Monatshefte für Chemie 108, 555—558 (1977)

**Monatshefte für Chemie**

# Molecular Constants of Some Hexahalide Anions

By

**M. L. Mehta**

Department of Physics, Government College, Barmer, India

*(Received August 16, 1976)*

Modified force fields have been applied to the hexachlorides and hexabromides anions of technetium. Mean amplitudes of vibration are also calculated at 0 K and 298 K. Trends of calculated data are discussed. The observed frequencies are 100% fitted by both the modified force fields used.

## Introduction

Recently, *LaBonville* et al.[1] have made a systematic comparison of five force fields for several hexahalides of $XY_6$ type of molecules and ions. They have shown the superiority of modified orbital valence force field (*MOVFF*) over other four force fields. The present author[2] has recently used *OVFF* and *UBFF* for K and Cs salts of $\mathrm{Tc}Y_6^{-2}$ ($Y$ = Cl or Br). In order to test the suitability of modified force fields viz. *MUBFF* and *MOVFF* for four hexahalide anions, the present investigation has been carried out.

## Force Constants

The vibrational spectra of anions under study have been tentatively assigned by *Schwochau* and *Krasser*[3]. These assignments have been used to carry out normal coordinate analysis using *Wilson*'s **GF** matrix method[4]. **G** and **F** matrices used here are the same as those of *LaBonville* et al.[1]. For both the modified force fields (*MOVFF* and *MUBFF*), the number of force constants is five. The force constants are refined by the usual method of weighted least square introduced by *Mann* et al.[5]. An initial set of force constants is calculated from the linear expressions involving Raman frequencies, $\mathbf{F}_{33}$ and $\mathbf{F}_{44}$ calculated by *Müller*'s approximation[6] using infrared frequencies. With an improved set of force constants, a fresh Jacobian is calculated for each iteration. The force constants are refined until the calculated frequencies give best fit with the observed frequencies. All the calculations are done on IBM 360.

Table 1. *Observed and Calculated Frequencies and Corresponding Force Constants. Frequencies are in* $cm^{-1}$ *and Force Constants in mdyne/Å*

| Hexahalides | | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ | $\nu_5$ | $\nu_6$ | $K$ | $H$ or $D$ | $F$ | $F'$ or $h$ | $k$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $K_2TcCl_6$ | Obs. | 342 | 270 | 321 | 185 | 177 | — | — | — | — | — | — |
| | *MOVFF* | 342 | 270 | 321 | 185 | 177 | 118 | 1.17 | 0.04 | 0.28 | —0.03 | 0.16 |
| | *MUBFF* | 342 | 270 | 321 | 185 | 177 | 109 | 1.17 | 0.01 | 0.28 | 0.01 | 0.16 |
| $Cs_2TcCl_6$ | Obs. | 335 | 265 | 309 | 181.5 | 177 | — | — | — | — | — | — |
| | *MOVFF* | 335 | 265 | 309 | 181.5 | 177 | 125 | 1.08 | 0.07 | 0.27 | —0.02 | 0.16 |
| | *MUBFF* | 335 | 265 | 309 | 181.4 | 177 | 112 | 1.11 | 0.02 | 0.27 | 0.00 | 0.17 |
| $K_2TcBr_6$ | Obs. | 208 | 176 | 250 | 123.4 | 115 | — | — | — | — | — | — |
| | *MOVFF* | 208 | 176 | 250 | 123.4 | 115 | 105 | 1.04 | 0.24 | 0.24 | 0.05 | 0.04 |
| | *MUBFF* | 208 | 176 | 250 | 123.4 | 115 | 79 | 1.14 | 0.06 | 0.18 | 0.01 | 0.19 |
| $Cs_2TcBr_6$ | Obs. | 204 | 176 | 242 | 119.7 | 112 | — | — | — | — | — | — |
| | *MOVFF* | 204 | 176 | 242 | 119.7 | 112 | 106 | 1.01 | 0.25 | 0.22 | 0.05 | 0.07 |
| | *MUBFF* | 204 | 176 | 242 | 119.7 | 112 | 77 | 1.11 | 0.06 | 0.15 | 0.00 | 0.24 |

Table 2. *Mean Amplitudes of Vibration in Å*

| Hexahalides | $T = 0$ K | | | $T = 298$ K | | |
|---|---|---|---|---|---|---|
| | $u(X—Y)$ | $u(Y \ldots Y \text{ short})$ | $u(Y \ldots Y \text{ long})$ | $u(X—Y)$ | $u(Y \ldots Y \text{ short})$ | $u(Y \ldots Y \text{ long})$ |
| $K_2(TcCl_6)$ | 0.0457 | 0.0685 ± 0.0005 | 0.0572 | 0.0576 | 0.1073 ± 0.0024 | 0.0738 |
| $Cs_2(TcCl_6)$ | 0.0464 | 0.0687 ± 0.0006 | 0.0578 | 0.0592 | 0.1071 ± 0.0024 | 0.0752 |
| $K_2(TcBr_6)$ | 0.0409 | 0.0560 ± 0.0006 | 0.0477 | 0.0584 | 0.1041 ± 0.0030 | 0.0738 |
| $Cs_2(TcBr_6)$ | 0.0414 | 0.0596 ± 0.0003 | 0.0478 | 0.0595 | 0.1063 ± 0.0033 | 0.0741 |

The observed, calculated frequencies and force constants using *MOVFF* and *MUBFF* are reported in Table 1. The notations of force constants given in Table 1 are the same as those of *LaBonville* et al.[1].

