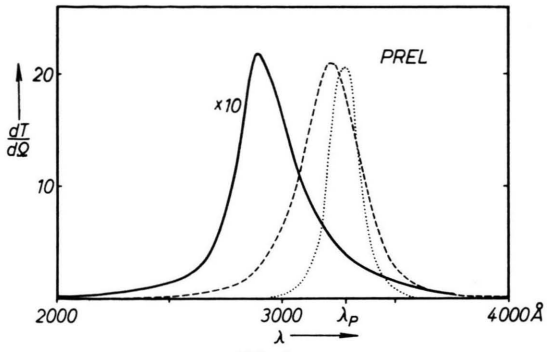

Abb. 3 a.

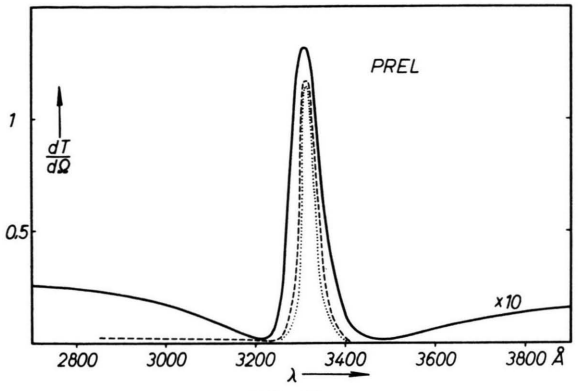

Abb. 3 b.

gegangenen Lichtes bemerkbar macht als Folge der oben erwähnten Anregung der strahlenden Oberflächenmode. Dieses Phänomen, das mit Hilfe der Fresnelschen Gleichungen und der zugehörigen optischen Konstanten beschrieben wird, ist schon längere Zeit an Alkalimetallen als sogen. vektorabhängige Lichtabsorption beobachtet worden [8, 9]. Es bedingt auch den sogen. selektiven Oberflächenphotoeffekt, erkenntlich an der hohen lichtelektrischen Ausbeute bei gewissen Wellenlängen [10]. Die atomphysikalische Deutung als Wirkung der Plasmafrequenz ist jedoch erst neueren Datums [11].

[8] R. Fleischmann, Nachr. Ges. D. Wiss., Göttingen 1931, Nr. 20 sowie Z. Physik **174**, 102 ff. [1963].

[9] Die damals beobachtete Abweichung der Lage des Transmissionsminimums von der Plasmafrequenz ω_p ist durch die Inhomogenität der damals verwendeten Schichten zu erklären, vgl. hierzu J. Bösenberg, Z. Phys. (im Druck).

[10] Vgl. hierzu B. Gudden, Lichtelektrische Erscheinungen, Springer-Verlag, Berlin 1928, S. 89 ff. und neuerdings W. Steinmann u. M. Skibowski, Phys. Rev. Letters **16**, 989 [1966].

[11] M. Hattori, K. Yamada u. H. Suzuku, J. Phys. Soc. Japan **18**, 203 [1963]. — A. J. McAlister u. E. A. Stern, Phys. Rev. **132**, 1599 [1963].

Abb. 3. Intensität (in willkürlichen Einheiten) der PREL nach Gl. (7); sonst wie bei Abb. 2. $\Theta=\Theta_0=30°$. Zum Vergleich punktiert die Funktion $|1-1/\varepsilon^2|^2$. $\sigma=1200$ Å; $\Phi=90°$ (s. hierzu [5]).

Correlation of the Mean Amplitude Quantities σ_r with the Covalency of a Chemical Bond

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(Z. Naturforsch. **23 a**, 617—618 [1968]; received 25 January 1968)

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 σ_r was tentatively suggested. However, since in an earlier work [2] the existence of a definite linear relationship between the Urey-Bradley [3] stretching force constants K and the percent ionic character of the MX bond of the hydrogen halides as well as of 27 tetrahalogens † was demonstrated by us, it was naturally tempting to search for such a correlation between the mean amplitude quantities σ_r of the said molecules and the percent ionic character (% I. C.) given by the Hannay-Smyth equation [4].

Percent Ionic Character $= 16\,|\chi_M - \chi_X| + 3.5(\chi_M - \chi_X)^2$

where χ_M and χ_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 σ_r and the covalency of the MX bond. In fact, the relationship can be given by

$$\sigma_r^{-1} = k(\%\,\text{I. C.} + \Theta)$$

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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[2] W. A. Yeranos and J. D. Graham, Spectrochim. Acta **23 A**, 732 [1967].

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

[4] N. B. Hannay and C. P. Smyth, J. Am. Chem. Soc. **68**, 171 [1946].

[5] H. O. Pritchard and H. A. Skinner, Chem. Rev. **55**, 767 [1955].

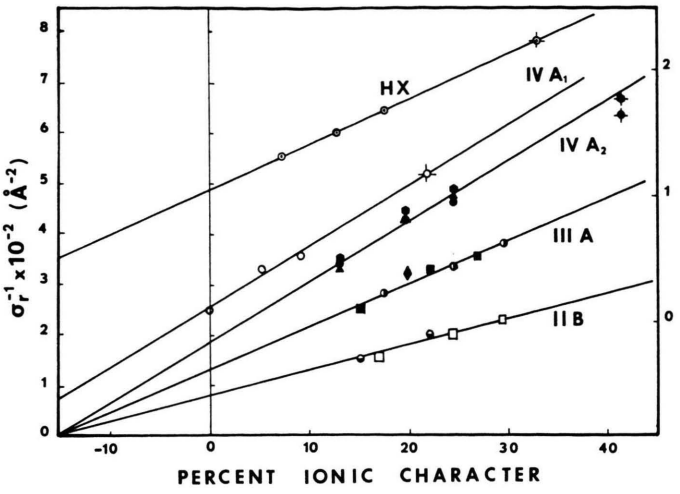

Fig. 1. Correlation of the Mean Amplitude Quantities σ_r with percent ionic character. The carbon tetrahalides are given ○, the silicon by ●, the tin by ▲, the germanium by ◆, the indium by ■, the gallium by ◑, the thallium by ◆, the zinc by □, the cadmium by ◒, and the hydrogen halides by ⊙. The σ_r^{-1} scale on the right is for the hydrogen halides.

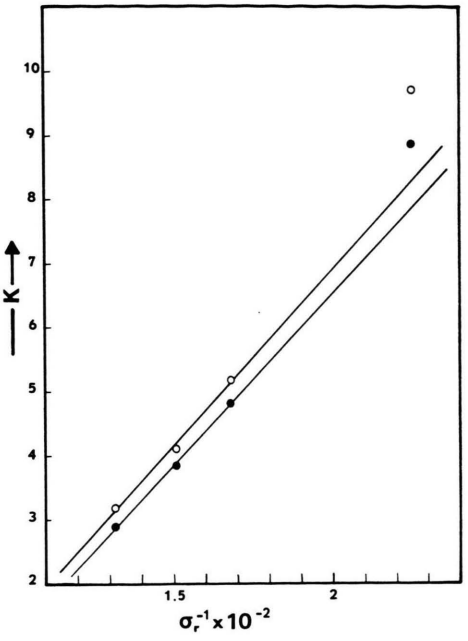

Fig. 2. σ_r^{-1} vs. Force Constants for the Hydrogen Halides. (i) Values depicted by ○ are without anharmonicity corrections, and (ii) values depicted by ● are with anharmonicity corrections.

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 298 °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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* Its vapor pressure at 0 °C is 25 mm [5].