Vibrational Broadening of a Charge-transfer Band in an Inorganic Crystal

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FEW, if any, quantitative measurements of bandwidth in the spectra of transition-metal complexes have ever been reported. Orgel[1] remarked on the qualitative differences in bandwidths between the various transitions of Mn^{2+} in aqueous solution and others[2,3] have shown how the broad, near-Gaussian, shapes of most transition-metal spectra at room temperature could be theoretically accounted for as the projection of the lowest vibrational wavefunction of the electronic ground-state on a nearly linear part of the potential-energy curve of the upper state. In contrast, solid-state physicists have studied the interaction of electronically excited-states of point defects in crystals with lattice vibrations and have shown[4] that when the defect suffers a large nuclear displacement Δq in the excited state, the halfwidth of the resulting Gaussian band-envelope is given by

$$(\Delta\nu_{\frac{1}{2}})^2 = \Sigma 4\ln 2.\hbar\omega_{ii}^{32}\,\Delta q\,\coth(\hbar\omega_i/2\boldsymbol{kT}) \qquad (1)$$

if the assumption is made that ground- and excited-state frequencies are identical. From observations of halfwidths as a function of temperature, 'effective' vibrational frequencies may therefore be derived.

To deal with continuous lattices, two extreme models have been proposed: the 'configurational co-ordinate' model,[5] which assumes that a very small number of vibrational modes *i*, localized around the defect, are important, and a model which takes as its starting point the plane-wave vibrations of the pure lattice.[6] One difficulty in assessing the range of validity of these two approaches has been that for the cases of strong electron–phonon interaction which have been studied so far, such as *F*-centres in alkali-metal halides,[7] the energy range expected of the local modes overlaps that of the lattice modes. In inorganic crystals containing discrete complex ions, on the other hand, the internal modes of the complexes are well separated from lattice modes and, from the similarity of the far-i.r.

and Raman spectra of such ions as $PtCl_6^{2-}$ in solution and in the solid state,[8] very little modified by the crystalline field. The spectra of such ions should therefore provide a good test of equation (1).

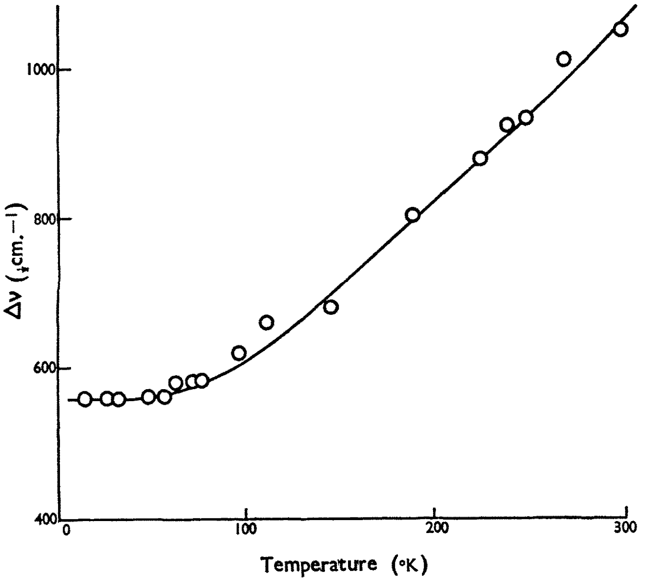

FIGURE. *Halfwidth of the band at* 22,100 cm^{-1} *for* $OsBr_6^{2-}$.

In the course of experiments on the charge-transfer spectra of various hexahalide complexes doped into single crystals of hexahalogenostannate salts,[9,10] we have measured the temperature dependence of some of the bands of $OsBr_6^{2-}$ between 300 and 4° K. In both hexachloro- and hexabromoiridates, a good deal of vibronic fine structure becomes resolved on lowering the temperature to 4° K, but in the osmates the bands, though considerably narrowed, remain smooth, and even at the lowest temperatures no vibrational progressions could be seen. To discover more about the vibrations broadening these transitions we therefore tested equation (1) by using the 22,100 cm.$^{-1}$ band of $OsBr_6^{2-}$, which is particularly suitable for the purpose as it is not overlapped by other bands. The host lattice was $(EtNH_3)_2SnBr_6$. The halfwidths recorded in the Figure were obtained during both heating and cooling runs, and no discontinuities were observed which could be attributed to phase transitions. The temperature was measured by a 0·03 atomic % iron–gold *vs.* Chromel thermocouple in close contact with the sample block, and the spectrophotometer was a Unicam SP 700. The line drawn through the experimental points (Figure) was calculated from equation (1) using ω = 188 cm.$^{-1}$ and shows a good fit to the data over the entire temperature range. By plotting the product of the height and halfwidth *vs.* temperature we found that the oscillator strength of the transition was almost constant, actually increasing by 2—3% between 300 and 4° K. The transition is therefore electric-dipole allowed, as required by the assignment to a charge-transfer excited-state, so that progressions in totally symmetric vibrational modes of the excited state should alone be excited, if the 0th vibrational level of the electronic ground-state is fully populated.[11] No Raman spectra of $OsBr_6^{2-}$ are available, because it is so deeply coloured, but among the neighbouring elements, $ReBr_6^{2-}$ has ν_1 at 213 cm.$^{-1}$[12] and $PtBr_6^{2-}$ at 207 cm.$^{-1}$.[13] The close agreement between these values and that of 188 cm.$^{-1}$ derived from the temperature dependence of the halfwidth of our charge-transfer band make it probable that in the latter, it is indeed the totally symmetric osmium–bromine stretching mode which is primarily responsible for the line-broadening as required by the 'configuration coordinate' model. This is the first occasion on which the frequency responsible for broadening an optical transition of a metal complex has been identified by this means. We also draw attention to the simplicity of the experiment, and the range of applicability of this kind of analysis.

From the experimental halfwidth at low temperature, equation (1) also allows Δq, and hence the displacement of the upper-state potential minimum, to be calculated. In the present example, $\Delta q = 6{\cdot}78 \times 10^{-21}$ cm.g.$^{\frac{1}{2}}$, equivalent to a displacement of 0·06 Å. This small value is compatible with our assignment[9] of the band as one of the spin–orbit components of the excited configuration $t_{2u}^5 t_{2g}^5$, in which an electron has been transferred from purely non-bonding ligand t_{2u} to the metal. More complicated expressions than equation (1) may, of course, be derived by removing the restriction that the ground- and excited-state vibrational modes be identical, but the greater number of theoretical parameters makes them difficult to test experimentally. We are continuing these experiments with other metal complexes.

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