rather satisfactory and indicates that no important terms have been neglected in the theoretical (ab initio) evaluation of these quantities. It is too early to say whether the very small remaining differences between observed and calculated values are significant.

A detailed account of the work on the dissociation energies is being published elsewhere.[9] The work on the ionization potential will be expanded and will be published in more detail later.[10]

I am greatly indebted to Dr. P. R. Bunker and Dr. U. Fano for communicating to me their unpublished theoretical results, and to Dr. P. Thurnauer and Miss B. J. McKenzie for much help in the evaluation. Mr. Shoosmith carried out the experiments with his usual thoroughness and skill, and Dr. A. E. Douglas helped with critical comments. To all of them I should like to express my thanks.

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SPECTROSCOPIC IDENTIFICATION OF EXCITED ATOMIC AND MOLECULAR STATES IN ELECTRON-BOMBARDED LIQUID HELIUM*

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Optical and infrared emission spectra of electron-bombarded liquid helium reveal the presence of a number of excited singlet and triplet states of the He_2 molecule, including the $a^3\Sigma_u^+$ metastable state. The observed liquid spectra show vibrational and unresolved rotational structure. There is also preliminary evidence that excited atomic states, including the metastable 2^3S_1 state, are populated in the liquid.

The existence of energetic neutral localized excitations, created in liquid helium by an immersed radioactive source, has been established in recent work by Surko and Reif.[1] Also, indirect evidence of long-lived excitations and of an effective energy-transfer mechanism to colloidally suspended impurities has been reported by Jortner et al.[2] (See also Fischbach, Roberts, and Hereford.[3]) However, none of these experiments has provided any information on the identity or structure of the excitations. In this Letter we report the spectroscopic identification of electronically excited He_2 molecules in electron-bombarded liquid helium. In particular, it is found that the metastable $a^3\Sigma_u^+$ state is populated at a rapid rate. Preliminary spectroscopic data also suggest the presence in the bombarded liquid of metastable 2^3S_1 atoms. Both species are known to have very long natural lifetimes and to be quite stable against collisions in gaseous helium.[4] Thus both would appear to be good candidates for the unidentified localized excitations found by Surko and Reif.[1,5]

Our experimental arrangement is illustrated in Fig. 1. A beam of electrons with nominal energy 160 keV is incident upon the liquid-helium sample through a thin (0.000 125-in.) metal foil,[6] which serves to separate the cryostat interior from the common vacuum space of the Dewar flask and electron-accelerator beam tube. This technique for exciting liquid samples has several advan-

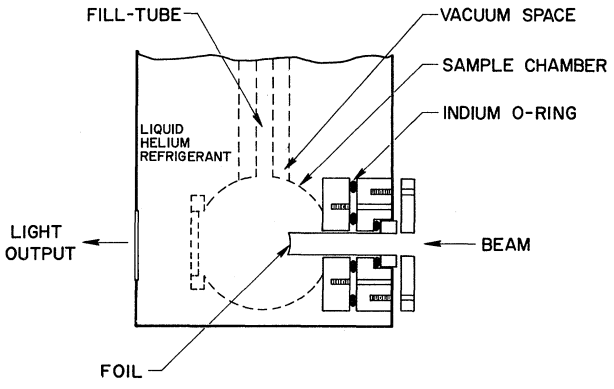

FIG. 1. Experimental apparatus.

tages over immersed radioactive sources for spectroscopic studies, the most obvious being the higher available flux of projectiles and the pulse capability for lifetime studies of transient excited species. For some of the experiments, high-purity helium was condensed into a separate vacuum-tight copper sample chamber (dotted lines in Fig. 1) immersed in the liquid-helium bath. With this arrangement, low-temperature gas spectra can be observed and impurity effects can be distinguished from pure-helium spectra by admitting metered quantities of impurity gases. Energy-transfer effects in liquid helium, such as those originally reported by Jortner et al.,[2] were observed upon addition of O_2, N_2, or neon.

Light emitted from the excitation region is viewed and analyzed through sapphire windows located on either side of the Dewar and on the electron-beam axis opposite the entrance foil. The emitted light is mechanically chopped, analyzed with a $\frac{1}{4}$-m Jarrell-Ash Ebert spectrometer, and detected synchronously with either an S-1 or S-20 photomultiplier tube.

