for bands arising from $v''=0$ but have not found them. Regions in which there is no NO absorption would permit observation of lines from 9,0; 10,0; and 11,0 of oxygen which are among the stronger of the Schumann–Runge bands. No pertinent lines have been found. Two features might suggest $v''=0$ oxygen absorption if observed under low resolution. One of these is the 1924.8 Å band. The 4,0 band head lies at 1924.2 Å, but our analysis indicates the identification stated earlier. In addition, if the 1924.8 Å band were 4,0, which is a weak band, then the 9,0–11,0 region should, but does not, show strong absorption. The second suggestive feature is a red degraded band at 1845.3 Å. (The oxygen 8,0 band head lies at 1946.4 Å.) This band is, however, NO β 9,0.

Strong evidence for the absence of $v''=0$ oxygen absorption comes from some auxiliary experiments. The absorption spectrum of oxygen at room temperature was obtained under spectrographic conditions comparable to those used in the flash photolysis. From the photolysis of NO_2 a maximum of 0.25 mm Hg of oxygen could have been formed. At a pressure of 0.5 mm of oxygen in the 35-cm path length the longest wavelength band visible was 8,0, while 50 mm Hg was needed to show the 4,0 band with the same intensity as the feature at 1924.8 Å.

Integrated absorption intensities have been measured for lines in several bands for samples of NO_2:Ar = 1:300, NO_2 = 0.5 mm Hg. These have been interpreted by using the "curve-of-growth" technique,[3] together with integrated absorption coefficients (f values), estimated from the work of Herbert and Nicholls[4] and of Bethke.[5] A check of the method, using narrower (17-μ) slits, against measurements on molecular oxygen at room temperature was satisfactory. Systematic errors in determining integrated intensities with 50-μ slits probably have led to *smaller* values for populations than actually exist. No correction for this has been made.

At 60 μsec after the flash we find about the same population, 2 to 8×10^{14} molecules/cc, in each of the levels $v''=2$ to 6. The estimates are reproducible within a factor of 2. We estimate a total of 1.5×10^{15} molecules/cc excited to these levels, which is to be contrasted with a possible total oxygen production of 1×10^{16} molecules/cc (0.25 mm Hg) from the reaction. Thus we conclude that excited oxygen molecules form a significant portion of the products from this reaction.

A detailed report of this work will be published later.

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Comments and Errata

Erratum: Kinetics of the Reaction Between Solvated Electrons and Water in Ethylenediamine

[J. Chem. Phys. **39**, 2388 (1963)]

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THE "note added in proof" on p. 2388 does *not* refer to the data given in Table I nor to the other conclusions of the work. It refers rather to the apparent build-up and decay of an intermediate inferred from several traces made at 750 mμ. Recent studies have failed to verify the existence of an intermediate.

Erratum: Truncated Reaction Operators

[J. Chem. Phys. **39**, 2429 (1963)]

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DUE to a printer's error, $C_{kq}(n)/N$ should be replaced by $C_{kq}(n)$ in Eq. (34). In the heading of Table II, Ψ_8 should be replaced by Ψ_q.

Discontinuous Change of Binding Type in the Series of Monohydrides

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VARIOUS facts, e.g., refractometric data, showed[1,2] the existence of continuous polarization effects. It was suggested that when such effects become sufficiently pronounced a discontinuous change of quantization, i.e., of the kind of subdivision of the electronic system into quantized groups may occur. The consideration of such a change, e.g., in the series of the hydrides LiH to HF, became imperative on the basis of the quanticule theory (Q.T.) of chemical binding.[3–5]

Accordingly, the molecule

$$LiH = Li^+H^- = (\bar{e}_2Li^{3+})(\bar{e}_2H^+)$$

consists of two mononuclear quanticules $\bar{e}_2$ quantized with respect to the nuclei Li^{3+} and H^+. Because of the

TABLE I. Internuclear distances (Å) and quotients Q'.

	LiH	BeH	BH	HC	HN	HO	HF
r_e	1.5953$_5$	1.3431	1.2325	1.1198	1.0372	0.9707	0.9171
Q'		1.1878	1.0897	*1.1006*	1.0796	1.0685	1.0584

considerable polarizability of H^-, its $\bar{e}_2$ is pulled towards Li^+ and the degree of polarity[6] of LiH is 0.77. In $BeH = Be^+H^- = \bar{e}Be^{2+}H^-$ the ion B^+ has an appreciable polarizability, its $\bar{e}$ is repelled by H^- and this quanticule formula (Q.F.) indicates appropriately that H^- is here nearly as strongly attracted and polarized as it is in $Be^{2+}H^-$. Proceeding to $BH = \bar{e}_2B^{3+}H^-$ etc., one has to expect that somewhere in the series the two electrons of H^- lose their mononuclear quantization because, when H^+ penetrates $F^- = (F^{7+})\bar{e}_8$, the molecule $HF = (H^+,F^{7+})\bar{e}_8$ results which contains the binuclear quanticule $\bar{e}_8$.

