CHAPTER III

RESULTS AND DISCUSSION

The frequencies of the molecules are available from Nakamoto's book[8] and are presented in Table 1. It can be seen from Table 1 that ν_1 of $N^{15}H_4^+$, NT_4^+, SnH_4 and SnD_4 and ν_2 of $[WSe_4]^{-2}$ have not been observed. These values can be predicted by the empirical plot method.

Table 1 Vibrational frequencies of tetrahedral molecules (cm^{-1})

Molecule	$\nu_1(a_1)$	$\nu_2(e)$	$\nu_3(f_2)$	$\nu_4(f_2)$
$N^{14}H_4^+$	3040	1680	3145	1400
$N^{15}H_4^+$	-	(1646)	3137	1399
ND_4^+	2214	1215	2346	1065
NT_4^+	-	976	2022	913
CH_4	2917	1534	3019	1306
SiH_4	2180	970	2183	910
GeH_4	2106	931	2114	819
SnH_4	-	758	1901	677
CD_4	2085	1092	2259	996
SiD_4	(1545)	(689)	1597	681
GeD_4	1504	665	1522	596

Table I (Continued)

Molecule	$\nu_1(a_1)$	$\nu_2(e)$	$\nu_3(f_2)$	$\nu_4(f_2)$
SnD_4	-	539	1368	487
$[WO_4]^=$	931	373	833	320
$[WS_4]^=$	460	(179)	480	195
$[WSe_4]^=$	278	-	310	115

Frequencies in brackets mean uncertainties.

3.1 Empirical plots (Figs. 2,3,4,5,6)

By plotting ν's against the masses of the central atoms or X atoms, in a series of MX_4 molecules, the unobserved frequencies of ν_1 ($N^{15}H_4^+$, NT_4^+, SnH_4, SnD_4) and ν_2 $[WSe_4]^=$ can be predicted. They are listed below:-

Table 2 Prediction from plots

Molecule	$\nu_1(cm^{-1})$	$\nu_2(cm^{-1})$
$N^{15}H_4^+$	3032±10	
NT_4^+	1893±20	
SnH_4	1890±15	
SnD_4	1352 1890±15	
$[WSe_4]^=$		82.5±10

3.2 Product rule

By using equations (XII) and (XIII), the predicted frequencies are listed in Table 3

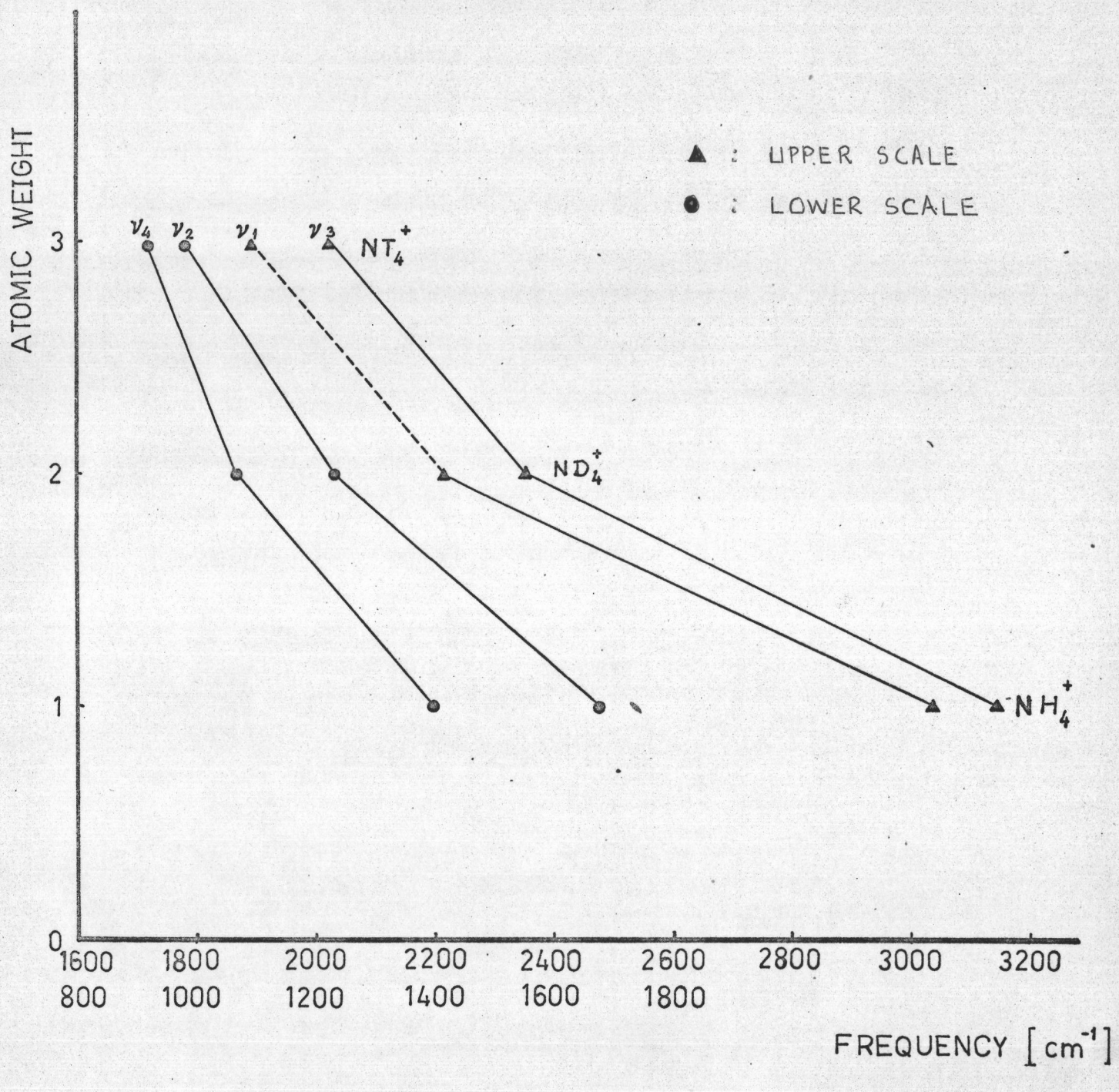

Fig. 2 Empirical plot of $N^{14}H_4^+$ family.