A thorough photographic study was undertaken to establish conditions under which local boiling might be induced by the incident electron beam. Most of our data were taken with the liquid-helium sample at a temperature of about 1.7°K, well below the 2.2°K λ-point transition to the liquid-helium II (superfluid) phase. In this temperature range liquid helium II does not boil even under reduced vapor pressure, because its anomalously large effective thermal conductivity precludes the establishment of significant thermal gradients. Photographs of the excitation region (which is about 1 cm in diameter and extends some 4 mm into the liquid, the latter figure being the range of 160-keV electrons in the liquid) established that no boiling occurs in liquid helium II for beam currents below approximately 30 μA (i.e., about 5 W); at somewhat higher currents, the precise value depending upon the initial liquid temperature and capacity of the pumps used to exhaust the vapor above the liquid, vigorous boiling in the excitation region appears suddenly and expands within a matter of seconds through out the liquid-helium bath. Thus, our photographic study suggests that heat energy deposited by the beam is distributed very effectively throughout the liquid helium II, and no boiling occurs unless the heat input from the incident electron beam is sufficient to overwhelm the pumps and drive the entire bath above the 2.2°K transition temperature. All experimental data were taken with beam currents less than 15% of this critical value. Optical emission from the excited liquid is easily visible to the naked eye with excitation currents below 1 μA. As an additional precaution, data were taken over a wide range of beam currents and it was ascertained that shapes of spectral features were beam independent, and intensities were directly proportional to current. Sudden narrowing of the spectroscopic features and sharply increased peak line intensities (i.e., gaslike spectra) are observed when boiling is deliberately induced.

Some 30 resolved special emission features are observed in electron-bombarded liquid helium in the wavelength interval from 6000 to 11 000 Å; all but six can be identified as excited molecular-helium transitions, and three of the remaining features probably result from atomic-helium transitions. The spectrum is shown in low resolution in Fig. 2, with the spectral features identified. Identification was facilitated by compar-

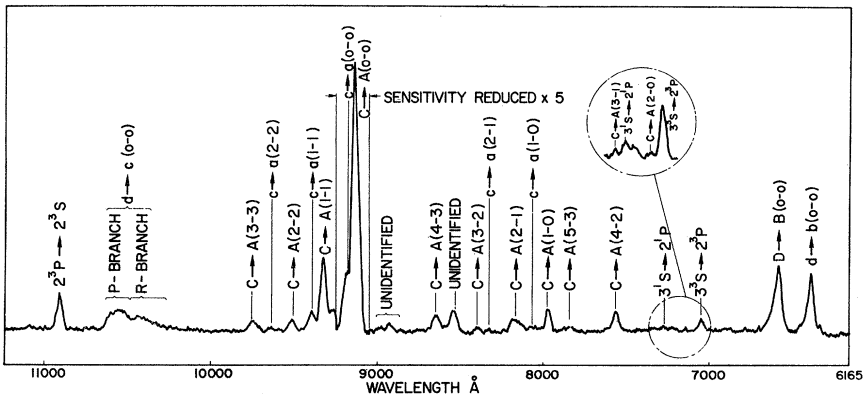

FIG. 2. Emission spectrum of electron-bombarded liquid helium, observed using $\frac{1}{4}$-m Jarrell-Ash spectrometer with 0.5-mm slits (instrumental resolution ~50 Å) and S-1 photomultiplier.