In an attempt to answer[3,4] the question where, e.g., in the above series, the discontinuous change from the quantization $\bar{e}_{n-1}M^{n+}H^-$ to $(H^+,X^{n+1})\bar{e}_{n+2}$ occurs, the binding strength (B.S.) in the neutral molecule was compared with that in the molecule ion. As a measure of B.S. the vibrational force constant or the internuclear distance was used. The ionization $\bar{e}_{n-1}M^{n+}H^- \rightarrow \bar{e}_{n-2}M^{n+}H^-$ should cause an increase in B.S. because the electrons $\bar{e}_{n-1}$ repel H^-, i.e., are antibinding. Hence a decrease of B.S. indicates the change $(H^+,X^{n+1})\bar{e}_{n+2} \rightarrow (H^+, X^{n+1})\bar{e}_{n+1}$ and that the $(n+2)$th electron moves predominantly in the binding region.[7,8]

In this way, on the one hand the formulas $\bar{e}Be^{2+}H^-$ and $\bar{e}_2B^{3+}H^-$ were confirmed, on the other hand $(H^+,O^{6+})\bar{e}_7$ was derived, but sufficient spectroscopic data were not available in 1943 to decide the type of quantization for CH and NH.

Present knowledge[9,10] of the ground states of molecules and molecule ions, as well as of their excited states, allows one to establish additional interrelations between them. To complete first the elucidation of the above series, the formulations left open in 1943 are $(H^+,C^{4+})\bar{e}_5$ and $(H^+,N^{5+})\bar{e}_6$, i.e., the discontinuous change occurs between $\bar{e}_2B^{3+}H^-$ (abbreviated BH) and $(H^+,C^{4+})\bar{e}_5$ (abbreviated HC).

Among the methods applied now for testing such discontinuities, space limitations allow the explanation only of that shown in Table I. If the Q.F. $\bar{e}_{n-1}M^{n+}H^-$ were valid in the whole series LiH to FH then, for reasons mentioned in comparing Li^+H^- with $\bar{e}Be^{2+}H^-$, the B.S. would increase regularly with increasing n. Since the relative change of n is larger in the transition from 1 to 2 than from 2 to 3, etc., one would expect that the quotient $Q' = r_n/r_{n+1}$ decreases regularly along the series. This is not the case, however: the value $BH/HC = 1.1006$ is larger than both adjacent Q'. This means that the B.S. in the existing stable $(H^+,C^{4+})\bar{e}_5$ is larger than in the unstable $\bar{e}_3C^{4+}H^-$.

An analogous irregularity of Q' occurs in the second octave for the value AlH/HSi showing, as do other data, a close analogy in the behavior of both octaves. In the series CuH to HBr, AgH to HI, and AuH to BiH, the gradation of properties from the first to the third group is different[4] from that for hydrides of the light metals; nevertheless, the change of quantization seems to take place also between the third and fourth group, e.g., between GaH and HGe. In the series KH to NiH, RbH to PdH, and CsH to PtH the available scarce spectroscopic data indicate only the quantization M^+H^-.

As to the molecule ions, the formulation M^+H^- for the neutral monohydrides of monovalent metals explains at once why for none of these hydrides, either of light or heavy metals, an ion $(MH)^+$ has been observed. The detachment of an electron leads, e.g., to Na^+H which dissociates into Na^+ and H. Monohydride ions of various higher valent elements are known and it is possible to predict that the discontinuity between the structures $\bar{e}_{n-2}M^{n+}H^-$ and $(H^+,X^{n+1})\bar{e}_{n+1}$ occurs at a higher value of n than for the neutral molecules $\bar{e}_{n-1}M^{n+}H^-$ and $(H^+,X^{n+1})\bar{e}_{n+2}$. In fact, the structures for the ions are: $(CH)^+$ [contrary to HC], $(SiH)^+$, $(PH)^+$, and with considerable probability, $(NH)^+$ for which the experimental data are not yet precise enough to make the decision final. On the other hand, the formulations $(HO)^+$ and $(HCl)^+$ are proved experimentally, $(HF)^+$ inferred from them, and $(HS)^+$ considered as probable but not yet certain.

Excited states of neutral molecules as well as ions $\bar{e}_mM^{n+}H^-$ can have the structure $\bar{e}^*\bar{e}_{m-1}M^{n+}H^-$, in which the excitation (*) of one of the antibinding electrons $\bar{e}_m$ causes an increase of B.S. On the other hand, in a state $\bar{e}_mM^{n+}(H^-)^*$ the binding is weaker and for alkali hydrides[11] very much weaker than in the ground state. The force constant of LiH decreases in the A state by a factor 36, those of NaH to CsH on the average by 16.