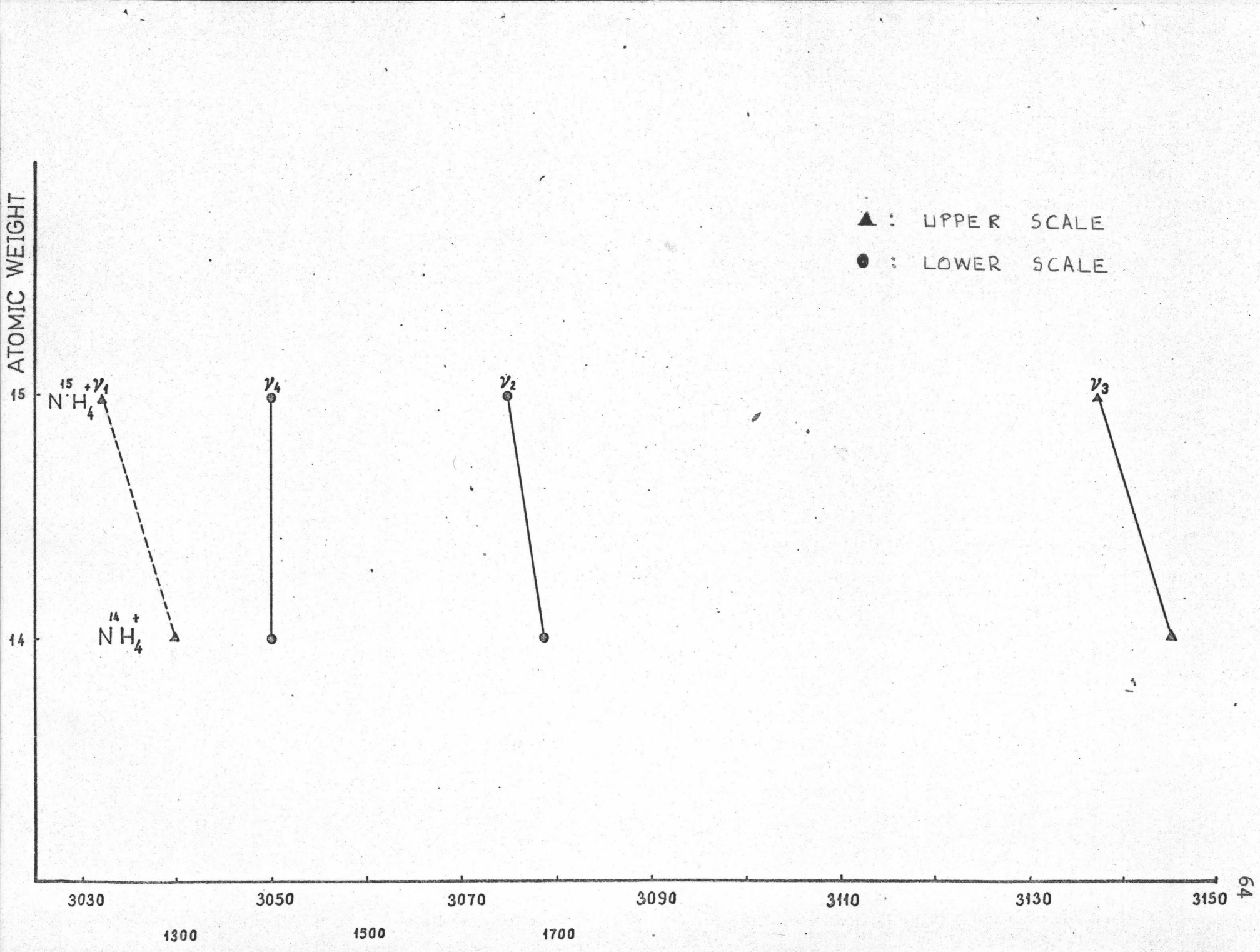

Fig.3 Empirical plot of $N^{14}H_4^+$ family.

