

results are applicable to the  $1s \rightarrow 2p$  transition bands  $a, b, d, f, h, i$  and transitions to higher states  $e, g, j$  are attributed to the same orbital results for semi-localized calculations.

The existence of  $e_2$  bands is assumed. This assumption that irradiation at a wavelength that causes a reversible change in the electron trap. The calculation of  $\nu$  for

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Professor G. Stein for

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## the Surface Processes

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call attention to an experiment observed when highly ionized, small, nonconductive particles of superficial conductivity are introduced into a tube, and its magnitude is a function of the ion (presumably  $e_2$ ). At a plasma concentration, the superficial conductivity has been estimated. The results were as follows: The particles passed down a tube at a rate of 1 cm/min, and probes were placed at various holes in the glass tube. The processes observed are of the same nature as those observed with the probes are almost the same on both sides, the results are the same (while normally

infinite in the absence of the plasma) is less than an order of magnitude during the passage of the plasma by the probes.

It is not the intention of this group to investigate the discovery further, since it was accidentally observed in the course of another program which engages our full attention. However, it is believed that this effect casts additional light on previously known probe effects in which sealing of probes directly into the ends of glass rods always results in apparent probe areas far greater than the area of metal exposed. This effect has been generally assigned to "working of the glass," but now appears to be a result of the superficial glass conductivity when a plasma containing electrons impinges upon the assembly. Furthermore, the possibility of superficial glass conductivity may account for the ease of disposal of charges of both signs which migrate as an ambipolar current to the walls of Geissler tubes, etc.

The speculation that proximity to an electron atmosphere is the cause of the conductivity is based on the well-known fact in gaseous electronics that the Schottky theory of the positive column implies the existence of either a surface or volume concentration of negative charge at any boundaries. It is therefore presumed that the mechanism of the superficial conduction is either electron mobility in an adsorbed layer on the surface, or a filling of the conduction bands of the surface layers of glass with electrons from the plasma as a donor. The latter viewpoint seems to be in better accord with the observed strong dependence upon the nature of the wall medium.

Pyrex glass is the most striking material that we have worked with, but similar though reduced effects are observed with Vycor. This work is an outgrowth of research supported by the National Science Foundation.

## Semilocalized Bond Orbital Treatment of the Allyl Radical

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IN calculations on the  $\pi$ -electron system of the allyl radical  $H_2C_a-C_bH-C_cH_2$ ,<sup>1,2</sup> the energy of the ground state  ${}^2A_2$  obtained by using the Berthier-Pople-Nesbet-type (BPN) SCF-LCAO-MOs without configuration interaction (CI) is  $3W_{2p} - 28.29$  eV, which is lower than that of the Hartree-Fock-type SCF-LCAO-MOs without CI ( $3W_{2p} - 27.15$  eV) and also that of the valence-bond (VB) method without ionic-homopolar-resonance (IHR) ( $3W_{2p} - 28.03$  eV). This is because the BPN  $1b_1$  MOs are one kind of the alternant orbital. Here, it is of interest to compare the above results with those of the semilocalized bond orbital

TABLE I. Electronic energies.<sup>a</sup>

State	WF	$\lambda_m$	$E(\lambda=\lambda_m)$	$E(\lambda=0)$	$E(VB+IHR)$
${}^2A_2$	$\Psi_1 + \Psi_2$	0.22	-28.88	-28.03	-28.94
${}^2B_1$	$\Psi_1 - \Psi_2$	0.08	-26.48	-26.05	-26.48
$\triangle$ or $\triangle$	$\Psi_1$ or $\Psi_2$	0.14	-28.20	-27.59	-28.21
$[{}^1A_{1g}]$	ethylene	0.15	-12.39	-11.73	-12.39
${}^2B_1$ ( $\triangle$ )	$\Psi_3$	0.00	-26.05	-26.05	-26.05
$[{}^1A_{1g}]$	ethylene	0.01	-5.71	-5.71	-5.71

<sup>a</sup> Values of energies in eV; energy zero is  $3W_{2p}$  and  $2W_{2p}$  for the allyl radical and the ethylene molecule, respectively.

(SLBO) treatment as an extension of the VB method, since these two calculations include partly, though each in a different way, the correlation energy.

The wave functions corresponding to canonical structures,  $\triangle$ ,  $\triangle$  and  $\triangle$ , respectively, were constructed as functions of a parameter  $\lambda$  as follows:

$$\Psi_1 = \begin{pmatrix} a+\lambda b & b+\lambda a & c \\ \alpha & \beta & \alpha \end{pmatrix} - \begin{pmatrix} a+\lambda b & b+\lambda a & c \\ \beta & \alpha & \alpha \end{pmatrix}$$

$$\Psi_2 = \begin{pmatrix} a & b+\lambda c & c+\lambda b \\ \alpha & \beta & \alpha \end{pmatrix} - \begin{pmatrix} a & b+\lambda c & c+\lambda b \\ \alpha & \alpha & \beta \end{pmatrix}$$

and

$$\Psi_3 = \begin{pmatrix} a+\lambda c & b & c+\lambda a \\ \alpha & \alpha & \beta \end{pmatrix} - \begin{pmatrix} a+\lambda c & b & c+\lambda a \\ \beta & \alpha & \alpha \end{pmatrix}.$$

Using these wave functions and their linear combinations  $\Psi_1 \pm \Psi_2$ , the minimized energies of the  ${}^2A_2$  and  ${}^2B_1$  states and of each of the canonical structures were calculated. The results are given in Table I, together with those of the VB method ( $\lambda=0$ ), and the VB+IHR method. The values of  $\lambda$ , corresponding to the minimum energy ( $\lambda_m$ ), differ considerably according to the states or the structures, but the charge distributions so obtained are scarcely different from those given by the VB+IHR method.<sup>1</sup> In comparison with each canonical structure, the larger value of  $\lambda_m$  for the  ${}^2A_2$  state indicates an increase of ionic contribution due to the resonance between these structures in the ground state. The energy of the  ${}^2A_2$  state obtained by the SLBO method is much lower than that obtained by the BPN method, and is very close to that given by the VB+IHR method. For the  ${}^2B_1$  state,  $\Psi_1 - \Psi_2$  gives a considerably lower energy than  $\Psi_3$ , while they have the same energy in the nonpolar case ( $\lambda=0$ ). This means that the contribution of polar structures between adjacent atoms, is much larger than the contribution of nonadjacent atoms. For each canonical structure, the energy depression by the SLBO method  $E(\lambda=0) - E(\lambda=\lambda_m)$  and the value of  $\lambda_m$  are fairly close to those for an ethylene molecule with the corresponding internuclear distances.