## Mean Amplitudes of Vibration

*Cyvin*'s secular equation[7] $|\Sigma\, \mathbf{G}^{-1} - E\, \Delta| = 0$ has been used for the evaluation of mean amplitudes of vibration. Here **G** is the kinetic energy matrix, $\Sigma$ is the symmetrized mean square amplitude matrix and $\Delta$, a temperature dependent quantity, can be expressed in terms of vibrational frequency as

$$\Delta = (h/8\,\pi^2\,\nu\, c) \cdot \coth\,(h\,\nu\, c/2\,kT).$$

Symbols used have their usual meaning. $\Sigma$ and **G** matrix used for these anions are the same as those of *Cyvin*[7].

On applying similarity transformation, the secular equation reduces into four one dimensional and a two dimensional secular equations. The solution of one dimensional secular equation is linear. For the solution of two dimensional secular equation, the **L** matrix approximation of *Müller*[6] has been used to calculate three symmetrized mean square amplitude of vibration using infrared active vibration ($\nu_3$ and $\nu_4$). $\nu_6$ is not experimentally observed. Therefore, the calculated value of $\nu_6$ has to be taken for the evaluation of mean amplitudes of vibration. Using *UBFF* and *OVFF*, the present author[2] has calculated two values of $\nu_6$ (One corresponds to each force field). Corresponding to two values of $\nu_6$, two values of $\Sigma\,(f_{2u})$ are evaluated. These evaluated $\Sigma$-matrix elements are linearly related to the mean amplitudes of vibration ($u$) for bonded and nonbonded interatomic distances[7]. Since only for $u\,(Y \ldots Y$ short) $\Sigma\,(f_{2u})$ comes in the expression, two values of $u\,(Y \ldots Y$ short) are calculated. Mean of these two values with deviation is calculated. Mean amplitudes of vibration are evaluated at 0 K and 298 K and are given in Table 2.

## Discussions

The obtained force constants show definite trends. The stretching force constant, $K$ and nonbonded repulsion constant, $F$, are higher for $K$ than for Cs salts. With respect to halide ligand, the stretching force constant $K$, gives the same results as observed by the present author[2].

The fundamental frequencies are 100% fitted by both the modified force fields. For all the anions *MOVFF* and *MUBFF* are equally good. *MOVFF* takes more iterations than *MUBFF* for convergence.

Mean amplitudes of vibration are higher for K than for Cs salts. Mean amplitudes of vibrations of all the anions under study have the trend

$$u\,(X - Y) < u\,(Y \ldots Y\,\text{long}) < u\,(Y \ldots Y\,\text{short})$$

at both the temperatures and increase with it. Similar results have been found for a number of molecules and anions of $XY_6$-type earlier[7, 8] also. The experimental values of mean amplitudes of vibration for the anions under study are not available, therefore, the calculated data cannot be compared.

## Acknowledgements

The author wishes to thank Prof. *A. Müller*, University of Dortmund, Germany, and Prof. *S. J. Cyvin*, Technical University of Norway, for constructive criticism and University Grants Commission, New-Delhi, India for financial assistance.

## References

[1] *P. LaBonville, J. R. Ferraro, M. C. Wall, S. M. C.*, and *L. J. Basile*, Coord. Chem. Rev. **7**, 257 (1972).

[2] *M. L. Mehta*, J. Molec. Spectrosc. **42**, 208 (1972).

[3] *K. Schwochau* and *W. Krasser*, Z. Naturforsch. **24 a**, 403 (1969).

[4] *E. B. Wilson, J. C. Decius*, and *P. C. Cross*, Molecular Vibrations. New York: McGraw-Hill. 1955.

[5] *D. E. Mann, T. Shimanouchi, J. H. Meal*, and *L. Fano*, J. Chem. Phys. **27**, 43 (1957).

[6] *A. Müller*, Z. Phys. Chem. (Leipzig) **328**, 116 (1968).

[7] *S. J. Cyvin*, Molecular Vibrations and Mean Square Amplitudes. Amsterdam: Elsevier. 1968.

[8] *M. L. Mehta*, Spectrosc. Letters **2**, 327, 383 (1969); Ph. D. Thesis, University of Jodhpur, India, 1971.

Correspondence and reprints:
*Dr. M. L. Mehta*
*Department of Physics*
*Government College*
*Telion ka Bas*
*344001 Barmer*
*India*