ison with spectra obtained in the same apparatus from electron-bombarded gaseous helium at 4.2°K over a range of densities from about 7.5 $\times 10^{19}$ atoms/cm (30 Torr) to about 10^{21} atoms/cm (350 Torr). (The latter density is only a factor 20 lower than the liquid density.) The principal (0-0) vibrational bands resulting from $d^3\Sigma_u^+ \rightarrow b^3\Pi_g$, $d^3\Sigma_u^+ \rightarrow c^3\Sigma_g^+$, $c^3\Sigma_g^+ \rightarrow a^3\Sigma_u^+$, $D^1\Sigma_u^+ \rightarrow B^1\Pi_g$, and $C^1\Sigma_g^+ \rightarrow A^1\Sigma_u^+$ molecular transitions are readily identified in the gas spectra by means of characteristic rotational structure.[7,8] Each of these bands is observed also in the liquid, though the features are substantially broader (typically about 20 Å) and shifted in wavelength toward the violet by a few wave numbers. Figure 3 shows a comparison of the $d \rightarrow b$ and $D \rightarrow B$ bands observed under high resolution in dense gas and liquid. The similarities are obvious, with the liquid spectra exhibiting "averaged out" rotational envelopes that correspond closely to the rotational structure observed in the gas.[9] The similarities between gas and liquid spectra are just as convincing for the $c \rightarrow a$, $C \rightarrow A$, and $d \rightarrow c$ transitions. For this reason we identify the liquid features of Figs. 2 and 3 with the corresponding gas features and infer that excited species of the He_2 molecule exist in the liquid. As indicated in Fig. 2, most of the remaining spectral features can be identified as other vibrational bands of the $d \rightarrow c$, $c \rightarrow a$, and $C \rightarrow A$ transitions.[8] Other bands of the $d \rightarrow b$ and $D \rightarrow B$ transitions are neither expected nor observed because the nearly identical internuclear separations[7] and interaction-potential wells of the upper and lower states imply negligible Franck-Condon factors for these transitions other than between states of the same vibrational quantum number; the allowed $d \rightarrow b$ and $D \rightarrow B$ bands originating on low vibrational states almost coincide with the stronger (0-0) transitions and are therefore unobservable.

In thermal equilibrium at 4.2°K or below, only the lowest vibrational and rotational levels of the various electronic states of the molecule should be populated. Yet we find all radiating states to be vibrationally excited, the d and D states to be rotationally excited, while only ground rotational levels of the c and C states are populated. The upper levels in all cases are Rydberg Σ states with large-radius electron orbits (6-10 Å); however the outer electrons for the d and D states are in $s\sigma$ united atom orbitals, while those for the c and C states are in $p\sigma$ united atom orbitals.[7] The former are nearly spherical while the latter are dumbbell shaped; thus, it does not seem unreasonable that collisions in the dense gas or liquid would be relatively ineffective in thermalizing the populations of the rotational sublevels of the spherical d and D states, while very effectively thermalizing the nonspherical c and C state rotational-level populations.

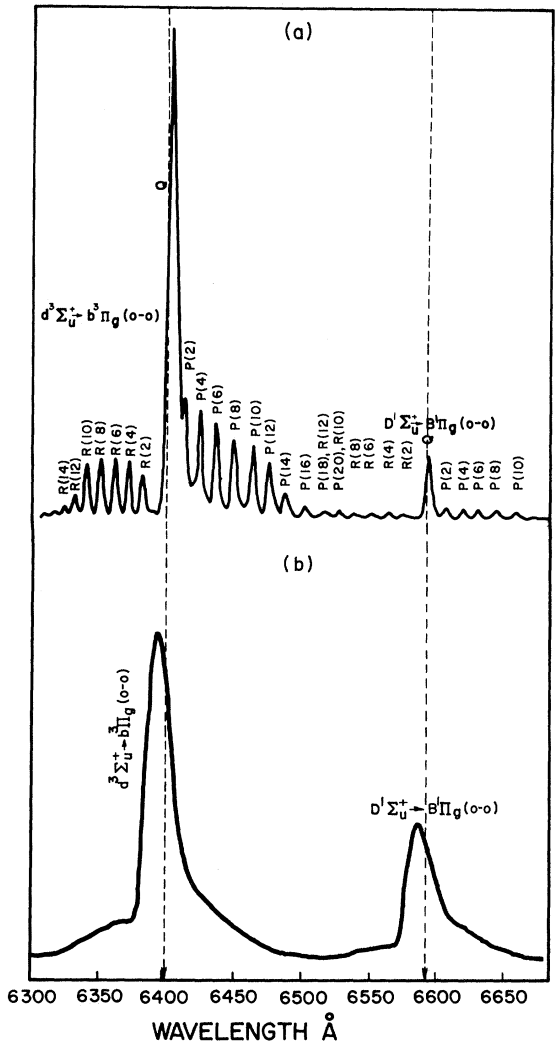

FIG. 3. The $d^3\Sigma_u^+ \rightarrow b^3\Pi_g^+$ (0-0) and $D^1\Sigma_u^+ \rightarrow B^1\Pi_g^+$ (0-0) bands observed with high resolution from electron-bombarded (a) dense gas (150 Torr at 4.2°K) and (b) liquid at 1.7°K. The vertical dashed lines indicate the positions of the free-molecule band origins.

