Methyl- α -D-3-oxo-glucopyranoside.

and Ballun⁷, by refluxing the oxo-glucoside for 3 h in unbuffered aqueous ethanol (30 % water) at pH 6. They were reduced with sodium amalgam (2.5 % sodium) for 4 h in aqueous solution buffered to pH 6. The amalgam was added at intervals over 4 h and the pH was kept at 6 by the addition of small amounts of acetic acid, the product was then deionised. The borohydride reduction was done in aqueous solution buffered to pH 9.5 for 5 h and the product was then deionised.

The reduction products were hydrolysed with 0.5 N sulphuric acid for 16 h at 100°, neutralised with Amberlite IR-4B (free base) and the solution obtained was concentrated. The sugars were separated by paper chromatography and a quantitative quadruple estimation was made using the procedure of Saeman *et al.*⁸. Schleicher and Schüll No. 2043a papers were used and the chromatograms were eluted with ethyl acetate-acetic acid-water, 3:1:3 (upper phase).

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Some Remarks about the Shape of Gaussian Error Curve of Absorption Bands

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As it is well known in literature, the Gaussian error curve is often a good approximation of absorption band shape for transition group complexes¹. In the theory of electronic transitions in molecules² this behaviour can be understood as the projection of the (squared) vibrational wavefunction of the electronic groundstate on the potential curve of the excited electronic state. If the electronic groundstate has a parabolic potential curve as function of the internuclear distance, and if the temperature is so low that only the groundstate ($n=0$ in $E = (n + \frac{1}{2})h\nu_0$) of the harmonic oscillator is populated, the Gaussian shaped wavefunction will produce a nearly Gaussian shaped absorption band (by projection on a linear potential curve of the excited electronic state) viz.

$$\varepsilon = \frac{\sigma}{\sigma_0} \varepsilon_0 \exp \left[-\frac{(\sigma - \sigma_0)^2}{\delta^2} \right] \ln 2 \quad (\text{I})$$

where the indices zero on the wavenumber σ and extinction coefficient ε refer to a point near to the band maximum. The

factor $\frac{\sigma}{\sigma_0}$ explains partly that fact¹ that $\delta(-) < \delta < \delta(+)$, where $\delta(-)$ and $\delta(+)$ are the halfwidths of two halves of non-corrected Gaussian curves towards smaller and larger σ . Dr. Klixbüll Jørgensen has pointed out that in this approximation, the maximum occurs at $\sigma = \sigma_0 + \frac{\delta^2}{\sigma_0 2 \ln 2}$ and the ratio between the two half-widths is $\frac{\delta(+)}{\delta(-)} \cong 1 + \frac{\delta}{\sigma_0 \ln 2}$. Reasonable values for the slope of the excited state's potential curve, as implied from ligand field theory³⁻⁵, agree well with the observed values of δ .

It is obvious that for a mixture, where the electronic groundstate is populated e.g. $\sim 75\%$ ($n=0$), 20% ($n=1$), 4% ($n=2$), 1% ($n=3$), a Gaussian shape cannot be obtained of the absorption band. On the other hand, the present note will draw attention to the fact that high temperature and Maxwell-Boltzmann distribution also produces a Gaussian probability distribution in the harmonic oscillator, and thus, a nearly Gaussian-shaped band (I) will also be expected here. We have three cases, which can be experimentally distinguished, viz:

1. $kT \ll h\nu_0$ Nearly Gaussian-shaped band, independent of T for a small heating, δ proportional to $(fm)^{-1/4}$, f is the force constant and m the effective mass.
2. $kT \sim h\nu_0$ The band is not Gaussian-shaped to any good approximation.
3. $kT \gg h\nu_0$ Nearly Gaussian-shaped band, proportional to $\sqrt{T}$ and to $f^{-1/4}$, independent of m .

The proof of the third case is the following: The Maxwell-Boltzmann probability of oscillation with amplitude from a to $a + da$ in a system of harmonic oscillators is given by

$$P(a, da) = \frac{f}{kT} \exp\left(-\frac{fa^2}{2kT}\right) a da$$

Probability of finding a classical harmonic oscillator vibrating with the amplitude a in a position from x to $x + dx$ is given by:

$$P_{a(x, dx)} = \frac{dx}{\pi \sqrt{a^2 - x^2}}$$

Total probability of position from x to $x + dx$ in a system of oscillators vibrating with various amplitudes in thermal

equilibrium is given by:

$$\begin{aligned} P(x, dx) &= \int_{a=x}^{\infty} P(a, da) P_{a(x, dx)} = \\ &= \frac{f}{\pi kT} dx \int_{a=x}^{\infty} \frac{\exp\left(-\frac{fa^2}{2kT}\right)}{\sqrt{a^2 - x^2}} a da = \text{(II)} \\ &= \frac{\sqrt{\pi}}{\sqrt{2\pi kT}} \exp\left(-\frac{fx^2}{2kT}\right) dx \end{aligned}$$

It is seen from (II) that the half width for Gaussian error curve based on the assumption of ligands high vibrational excitement should be proportional to $\sqrt{f/T}$ and unrelated to mass of ligands. Measurements seem to show the half width of absorption bands being nearly unchanged by exchange of ligands in spite of great differences in their masses. Small effects can easily be related to force constants. In such a manner the assumption of high vibrational excitement seems to be more probable. Further confirmations are to be searched by examining the temperature dependance of absorption band half width.

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