In the ground state of neutral and singly ionized hydrides $(H^+,X^{n+})\bar{e}_m$ all $\bar{e}_m$ seem to be moving predominantly in the binding region and the excitation to a state $(H^+,X^{n+})\bar{e}_{m-1}\bar{e}^*$ causes, in most cases, a diminution in B.S. The relatively small increase in B.S. which occurs in states A of HC and a of HN is interpreted as a differential effect[7]: the weakening of the binding due to $\bar{e}^*$ is overcompensated by the strengthening of the binding due to the electrons $\bar{e}_{m-1}$. They are less intensively repelled by $\bar{e}^*$ and have a greater probability of being found in the binding region than they have in the ground state.

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Notes

Hole Traps at the Surface of Anthracene Crystals*

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THE most direct method of detecting trapping sites in an insulator is the conductivity glow curve technique in which the crystal is irradiated at low temperature and then warmed at a uniform rate in the dark. Carriers trapped at the low temperature become thermally released at some higher temperature giving rise to a maximum in the dark current. Measurements of this kind have been carried out on anthracene[1,2] single crystals and a discrete set of traps were found 0.77 ± 0.07 eV from the band edge. The nature of the trapping site and the sign of the trapped carrier remained undecided although it was shown that the introduction of tetracene impurity or extensive x irradiation had the effect of removing the conductivity glow peak. Thus it was concluded that the trapping center was not a substitutional site or some structural defect in the crystal lattice.

However, this behavior can be explained in terms of surface sites occupied by adsorbed oxygen molecules. It is well known that a reversible oxygen adsorption process affects the surface photocurrent of anthracene by the formation of a negatively charged layer.[3,4] Thus there are two possible trap mechanisms, viz., electrons trapped on adsorbed oxygen molecules, or holes trapped at the crystal surface adjacent to a molecule of adsorbed oxygen. Conductivity glow curves were studied in three distinct ranges of oxygen pressure: (a) $<10^{-3}$ mm so that the gas was desorbed at both the low (150°K) and high (330°K) temperature extremes of the experiment, (b) about 1 mm so that the gas was adsorbed almost completely at the low temperature yet was desorbed at room temperature, and (c) >40 mm so that the surface was always essentially covered. In experiment (b) the prominent peak[1,2] at about 0°C was readily obtained. In experiment (a) the corresponding conductivity peak could not be detected with our apparatus since it was reduced by at least a factor of 50. We conclude that the glow peak is associated with the presence of adsorbed oxygen. In experiment (c) the conductivity peak was even larger than in (b) so that the removal of the negative charge from the oxygen molecules prior to desorption is not necessary for production of the glow peak. Therefore the peak is created in the process of freeing positive holes from the vicinity of adsorbed oxygen.

Earlier work[3,5] has established that the rate at which the anthracene/oxygen system reaches equilibrium depends on the intensity of illumination. There is a number of ways to explain how the negative charge is acquired by the adsorbed oxygen. Free electrons and holes may be formed in the crystal bulk with the electrons becoming localized on the oxygen after diffusion to the surface. A more likely explanation involves migration of either a singlet or triplet exciton to the surface where a complex intersystem crossing occurs from a state represented approximately by a triplet exciton localized by a triplet ground-state oxygen molecule to a charge transfer state describing a positive hole trapped near the ion O_2^-. The latter model invoking an adsorbed oxygen molecule as an acceptor site receives some support from the observation[6] that oxygen quenches the delayed fluorescence from microcrystalline aromatic hydrocarbons. Other authors[7,8] have presented evidence to show that a bulk generation of carriers does occur but that this is small compared with the production at the surface.[9] The earlier observation that the presence of tetracene impurity reduces the current glow peak is readily interpreted as providing a very efficient alternate path for the degradation of the energy from the singlet exciton state. Heavy x irradiation must form a layer of anthraquinone which is known[3] to compete with oxygen for the surface sites.

Recent investigations of the space-charge-limited currents in anthracene[10,11] have provided considerable information about trapping processes. Once more positive holes are shown to be the carriers localized in a deep trap (about 0.8 eV or more from the hole band) as well as a series of traps whose density per unit energy range decreases exponentially with energy from the hole band. We have found no evidence for the existence of this series of traps but note that there would be other bound states for the hole about the O_2^- ion apart from the deepest in which the hole and gas ion are closest. However, before we can claim that the traps measured by these different techniques are the same it must be shown that adsorbed oxygen was present in all cases. Adolph and co-workers[11] illuminated