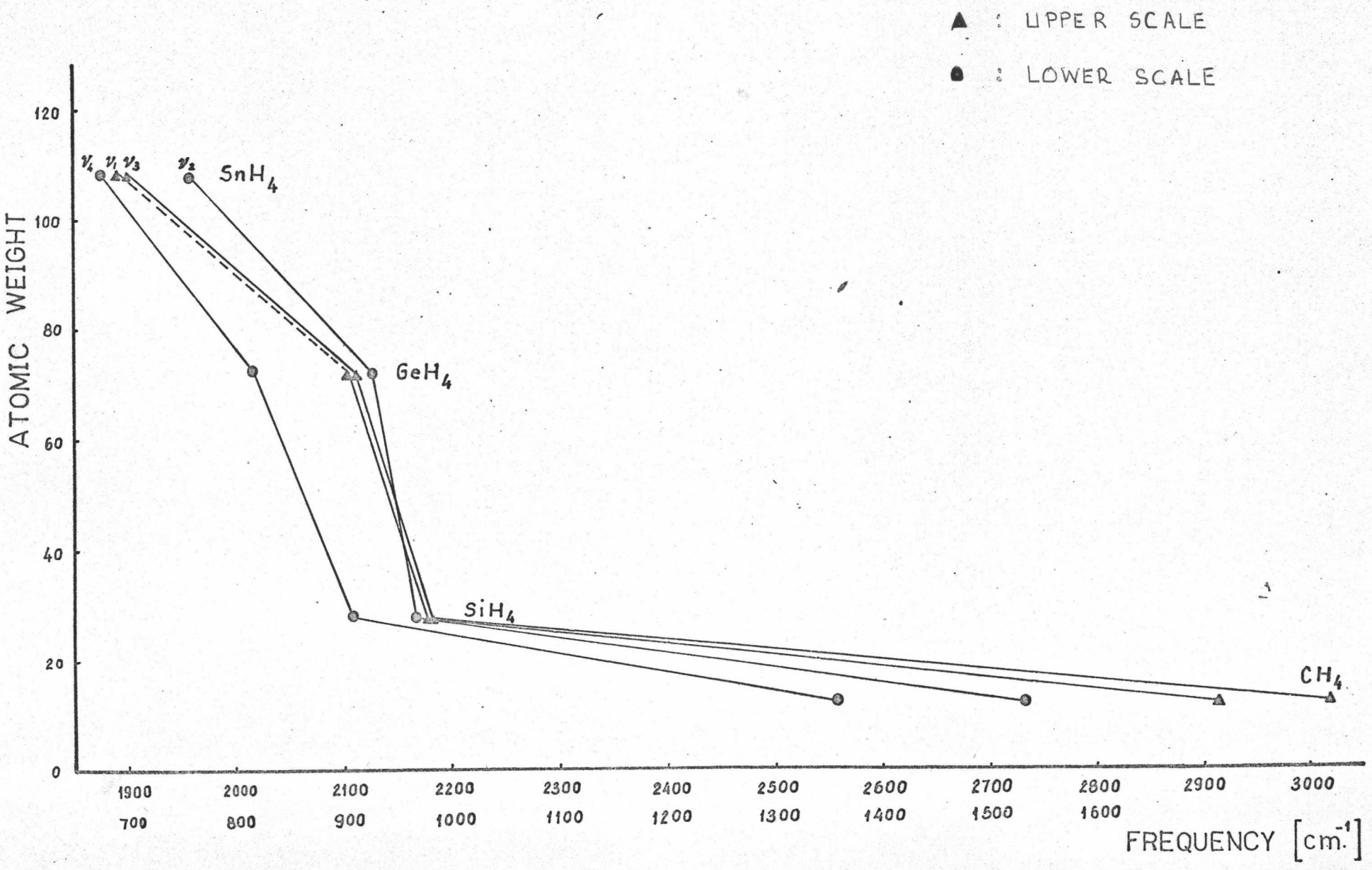

Fig. 4 Empirical plot of CH_4 family.

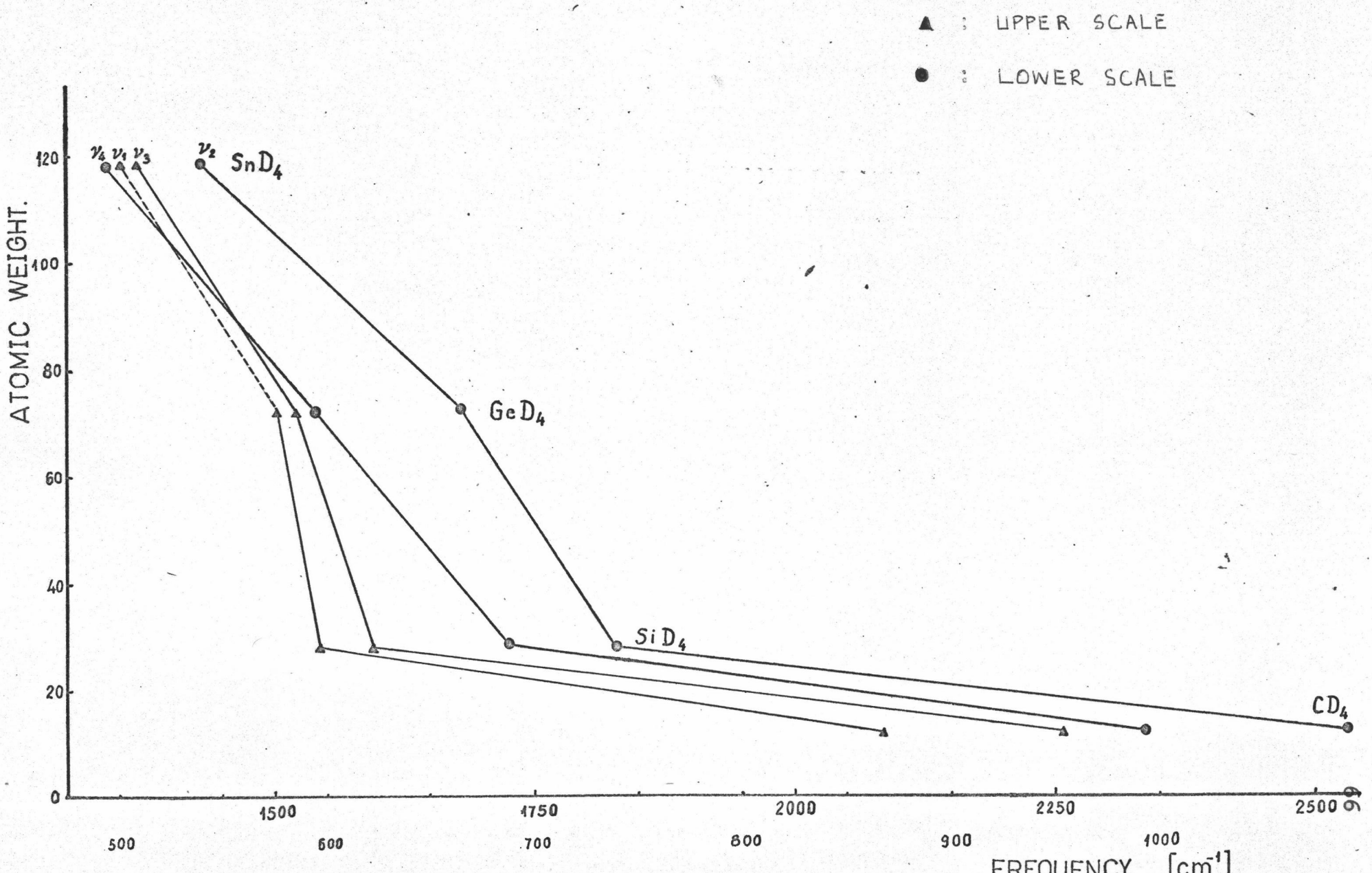

Fig. 5 Empirical plot of CD_4 family.

