Monatshefte für Chemie 110, 857—860 (1979)

**Monatshefte für Chemie**



# Normal Coordinate Treatment of Actinide(IV)-Hexabromides

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*(Received 21 October 1977. Accepted 11 November 1978)*

Molecular force field studies of hexabromo-thorates(IV) and -uranates(IV) have been carried out using four different force field models. Weighted least square adjustment has been used to fit the observed frequencies. Mean amplitudes of vibration have also been calculated at 0 °K and 298 °K. The trends of force constants and mean amplitudes have also been discussed.

*(Keywords: Force field; Mean amplitudes of vibration, hexahalides;* $ThBr_6$; $UBr_6$)

*Normal-Koordinaten Berechnungen an Actiniden(IV)-hexabromiden*

Es wurden für die Rechnungen an Hexabromo-thoraten(IV) und -uranaten(IV) vier verschiedene Modelle herangezogen. Die beobachteten Frequenzen wurden mittels gewichteter Kleinster-Fehlerquadrat-Methode angepaßt. Die Trends bei den Kraftkonstanten und den mittleren Amplituden der einzelnen Verbindungen werden diskutiert.

## Introduction

In a recent spectroscopic study the present author[1] has done a normal coordinate treatment (NCT) for hexahalides of the $XY_6$ type. *Brown* et. al.[2] have recorded the infrared and *Raman* spectra of actinide(IV) hexahalogeno complexes. Complete vibrational data of $ThBr_6^{-2}$ and $UBr_6^{-2}$ anions have only been reported. According to group theory the molecules of $XY_6$ type belonging to $O_h$ point group are expected to have six fundamentals, of which $\nu_1$, $\nu_2$, and $\nu_5$ give rise to *Raman* active and $\nu_3$ and $\nu_4$ are permitted in ir. The sixth fundamental $\nu_6$ is inactive in both ir and *Raman* spectra. Using the observed fundamental vibrations, NCT is attempted using orbital valence force field (OVFF), *Urey-Bradley* force field (*UB*FF), modified OVFF and modified *UB*FF models. Mean amplitudes of vibration of these ions have also been calculated at 0° K and 298° K.

0026-9247/79/0110/0857/$ 01.00

Table 1. *Observed and calculated frequencies in* $cm^{-1}$ *and corresponding force constants in* mdyn/Å *for hexabromides*

| Hexabromide | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ | $\nu_5$ | $\nu_6$ | $K$ | $H$ or $D$ | $F$ | $F'$ or $h$ | $k$ | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $ThBr_6^{-2}$ | | | | | | | | | | | | |
| Obs | 181 | 150 | 179 | 81 | 82 | — | — | — | — | — | | 1 |
| OVFF | 177 | 144 | 188 | 80 | 83 | 53 | 0.86 | —0.01 | 0.16 | —0.01 | | |
| *UB*FF | 180 | 143 | 187 | 81 | 82 | 53 | 0.83 | —0.01 | 0.17 | —0.01 | | |
| MOVFF | 181 | 150 | 179 | 81 | 82 | 53 | 0.86 | 0.00 | 0.15 | 0.00 | 0.09 | |
| M*UB*FF | 181 | 150 | 179 | 81 | 82 | 54 | 0.86 | 0.00 | 0.15 | 0.00 | 0.09 | |
| $UBr_6^{-2}$ | | | | | | | | | | | | |
| Obs | 181 | 150 | 180 | 81 | 83 | — | | | | | | 1 |
| OVFF | 178 | 145 | 188 | 81 | 84 | 56 | 0.86 | 0.00 | 0.16 | —0.01 | | |
| *UB*FF | 180 | 144 | 187 | 81 | 83 | 54 | 0.84 | —0.01 | 0.17 | —0.01 | | |
| MOVFF | 181 | 150 | 180 | 81 | 83 | 55 | 0.86 | 0.00 | 0.15 | —0.01 | 0.08 | |
| M*UB*FF | 181 | 150 | 180 | 81 | 83 | 55 | 0.87 | 0.00 | 0.15 | 0.00 | 0.08 | |

Table 2. *Mean amplitude of vibration in* Å

| | $T = 0\,°K$ | | | $T = 298\,°K$ | | |
|---|---|---|---|---|---|---|
| Hexabromide | $u$(X—Y) | $u$($Y \ldots Y$ short) | $u$($Y \ldots Y$ long) | $u$($X$—$Y$) | $u$($Y \ldots Y$ short) | $u$($Y \ldots Y$ long) |
| $ThBr_6^{-2}$ | 0.0407 | 0.0773 | 0.0515 | 0.0653 | 0.1603 | 0.0854 |
| $UBr_6^{-2}$ | 0.0405 | 0.0768 | 0.0515 | 0.0650 | 0.1588 | 0.0854 |

## Force Constants

The usual method of *Wilson*'s GF matrix[3] has been used to carry out NCT. The number of force constants is less than the secular equations, therefore, the method of least squares is used for the best fit of observed fundamentals. The method of calculation has already been reported[4,8]. All the calculations were done on an IBM 360 computer. Observed and calculated frequencies and corresponding force constants using OVFF, *UB*FF, MOVFF and M*UB*FF are reported in Tab. 1. The cited reference[5] may be consulted for the precise definitions of force constant notations used in Tab. 1.

Comparing the observed and calculated frequencies, it is clear that the bending vibrations ($\nu_4$ and $\nu_5$) are almost fitted by all the force field models where as the stretching frequencies are 100% fitted by modified fields only. The calculated frequency $\nu_6$ is approximately equal to $\nu_5/\sqrt{2}$ as calculated theoretically by *Brown* et. al.[2]. The force constants $K$ and $F$ are just equal for both the hexabromides. Comparing the stretching force constant $K$ of $(NEt_4)_2\,UCl_6$ evaluated by *Shamir* et. al.[6] with that of our result for $(NEt_4)_2\,UBr_6$, the usual trend $K_{U\text{-}Cl} > K_{U\text{-}Br}$ is observed. For both the hexabromides, M*UB*FF took the least number of iterations for convergence.

## Mean Amplitudes of Vibration (MAV)

For the evaluation of MAV *Cyvin*'s secular equation $|\Sigma G^{-1} - \Delta E| = 0$ has been used. The symbols used here have their usual meanings. The $L$-matrix according to *Müller*[7] is used for the complete solution of the symmetrized mean square amplitudes of vibration ($\Sigma$) for $f_{1u}$ mode of vibrations. MAV are calculated at 0 °K and 298 °K and reported in Tab. 2.

The calculated MAV have the usual trend $u$(X–Y) < $u$(Y ... Y long) < $u$(Y ... Y short) and increase with temperature, as observed for a large number of $XY_6$ type of molecules and anions[1,4,8]. There is very small differences between these quantities for both the anions.

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