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 destroys 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 correspondence with their respective correlations of the Urey-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.

**Predicted Root-Mean-Square Amplitudes of XeO$_4$**

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The root-mean-square amplitudes of vibration of both the Xe—O and the O...O interatomic distances of XeO$_4$ have been theoretically estimated to be 0.0373 Å and 0.0742 Å respectively at 290 °K. Although the experimental parameters for XeO$_4$ are not yet available, it is hoped that the results of this investigation could, at least, be used as first approximations in any future electron diffraction data refinements of XeO$_4$.

In a recent investigation 1 we presented a study of the root-mean-square amplitudes of vibration of the bonded and non-bonded interatomic distances of XeF$_2$ and XeF$_4$ within the framework of the Morino-Cyvin formalism 2,3. In the present work, we extend this investigation to the study of yet another xenon compound, that of xenon tetroxide.

Xenon tetroxide, it should be mentioned, is an unstable compound 4, solid samples of which have exploded at temperatures as low as —40 °C! Nonetheless, it can be handled at room temperature and since its infrared spectrum in the gaseous phase* has been

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1 W. A. YERANOS, Molec. Phys. 12, 529 [1967].
* Its vapor pressure at 0 °C is 25 mm 5.
obtained and studied, there is every reason to believe that some day its electron diffraction parameters shall be reported too. Anticipating this, we report our study of the root-mean-square amplitudes of vibration of the bonded and the non-bonded interatomic distances of XeO_4, not so much as to provide numbers which will later be matched to the experimental values, but rather as numbers which can, at worst, be used as first approximations in future electron diffraction data refinements of XeO_4. In short, we have asked infrared spectroscopy to come to the help of a future electron diffraction study.

1. Theory

Within the Morino-Cyvin formalism the mean-square amplitude matrix \( \Sigma \) for a vibrating molecule at a given temperature is given by:

\[
\Sigma = L \tilde{A}L^T,
\]
where \( \tilde{A} \) is a diagonal matrix having:

\[
\tilde{A}_i = \frac{k}{4 \pi c} \frac{h c \tilde{v}_i}{2 k T}
\]
on its diagonal, and where \( L \) is the transformation matrix from the normal cordinates \( Q \) to the symmetry coordinates \( S \), such that

\[
S = LQ.
\]

The matrix elements of the mean-amplitude matrix, on the other hand, are given by:

\[
\Sigma(i,j) = \langle S_i \tilde{S}_j \rangle
\]
where \( \langle S_i \tilde{S}_j \rangle \) can be expanded as a linear combination of the mean-square quantities \( \sigma_{\xi \eta} \) which are themselves defined as:

\[
\sigma_{\xi \eta} = \langle r_{a \xi} r_{b \eta} \rangle
\]
and where \( a \) and/or \( b \) are equal to 1 respectively, if \( \xi \) and \( \eta \) are internal coordinates which define angle deformations, and zero otherwise. It should, furthermore, be noted that in practice the mean-square quantities of the bonded and non-bonded interatomic distances are the most important ones and can, in principle at least, be determined from electron diffraction data.

2. Determination of Root-Mean-Square Amplitudes of Vibration and Discussion

The infrared spectrum of XeO_4 has been reported by Claassen while a theoretical vibrational analysis of the said molecule has been presented by the author himself. The set of Urey-Bradley force constants was obtained by the latter not only reproduces quite well the experimentally observed infrared bands, but provides us also with tentative values for the missing Raman frequencies and, in as far as the present work is concerned, is instrumental in the determination of the \( L \) matrix of XeO_4.

Using the symmetry coordinates presented by us in a previous publication we have, for the \( \Sigma \) matrix of an MX_4 molecule of \( T_d \) symmetry, the following matrix elements:

\[
\begin{align*}
\Sigma(1,1) & = \sigma_r + 3 \sigma_{rr} , \\
\Sigma(2,2) & = \sigma_a - 2 \sigma_{aa} + \sigma_{aa}' , \\
\Sigma(3,3) & = \sigma_r - \sigma_{rr} , \\
\Sigma(3,4) & = \Sigma(4,3) = \sqrt{2} (\sigma_{ra} - \sigma_{ra}') , \\
\Sigma(4,4) & = \sigma_a - \sigma_{aa}' ,
\end{align*}
\]
where the primes in the mean-square quantities \( \sigma_{\xi \eta} \) represent trans interactions.