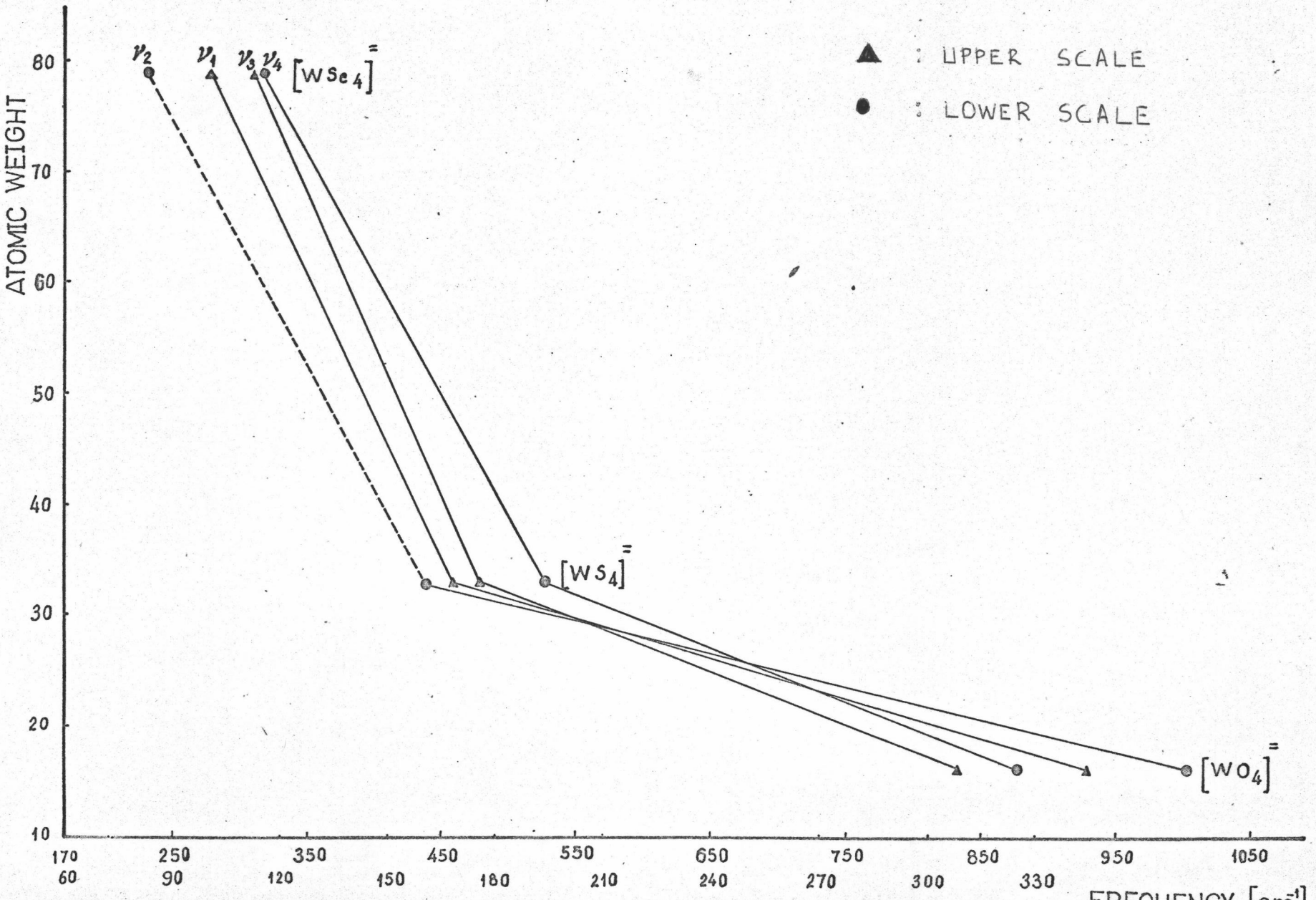

Fig. 6 Empirical plot of $[WO_4]^=$ family.

Table 3 Prediction from product rule

Molecule	ν_1
$N^{15}H_4^+$	3040±3%*
NT_4^+	1809±3% *
SnH_4	1900±2% ≠
SnD_4	1362±2% ≠

3.3 Urey-Bradley force field (UBFF)

Using 4 observed frequencies (Table 1), 4 force constants are calculated. They are listed in Table 4.

Table 4 Urey-Bradley force constants (10^5dyne.cm^{-1})

Molecule	K	H	F	F′
NH_4^+	5.218	0.552	0.068	0.048
ND_4^+	5.244	0.555	0.142	0.056
CH_4	4.725	0.500	0.081	0.033
SiH_4	2.700	0.166	0.031	-0.029
GeH_4	2.621	0.165	0.003	-0.016
CD_4	4.784	0.450	0.094	0.029
SiD_4	2.776	0.171	0.014	-0.036
GeD_4	2.664	0.168	0.005	-0.017

* based on NH_4^+/ND_4^+ ; ν_1 obs.=2214 and ν_1 calcd. = 2150. (Eq XII)

≠ usual % figures for product rule.

Table 4. (Continued)

Molecule	K	H	F	F′
$[WO_4]^=$	4.887	0.162	0.821	-0.003
$[WS_4]^=$	3.406	0.188	0.147	-0.004

Using unobserved frequencies predicted by empirical plots from Table 2 together with other three observed frequencies, we can calculate Urey-Bradley force constants. They are in Table 5.

Table 5 Urey-Bradley force constants (10^5dyne.cm.$^{-1}$)

Molecule	K	H	F	F′
NT_4^+	5.320	0.490	0.262	0.039
$^{15}NH_4^+$	5.264	0.529	0.049	0.028
SnH_4	2.150	0.111	-0.012	-0.015
SnD_4	2.200	0.112	-0.008	-0.015
$[WSe_4]^=$	2.685	0.012	0.227	-0.012

3.4 Discussion

The 4 force constants for each family are acceptable, when Tables 4,5 are compared.

3.4.1 The NH_4^+ family: K's, the major force constants show a slight increase as the hydrogen atom is substituted by heavier masses. This shows that the assumption of the product rule in this case is not as good as usual. But the overall pattern is acceptable. (Fig. 7).

