WG[b]	UF_6
f_r	3.57	3.62	3.76
f_{rr}	0.22	0.22	0.30
f'_{rr}	−0.50	−0.80	0.02
$f_{r\alpha} - f''_{r\alpha}$	−0.02	+0.02	−0.02
$f_\alpha - f'_{\alpha\alpha}$	0.15	0.17	0.12
$f'_{\alpha\alpha} - f'''_{\alpha\alpha}$	0.03	0.02	0.01
$f_{\alpha\alpha} - f''_{\alpha\alpha}$	0.002	0.003	0.01

[a] From McDowell, Asprey, and Paine, Ref. 6; see this reference for definitions.

[b] From Weinstock and Goodman, Ref. 2.

TABLE IV. Absolute integrated molar absorption coefficients A (in km mol^{-1}) for bands in PuF_6 compared with those in UF_6.

Band (cm^{-1} in PuF_6)[a]	A^b PuF_6	A (NpF_6)	A (UF_6)	(UF_6) relative[c] peak intensity
Fundamentals				
ν_3, 619	524 ± 0.3	674 ± 10	750 ± 15 $(710)^d$	2000
ν_4, 201	···	···	···	100
Combinations				
$\nu_1 + \nu_3$, 1248	4.1 ± 0.2	3.3 ± 0.1	2.8 ± 0.04	4.1
$\nu_2 + \nu_3$, 1143	4.5 ± 0.3	4.1 ± 0.1	4.1 ± 0.03	4.7
$\nu_1 + \nu_4$ (830?)	(e)	(e)	0.2	0.7
$\nu_3 + \nu_5$ 825	0.75 ± 0.06	1.1 ± 0.1	1.1 ± 0.3	1.9
$\nu_2 + \nu_4$ 725	0.6 ± 0.05	0.5 ± 0.05	0.4	0.7
$\nu_2 + \nu_6$ 702	1.7 ± 0.05	2.6 ± 0.1	5.0 ± 0.5	8.9

[a] The wave number of the corresponding band in NpF_6 is given in Table I.

[b] The uncertainties listed are three times the standard deviation of the measurements.

[c] From McDowell, Asprey, and Paine, Ref. 6.

[d] From Kim and Person, Ref. 5.

[e] Overlapped by 825 cm^{-1} band.

cating that the force constants are somewhat different. The XF stretching constant f_r is about 5% smaller for the PuF bond than for the UF bond, and the FXF bending constant is about 25% larger for the FPuF bend than for the FUF bend with intermediate changes for NpF_6. Band shapes in PuF_6 are quite similar to those in UF_6 (at this relatively low resolution, at least), indicating that the Coriolis constants in PuF_6 are similar to those in UF_6. There is some indication from the relative intensities that at least one of the cubic anharmonicity constants (k_{133}) may increase regularly from UF_6 to NpF_6 to PuF_6.

In fact the largest difference in the vibrational properties of PuF_6 compared to UF_6 and NpF_6 appears to be in the intensity of the ν_3 fundamental. This value definitely decreases from UF_6 to NpF_6 to PuF_6 (where it falls to 0.70 of the value for UF_6). It is of some interest, then, to reexamine the predictions for this intensity that were made for UF_6[3,4] and to extend them to PuF_6.

Two different procedures were followed to estimate intensities for UF_6, both based on empirical observations indicating transferable intensity parameters. In the first, Fox and Person[4] had noted that the vibrational transition moments (μ_{01}) for ν_3 transitions in XY_4 and XY_6 compounds appeared to be transferable from molecule to molecule for constant Y types. Thus, the transition moment for ν_3 of the known XF_4 and XF_6 molecules appeared to be 0.33 ± 0.06 D. Later measurements suggest that 0.37 ± 0.04 D might be better, and subsequent measurements on UF_6 indicated that it was 0.385 D for that molecule (hence, on the high side). We see here that the values in PuF_6 (0.335 D) and NpF_6 (0.379 D) are also in this range, but that for PuF_6 is slightly on the low side while that for NpF_6 is very slightly on the high side. The indication is that this procedure for predicting intensities works very well even for PuF_6, and that the difference between ν_3 intensities for PuF_6, NpF_6, and UF_6 is just a normal sort of variation that might be expected.

The other procedure for predicting the intensities of ν_3 in XF_6 molecules is to use the idea of invariance of the effective charge ζ_F on the F atom. This concept was introduced by King, Mast, and Blanchette[7] for H atoms in predicting hydrocarbon intensities, and has been examined extensively by King.[8] It was introduced for XF_6 molecules by Person and Overend,[3] who predicted an intensity for ν_3 of UF_6 of about 400 km mol^{-1}. This value is obviously too low for UF_6, but the prediction applies also to ν_3 for PuF_6 as well as for NpF_6. The predicted value (400 km mol^{-1}) is in better agreement with the experimental intensity of ν_3 of PuF_6 (524 km mol^{-1}), but also does not agree for ν_3 of NpF_6 (674 km mol^{-1}). From this viewpoint, we conclude that intensity parameters for the F atoms do finally change as we go down the Periodic Table from C to S to U, Np, and Pu. Some of the possible reasons for these kinds of variations have been discussed by Person,[9] but it is still early in the theory of infrared intensities to be able to discuss variations of intensity of this magnitude (A in PuF_6 = 0.7 Å in UF_6) any more quantitatively.

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