Collisions should be relatively ineffective in vibrational relaxation for molecular Rydberg states in which the orbital of the excited electron is nearly independent of internuclear separation.

It is important to note that the 3.7-Å average interatomic spacing in liquid helium is substantially less than the diameters of the large Rydberg molecules observed. The remarkably small wavelength shifts observed in the liquid

relative to the free molecule and the vibrational and rotational structure noted above suggest the existence of stable microscopic local voids (or "bubbles") in which the molecules reside—a situation somewhat reminiscent of the free-electron bubble in liquid helium.[10]

There is evidence also for the existence of excited helium atoms in the bombarded liquid, though the case is weaker than for the molecules because there is no distinctive vibrational and rotational structure to help in the identification. Nevertheless, the only three atomic lines, $3^3S \rightarrow 2^3P$, $3^1S \rightarrow 2^1P$, and $2^3P \rightarrow 2^3S$, that are observed in the dense gas appear to be present also in the liquid with slight wavelength shifts. We interpret the absence of atomic lines originating on states higher in energy than the 3^1S state at 22.92 eV in terms of the Hornbeck-Molnar process,[11] $He^* + He \rightarrow He_2^+ + e$, which very effectively quenches excited (He*) atoms in states with energy above the reaction threshold at approximately 23.0 eV.[11,12] Again, the remarkable similarity between atomic spectra in liquid and gas suggests the presence of a bubble.[13]

The following additional observations are recorded:

(1) While spectra obtained from low-density gas indicate that triplet and singlet molecular states are populated according to their 3:1 statistical weights, the dense gas and liquid exhibit relatively much more intense singlet spectra. We believe that the fluid is sufficiently dense to preclude the escape of most electrons from their parent ions following impact ionization of singlet ground-state helium atoms, though the secondary electrons so produced are themselves sufficiently energetic to excite or ionize other neighboring atoms. To the extent that parental recombination predominates, triplet states should be produced only by electron-exchange excitation involving the low-energy secondaries, with the bulk of the recombination events conserving spin, hence producing singlet states.

(2) By comparison with a standard lamp viewed through the spectrometer, we estimate that the $d \rightarrow b$, $D \rightarrow B$, $c \rightarrow a$, and $C \rightarrow A$ line intensities in the liquid correspond approximately to 1×10^{13}, 7×10^{12}, 3×10^{12}, and 3×10^{13} transitions per second per microampere of beam current, respectively.

(3) All molecular transitions observed in the liquid originate on Σ states. We are unable to detect the $b^3\Pi_g \rightarrow a^3\Sigma_u^+$ (0-0) band at approximately 2.1-μm wavelength with a PbS detector and band-pass filter combination. The sensitivity was such that the band should have been observable if 10% or more of the molecules known to reach the $b^3\Pi_g$ state through $d \rightarrow b$ transitions subsequently undergo $b \rightarrow a$ radiative transitions. The negative result suggests the possibility that $b^3\Pi_g$ and perhaps other non-Σ states are nonradiatively quenched in the liquid.

(4) Positions and shapes of spectral features observed in the liquid show no discernable dependence on the liquid temperature from 1.7 to 2.2°K.

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[5]Such an identification leaves unexplained the conversion of the neutral excitation to He_2^+ ions and electrons at the free liquid surface as observed by Surko and Reif. These authors also established in a magnetic deflection experiment that if the excitation is thermalized at their 0.5°K experimental temperature, then its magnetic moment is less than $0.2\mu_B$. If our identification is correct, it would therefore imply that their neutral excitation was not thermalized.

[6]HAVAR foil, manufactured by Hamilton Watch Company, Lancaster, Pa.

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[9]At 4.2°K and below, only the lowest rotational levels of the rotationally equilibrated c and C states are populated; therefore the $c \rightarrow a$ (0-0) and $C \rightarrow A$ (0-0) bands were observed at 20°K in the dense gas, where rotational structure confirmed the identification.

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