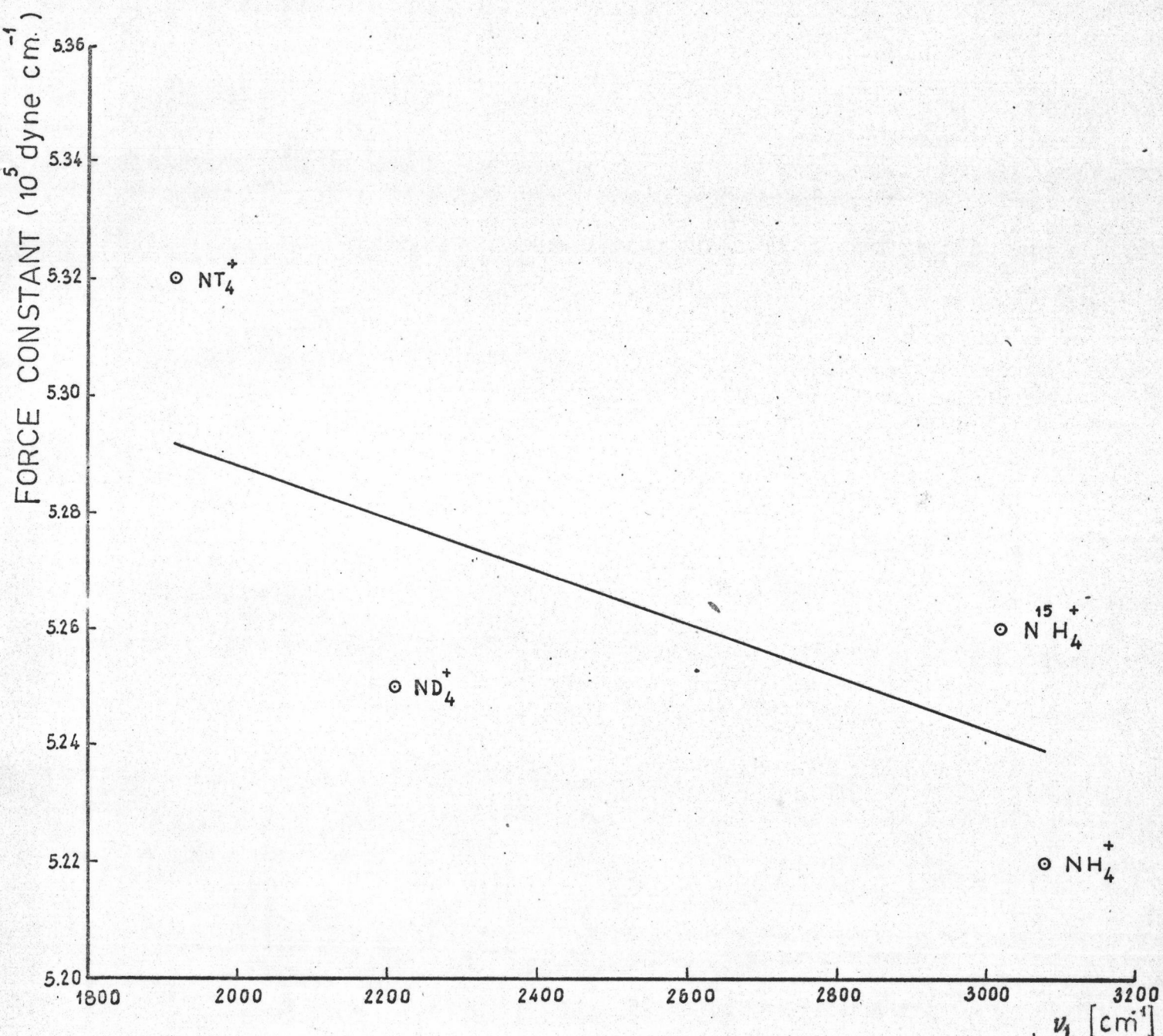

Fig. 7 Force constant (K) vs. ν_1 frequencies of NH_4^+ family.

3.4.2 The CH_4 and CD_4 families: All four force constants decrease as the central masses and the bond lengths are increased, e.g. in CH_4 family, 1.480, 1.535, and 1.76 A° (Fig. 11). This is physically reasonable. As the bond lengths are increased, so do the non-bonded distances between the X atoms. It is not surprising therefore, the strengths of K, H, F's become weaker. When K's are plotted against ν_1, a smooth curve results for both families (Fig. 8,9).

Further, the 2 sets of force constants (Table 5) for SnH_4, SnD_4 are comparable, showing that the assumptions of the product rule is indeed valid, which in turn indicates that the empirical plot method is satisfactory.

3.4.3 The $[WO_4]^=$ family: It is not as good as the other families because the observed frequencies are not in the same sequence, e.g. for

$$[WO_4]^= \; ; \; \nu_1 > \nu_3 , \quad \nu_2 > \nu_4$$
$$[WS_4]^= \quad \nu_1 < \nu_3 , \quad \nu_2 < \nu_4$$

Nonetheless the major force constants, K, show a decrease as the masses and bond lengths are (1.79, 2.17 and 2.32 A°) increased (Fig. 12). Again, this is physically reasonable. The K vs. ν_1 plot is again a smooth curve (Fig. 10)

3.5 Conclusion

This empirical plot method is applicable to other symmetrical molecules[9]. It is particularly good for molecules with hydrogen atoms, because the observed frequencies would be high and therefore the % errors would be low. Comparing table 2 and 3, it can be seen that the empirical plot method is better than the product rule.

