Correlation of the Mean Amplitude Quantities $\sigma_2$ with the Covalency of a Chemical Bond

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In a recent investigation $^1$ we presented a theoretical analysis of the mean amplitudes of vibrations of XeO$_4$ in which an inverse relationship between stretching force constants and the mean amplitude quantities $\sigma_2$ was tentatively suggested. However, since in an earlier work $^2$ the existence of a definite linear relationship between the Urey-Bradley $^9$ stretching force constants $K$ and the percent ionic character of the MX bond of the hydrogen halides as well as of 27 tetrahalogenes $^7$ was demonstrated by us, it was naturally tempting to search for such a correlation between the mean amplitude quantities $\sigma_2$ of the said molecules and the percent ionic character (% I.C.) given by the Hannay-Smith equation $^4$. 

\[ \text{Percent Ionic Character} = 16|z_M - z_X| + 3.5(z_M - z_X)^2 \]

where $z_M$ and $z_X$ are the Pauling electronegatives of the atoms forming the MX bond $^5$.

The theory as well as the details of the computational techniques involved in the present work have been given in our earlier papers $^1, 2$ and shall not be repeated here. Suffice it to say, however, that although the results are only correct to the first order, there seems, nonetheless, to be a definite linear relationship between the reciprocal of $\sigma_2$ and the covalency of the MX bond. In fact, the relationship can be given by

\[ \sigma_2^{-1} = k(\% \text{ I. C.} + \Theta) \]

where for the chlorides, the bromides, and the iodides $\Theta = 0.0$, and for the fluorides $\Theta = -10.5$. 

A critical examination of our preliminary results, as given by Fig. 1, reveals a number of intriguing points. First, it is noted that none of the fluorides falls on the curves traced by the other halides. One could blame this on anharmonicity. Fig. 2, unfortunately, shows, that the major part of the problem definitely lies

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$^4$ These include all available tetrahedral molecules of the II B, III A, and IV A families of the periodic Table.

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Abb. 3 a.

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somewhere else. Moreover, it is most intriguing to note
that if the percent ionic character of all the fluorides
were reduced by approximately 10 units then they all
behave "normally" and fall on the "expected" curves.
Naturally, one is tempted to "correct" the ionicity of
the fluorides, but, unfortunately, in so doing one de-
structors a great number of other correlations, including
our previous force constant correlation, and indeed
gains very little, if anything.

Secondly, it is extremely interesting to find that when
all of the curves are extrapolated beyond the origin
to $-15\%$ I.C., there seems to be a 1 to 1 corre-

dence with their respective correlations of the ÜBEY-
BRADLEY force constants $K$ with covalency (see Fig. 1
of Ref. 2). That is, curve for curve the slopes and the
intercepts seem to be more or less the same.

Of course, the most intriguing question is why? We
are presently working in that direction and will report
as soon as a mathematical formulation is obtained.