

FIG. 1. $1s \rightarrow 2p$ transition of an electron in liquid ammonia.

placed at infinity from the cavity center.

$$V(r) = -\frac{s_{\mu e}}{r_0^2} - \frac{s_{\alpha e^2}}{2r_0^4} - \frac{2\pi N \alpha e^2}{r_0 + 2r_{\rm NH_3}} \quad r < r_0 \quad (1a)$$

$$V(r) = -\frac{c^2}{r} \left(\frac{1}{D_{0p}} - \frac{1}{D_s} \right) \qquad r > r_0 \qquad (1b)$$

where r_0 is the e.c. radius, r_{NH_3} radius of solvent molecules, s number of solvent molecules surrounding the e.c., α polarizability of solvent molecule, μ dipole moment of solvent molecule, N number of solvent molecules per cc in the bulk, and D_{0p} and D_s optical and static dielectric constants.

Equation (1a) is based on a rough structural model. The third term was obtained from the expression

$$\int_{r_0+2r_{\rm NH_3}}^{\infty} \frac{\alpha e^2}{2r^4} 4\pi N r^2 dr$$

Equation (1b) is Landau's expression for a potential well formed by directed dipoles surrounding a negative charge. The approximate value of $r_0 = 3.6$ A is calculated assuming continuity of V(r), setting s=4.

The dipole rearrangement energy-II-required for formation of the potential well was calculated from an electrostatic model. The value $\Pi = 0.45$ ev was obtained.

In the potential well (1) an infinite number of stationary states $(W_1 W_2 \cdots)$ exists. For the higher states:

$$W_n = \frac{me^4}{2\hbar^2 n^2} \left(\frac{1}{D_{0p}} - \frac{1}{D_s} \right)^2 \quad n = 2, \, 3 \cdots .$$
 (2)

For the ground (1s) state W_1 is obtained from

$$H_{\mathfrak{o}}^{s} = W_{1} - \Pi \tag{3}$$

hence $W_1 = 2.1$ ev $W_2 = 1$ ev.

During the electronic transition the dipole arrangement is not changed. Hence we get

$$h\nu_{1\to n} = W_1 - W_n = H_e^s + \Pi - W_n. \tag{4}$$

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We assume that these numerical results are applicable to all systems of Table I. For the $1s \rightarrow 2p$ transition $h\nu = 1.1$ ev (see Fig. 1). The intense bands a, b, d, f, h, i refer to this transition. For transitions to higher states the series limit is 2.1 ev. The bands c, e, g, j are attributed to these transitions. The experimental results for ammonia are in agreement with these calculations.

Spectrophotometric evidence for the existence of en centers¹ may be found in the k band. This assumption is supported by the observation⁷ that irradiation at the *i* band wavelengths gives rise to a reversible change in the k band intensity, indicating that at low temperatures an e.c. may possibly act as an electron trap.

Our results make possible the calculation of v for liquid ammonia.

Setting⁸ a=1.6 ev from

$$a = H_e^s + \Pi + ev \tag{5}$$

we get v = -0.5 volt.

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Plasma Augmentation of the Surface Conductivity of Glasses

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'HE purpose of this note is to call attention to an effect which we have observed when highly ionized gases are in contact with normally nonconducting surfaces, especially glasses. Superficial conductivity is then observed over the nonconductor, and its magnitude seems to be a function of the ion (presumably electron) concentration in the plasma. At a plasma concentration of 10¹⁶ to 10¹⁷ ions/cc, superficial conductances of the order of 1 mho or less have been estimated. The technique of the experiments was as follows: a flowing hydrogen plasma was passed down a tube through a transverse magnetic field, and probes were introduced into the plasma through holes in the glass walls. Normally the plasma resistances observed are of the order of 1000 ohms, but when the probes are allowed to touch the glass walls on both sides, the indicated resistance between the probes (while normally

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call attention to an rved when highly mally nonconductrficial conductivity ctor, and its magnie ion (presumably a. At a plasma consuperficial conducwe been estimated. ts was as follows: ssed down a tube l, and probes were holes in the glass ces observed are of the probes are aln both sides, the bes (while normally

minite in the absence of the plasma) is less than an ohm 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 Shottky 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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TN calculations on the π -electron system of the allyl I radical $H_2C_a - C_bH - C_cH_2$,^{1,2} the energy of the ground state 2A2 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 $(3W_{2p}-27.15 \text{ ev})$ and also that of the valence-bond (VB) method without ionichomopolar-resonance (IHR) $(3W_{2p}-28.03 \text{ ev})$. 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.ª

State	WF	λ_m	$E(\lambda = \lambda_m)$	$E(\lambda = 0) I$	C(VB+IHR)
² A ₂	$\Psi_1 + \Psi_2$	0.22	-28.88	-28.03	-28.94
${}^{2}B_{1}$	$\Psi_1 - \Psi_2$	0.08	-26.48	-26.05	-26.48
\triangle or \triangle	Ψ_1 or Ψ_2	0.14	-28.20	-27.59	-28.21
$[{}^{1}A_{1g}$	ethylene	0.15	-12.39	-11.73	-12.39]
$^{2}B_{1}$ (\bigtriangleup)	Ψ_3	0.00	-26.05	-26.05	-26.05
$\begin{bmatrix} {}^{1}A_{1g} \end{bmatrix}$	ethylene	0.01	-5.71	-5.71	-5.71]

* Values of energies in ev: energy zero is $3W_{2p}$ and $2W_{2p}$ for the ally 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 λ 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

$$\Psi_{3} = \begin{pmatrix} a + \lambda c & b & c + \lambda a \\ \alpha & \alpha & \beta \end{pmatrix} - \begin{pmatrix} a + \lambda c & b & c + \lambda a \\ \beta & \alpha & \alpha \end{pmatrix} \cdot^{3}$$

Using these wave functions and their linear combinations $\Psi_1 \pm \Psi_2$, the minimized energies of the 2A_2 and ${}^{2}B_{1}$ 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 λ , corresponding to the minimum energy (λ_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.¹ In comparison with each canonical structure, the larger value of λ_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 ${}^{2}A_{2}$ 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 ${}^{2}B_{1}$ state, $\Psi_{1}-\Psi_{2}$ gives a considerably lower energy than Ψ_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 λ_m are fairly close to those for an ethylene molecule with the corresponding internuclear distances.