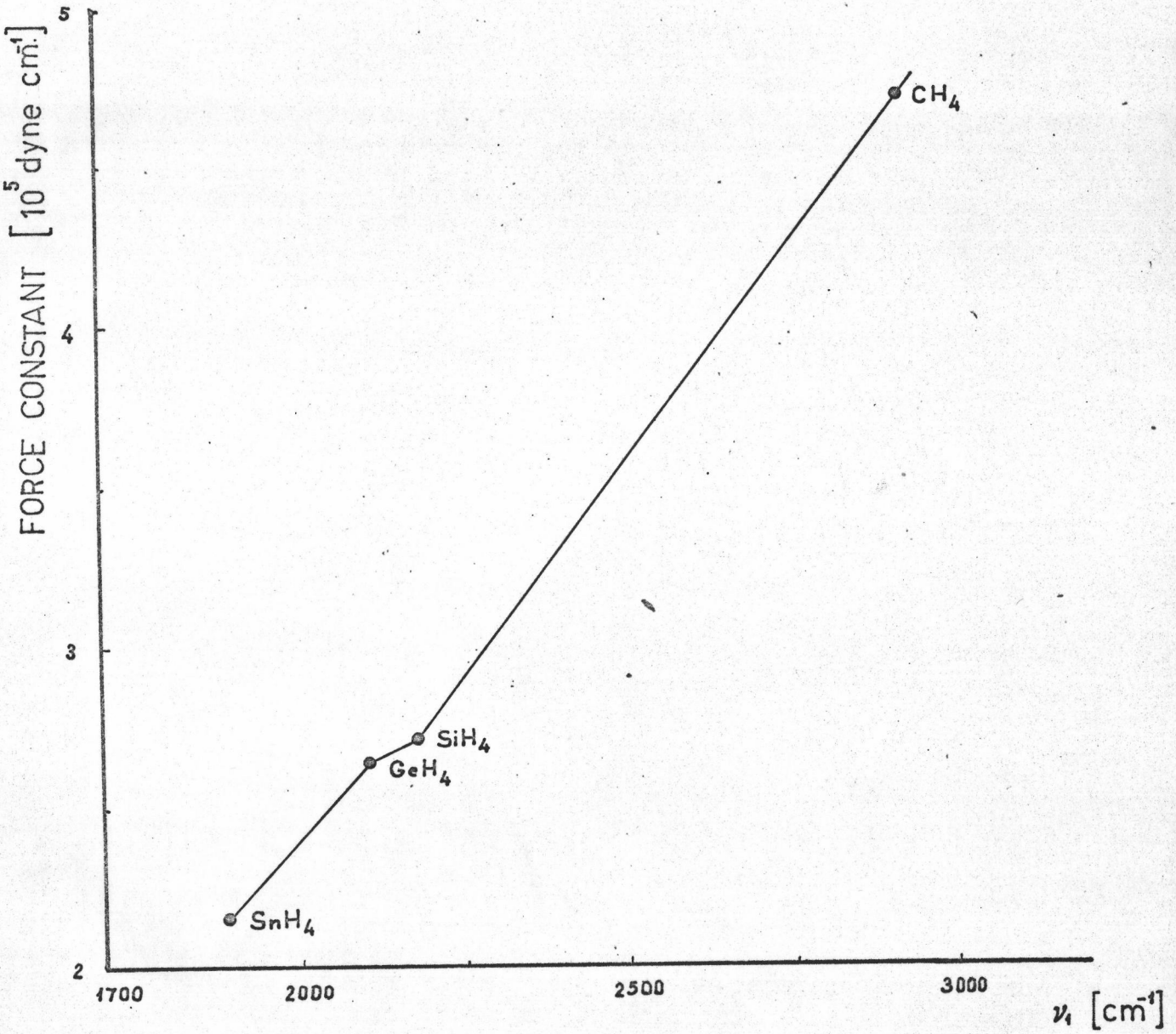

Fig.8 Force constant(K) vs. ν_1 of CH_4 family.

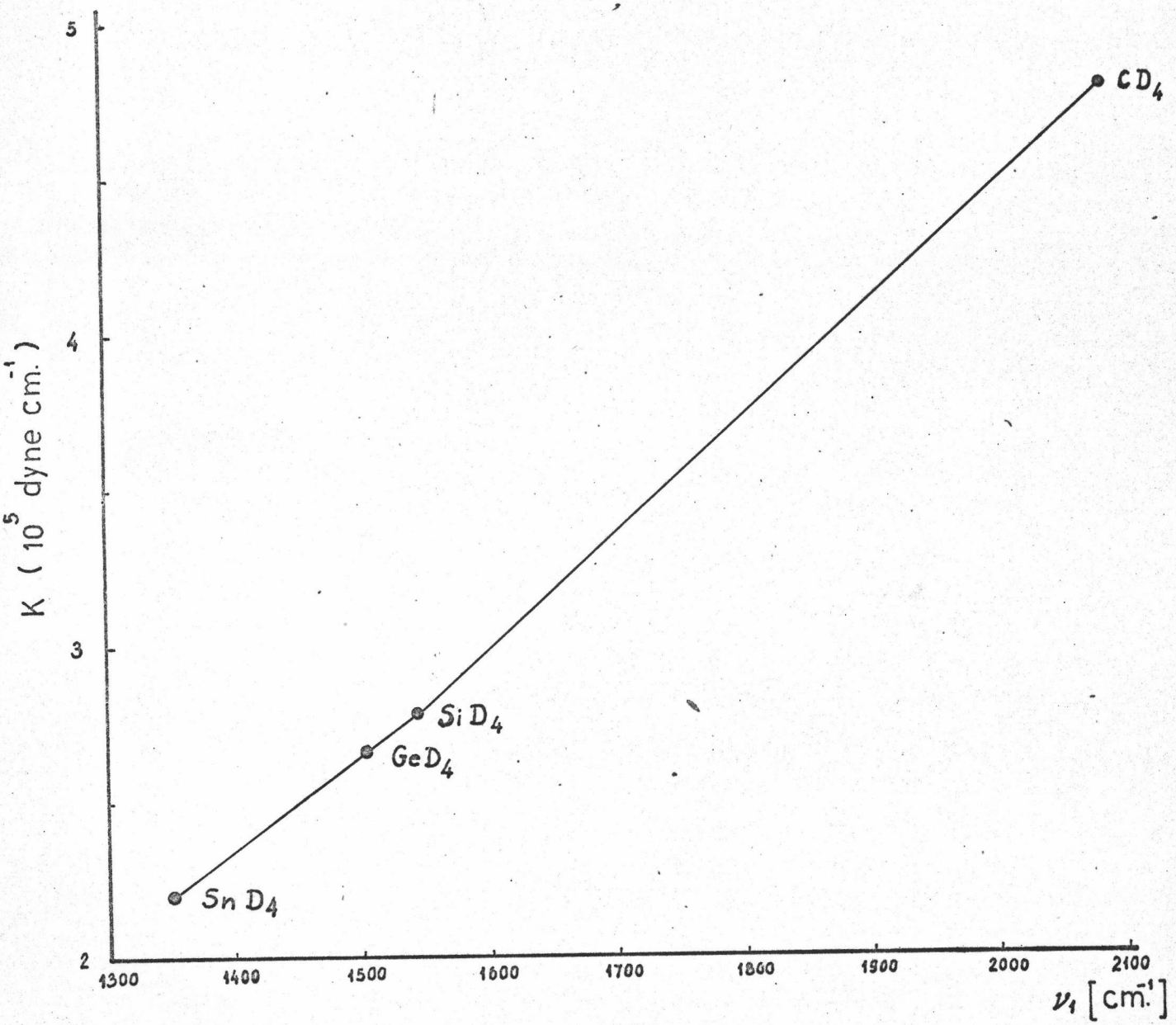

Fig. 9 Force constant (K) vs. ν_1 frequency of CD_4 family.