The above matrix elements, coupled with the following relations obtained from the redundancy condition:

\[
\sigma_a + 4 \sigma_{aa} + \sigma_{aa}' = 0 ,
\]
and

\[
\sigma_r + \sigma_{ra}' = 0 ,
\]
give us, for the mean-square quantities of the interatomic distances Xe-O and O...O, the following relationships:

\[
\begin{align*}
\sigma_r & = \frac{1}{2} [\Sigma(1,1) + 3 \Sigma(3,3)] , \\
\sigma_{rd} & = \frac{1}{2} [2 \Sigma(1,1) + \Sigma(2,2) + 2 \Sigma(3,3) + 2 \Sigma(3,4) + \frac{1}{2} \Sigma(4,4)] .
\end{align*}
\]

The results of our calculations for XeO_4 are given in Table 1, along with the root-mean-square amplitudes of vibration \( l_v(i,j) \) between atoms \( i \) and \( j \) which are defined as:

\[
l_v(i,j) = \sqrt{\sigma_{\xi \eta} .}
\]

| \( \Sigma(1,1) \) | \( 0.00119301 \) \( \text{Å}^2 \) |
| \( \Sigma(2,2) \) | \( 0.01691569 \) \( \text{Å}^2 \) |
| \( \Sigma(3,3) \) | \( 0.00145518 \) \( \text{Å}^2 \) |
| \( \Sigma(3,4) \) | \( \Sigma(4,3) \) | \( -0.00080858 \) \( \text{Å}^2 \) |
| \( \Sigma(4,4) \) | \( 0.01441861 \) \( \text{Å}^2 \) |
| \( \sigma_r \) | \( 0.00138964 \) \( \text{Å}^2 \) |
| \( \sigma_{rd} \) | \( 0.00550903 \) \( \text{Å}^2 \) |
| \( l_v(\text{Xe-O}) \) | \( 0.0375 \) \( \text{Å} \) |
| \( l_v(\text{O...O}) \) | \( 0.0742 \) \( \text{Å} \) |

Table 1. Results obtained for \( T = 298 \) °K.

6. R. W. James, Phys. Z. 33, 737 [1932].
** Observed: \( \tilde{v}_s(t_a) = 877 \) cm\(^{-1} \), \( \tilde{v}_s(t_b) = 306 \) cm\(^{-1} \).
Calculated: \( \tilde{v}_s(t_a) = 876 \) cm\(^{-1} \), \( \tilde{v}_s(t_b) = 305 \) cm\(^{-1} \).
\( \tilde{v}_s(t_c) = 906 \) cm\(^{-1} \), \( \tilde{v}_s(t_d) = 301 \) cm\(^{-1} \).
11. W. A. Yeranos and F. D. Foss, Molec. Phys. 9, 87 [1965].
\* By convention, if \( \xi \) and \( \eta \) are the same, the mean-square quantity involved is simply written as \( \sigma_\xi \).
An examination of the values of $\sigma_o$ and $\sigma_i$ for $\text{XeO}_4$ shows that they are almost half as much as their respective counterparts in $\text{XeF}_4$. This is indeed interesting if one remembers that the force constants of both molecules bear the inverse relationship $1/2$.

Preliminary results of the 27 tetrahedral molecules studied previously suggests a linear relationship between the percent ionic character with the reciprocal of the mean amplitude quantities $\sigma_i$. The complete study shall be submitted to this Journal as soon as available.

A Level-Crossing Investigation of the hfs in the $3^2P_{3/2}$-State of Sodium

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The first studies of the hyperfine structure (hfs) in the $3^2P_{3/2}$ state of $^{23}\text{Na}$ atoms $^1$ had yielded an ambiguity, concerning the sign and magnitude of the nuclear electric quadrupole moment of $^{23}\text{Na}$ ($I=3/2$), which could be removed by some recent double-resonance experiments $^3$—$^5$. In view of the difficulties in interpreting double resonance spectra in a case where the hfs level separations are comparable with the level-widths $^6$, it seemed worth-while to seek for a confirmation of the results in a level-crossing experiment $^7$—$^8$ by observing the field-dependence of the polarization of fluorescence radiation in a magnetic field. Such an experiment had been previously undertaken $^9$ but the authors were not able to deduce the hfs coupling constants from their measurements.

According to Breit $^{10}$ the intensity, $R(f,g)$, of laterally scattered fluorescence radiation is given by the formula

$$R(f,g) = C \sum_{m,m'} \frac{\langle m | f \cdot r | r \rangle}{1 - 2 \tau i \tau r(m,m')} g_{m'g}(m,m').$$

Here $f_{m} = \langle m | f \cdot r | \mu \rangle$, etc., where $f$ and $g$ are the polarization vectors of the exciting light and the observed fluorescent light, respectively. The eigenvectors of the excited state and of the ground state are $| m \rangle$ and $| \mu \rangle$, respectively. $\tau$ is the radiative lifetime of the excited atoms. $r(m,m') = (E_m - E_{m'})/h$ is the difference of term values in the excited state. In (1) it is assumed that the power density of the exciting light is constant over the hfs components of the atomic resonance and that no multiple scattering takes place. The first assumption is not exactly satisfied for the lamp in the present experiment.

The eigenvectors of the Na atoms were determined by diagonalizing the Hamiltonian for the atoms in a magnetic field with the aid of a computer. $R(f,g)$ was calculated as a function of the magnetic field for different values of the magnetic hfs splitting constant $A$.

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10 G. Breit, Rev. Mod. Phys. 5, 91 [1933].