excited state. According to the Franck-Condon principle, the principal vibration frequency excited in the transition should be one of symmetry E_{2g}. The two carbon frequencies in benzene corresponding to this symmetry have wave numbers of 606 and 1596 cm^{-1}. The latter one is of the type where, in the notation of Fig. 2, II and III move towards each other and out from the ring, and V and VI do the same. This frequency is not much lowered by substitution. It does, however, in the excited state of benzene drop to 1485 cm^{-1}, and may drop because of a weakening of the force constant in this partially ionized benzene ring. The experimental distance between the peaks of 0.06 ev corresponds to about 1300 cm^{-1} which seems a reasonable value for the frequency of this type of vibration in the Wurster ion.

The third hump which appears in the spectra of some substituted Wurster ions on the short wave-length side seems to show about the same displacement and may be attributed to the 0–2 vibrational transition.

9. THE INTENSITY OF ABSORPTION

The experimental intensity of absorption can be computed by evaluating approximately the area under the absorption curve. It is found that the observed intensity corresponds to an electron number of $f=0.09$.

The theory shows that the component of the dipole moment in the y axis (Fig. 2) is the one which does not vanish in the transition. The 6 matrix elements of this component for the transitions from the three states ϕ_-, Ψ_-, and $\psi_-{}^{\times}$ which make up the ground state, to the states Φ_0, Ψ_0, which constitute the excited state, were evaluated. It is seen that the dipole moment corresponding to a transition from Ψ_- to Ψ_0 is very large. It corresponds to a charge of one electron multiplied by the distance from the nitrogen atom to the center of the molecule, 2×1.39A. The dipole moment corresponding to a transition from Φ_- to Φ_0 corresponds to a length of 0.72×1.39A. All other matrix elements are very much smaller since the corresponding eigenfunctions differ in the orbitals of at least 2 electrons.

The coefficients with which the various states (1′) to (6′) enter into the ground and excited state may be computed from the determinants at the end of Section 6. The result is that for $\Delta=1.92$ the calculated transition probably corresponds to an electron number of $f=0.34$, in fair agreement with experiment.

Substitution of CH_3 groups on the nitrogen atoms corresponds to a decrease in Δ. This means that the energies of the states Ψ_- and Ψ_0 are lowered. Consequently, the extent to which these states contribute to the ground and excited state, respectively, is increased. Since the matrix element of the dipole moment for transition from Ψ_- to Ψ_0 is the largest term in the total dipole moment, it is seen that a decrease in Δ will bring about an increase in intensity, as is observed in Fig. 1.

DISCUSSION

R. S. Mulliken, *University of Chicago:* Besides its importance for the problem discussed, this interesting paper will be very useful as a guide in other future calculations by the LCAO molecular orbital method. Regarding the quantity Δ, it is not clear to me that one can in general set such a quantity directly equal to a difference of two ionization potentials; however, this is not crucial here, since the empirical difference in ionization potentials is not actually used.

The explanation of the effect of CH_3 substitution in the NH_2 groups in reducing $h\nu$ and increasing the intensity of the absorption bands, by ascribing the effect to a reduction of the N atom ionization potential and therefore of Δ, seems to be very satisfactory, at least qualitatively. I believe, however, that an additional element, namely hyperconjugation between the CH_3 groups and the system of unsaturation ($2p\pi$) electrons extending through the molecule, may also contribute to an appreciable degree. Even if it had no effect on Δ, hyperconjugation (like conjugation—which is already taken into account in the computations) could cause changes in ionization potential and in excitation energy. Actually, conjugation and hyperconjugation in general cause what Dr. Sklar, in his papers on substituted benzenes, calls "migration of charge,"

and so also affect Δ. In general, migration of charge arises both from the existence of atomic Δ's and from conjugation or hyperconjugation.

The factor of about 3 by which the computed f value for the transition in the Wurster's salt prototype exceeds the observed is the usual factor by which the computed exceeds the observed intensity for $N \rightarrow V$ transitions in LCAO molecular orbital computations for moderate-sized molecules. Some computations by Mrs. C. A. Rieke and the writer on the hydrogen molecule indicate how such a factor can be understood. Essentially, the Z values for the atomic orbitals used should be adjusted, and differently for different electronic states of a molecule. Unfortunately, such adjustments cannot be made without greatly complicating the theoretical computations; the ordinary LCAO method depends upon the use of the same atomic orbitals for all states. Hence, except in a few cases of particular importance, the LCAO method must probably suffice for some time to come.