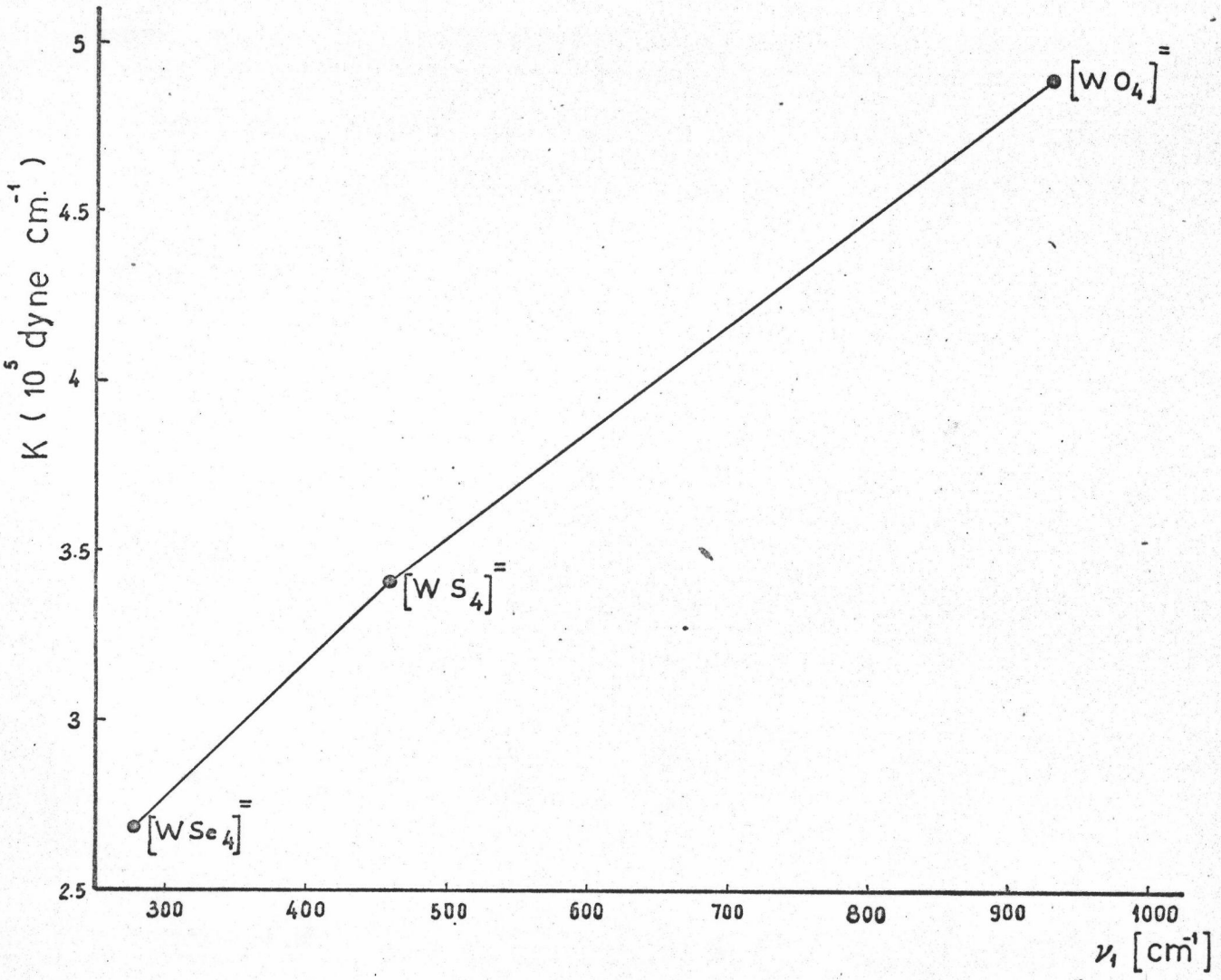

Fig.10 Force constant (K) vs. ν_1 frequencies of $[WO_4]^{=}$ family.

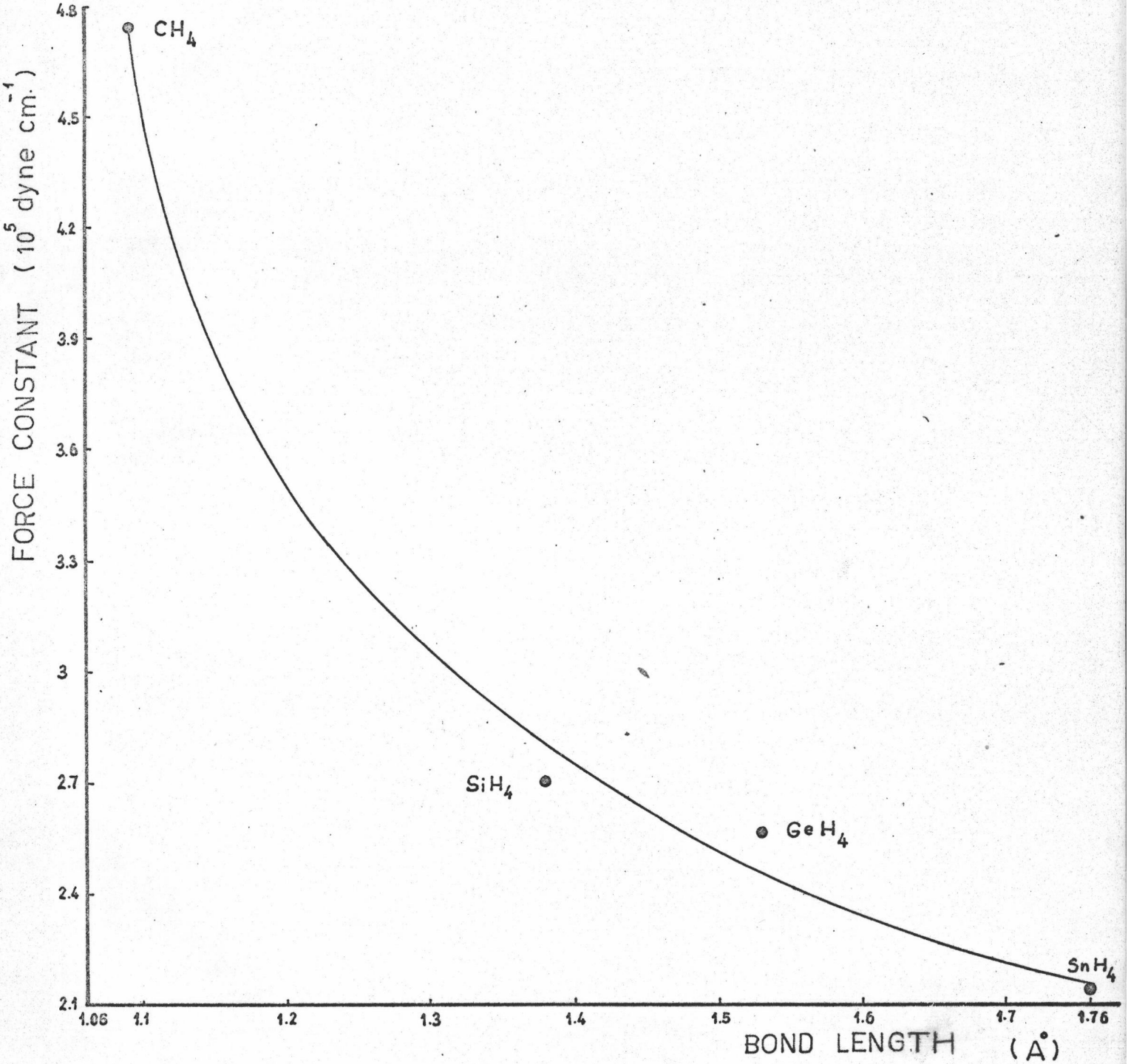

Fig.11 Force constant (K) vs. bond length of M-X of CH_4 family.

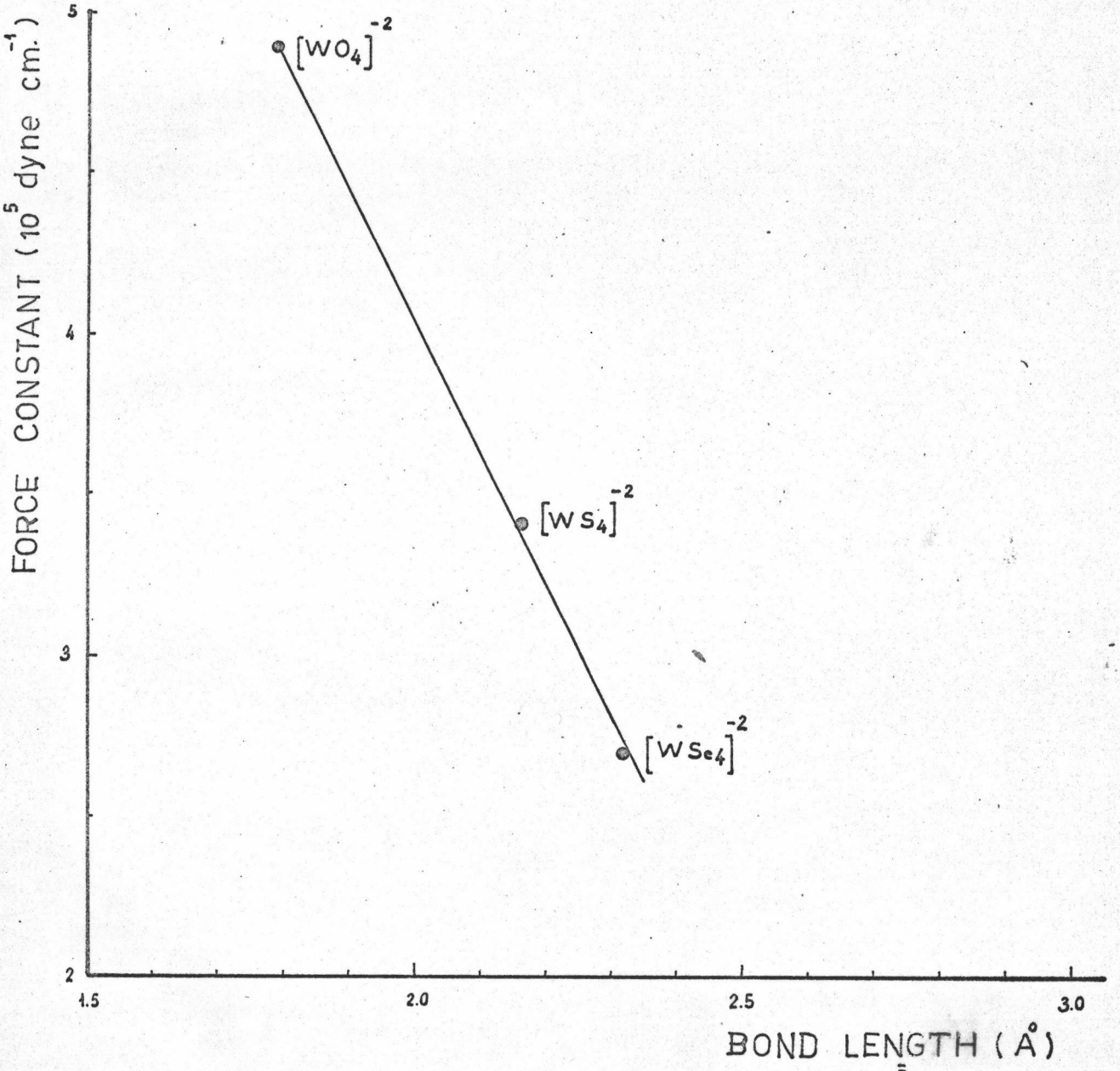

Fig.12 Force constant (K) vs. bond length of M-X of $[WO_4]$ family.