

## SPECTROSCOPIC STUDY OF LIQUID HELIUM IN THE VACUUM ULTRAVIOLET\*

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(Received 5 September 1969)

The absolute reflectance of liquid helium was measured as a function of wavelength between 1000 and 518 Å. The main feature of the data is a large peak in reflectance located at 574 Å and having a width (at half-maximum) of 15.5 Å. The absolute reflectance at the maximum is  $0.12 \pm 0.01$ . The peak appears to correspond to the  $1^1S_0 \rightarrow 2^1P_1$  atomic transition. Very small structure near 597 Å may correspond to a forbidden atomic transition.

Considerable interest has been shown in studies designed to elucidate the nature of the excited electronic states in condensed matter. In particular, the appealing simplicity of the rare-gas solids and liquids has stimulated investigations in several of these substances.<sup>1</sup> Among these, liquid helium (which has not been studied heretofore) would seem most worthy of attention because of the extreme simplicity of the He atom, the weak interaction between the atoms which are very loosely packed in the liquid, and the possibility of investigating a liquid close to 0°K. In addition, such a study of liquid helium might help to clarify the nature of the energetic neutral excitations which have recently been observed to travel freely through the superfluid.<sup>2</sup> In the present Letter, we report the results of a spectroscopic investigation of liquid helium at 1.2°K in the wavelength range between 1000 and 518 Å.<sup>3</sup>

Such a spectroscopic study of liquid helium presents particular difficulties, both because of the cryogenic problems involved, and because the excited states of He lie in the vacuum ultraviolet (v-uv) region of the electromagnetic spectrum. In this region conveniently available light sources have very low output powers; furthermore, there exist neither vacuum-tight transparent windows nor good reflectors for the v-uv radiation.<sup>4</sup> These difficulties can be minimized by studying the reflection of the radiation from the surface of the liquid helium.<sup>5</sup>

Our experimental arrangement is shown in Fig. 1. The monochromator is a McPherson Model No. 235 (Seya-Namioka design, with a reflection grating of 0.5 m focal length). To avoid using any mirrors whose poor reflectances would reduce the intensity of the v-uv light, the monochromator is mounted vertically so that v-uv light emerges directly downward and is incident

normally (within 10°) upon the liquid helium in the cryostat. To collect the maximum amount of light, this cryostat was specially designed to minimize the length of the light path from the

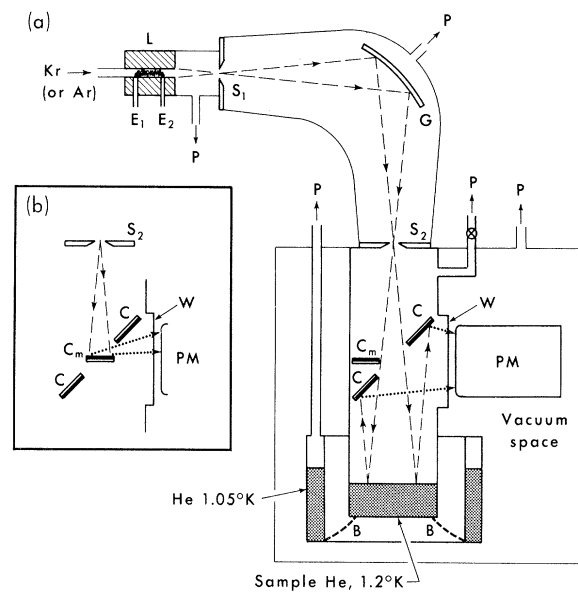


FIG. 1. Diagram of the apparatus. (a) v-uv radiation from the light source  $L$  passes into the monochromator through the entrance slit  $S_1$ , is diffracted from the reflection grating  $G$ , passes through the exit slit  $S_2$ , reflects from the surface of the sample of liquid helium, and then strikes the sodium-salicylate converter  $C$ . Visible light produced by  $C$  passes through the Mylar window  $W$  to the photomultiplier tube  $PM$ . Voltage pulses applied to the electrodes  $E_1$  and  $E_2$  produce a Kr (or Ar) gaseous discharge in the lamp  $L$ . The helium sample is cooled indirectly by copper bars  $B$  attached to a helium bath at 1.05°K. Pipes leading to the vacuum pumps are denoted by  $P$ . (Not shown is the remainder of the Dewar which includes another helium reservoir at 4.2°K and a liquid  $N_2$  reservoir.) (b) The movable converter  $C_m$  is shown in position to monitor the v-uv radiation emerging from the monochromator.

monochromator to the liquid and thence to the detector. Since no transparent windows are available, the v-uv light necessarily traverses helium vapor in the region above the liquid. Absorption of light in the vapor is minimized by keeping the liquid at the lowest practicable temperature (1.2°K) and thereby reducing its vapor pressure to about 0.6 Torr. In addition, since most of the absorption occurs in the high-density vapor near 1°K, the amount of such low-temperature vapor is minimized by a copper aperture kept at 4°K and placed close (~1 cm) above the liquid surface.

The v-uv light is generated by a gas discharge, pulsed at 35 Hz, which yields a dense broadened line spectrum. Krypton gas is used because it provides highest intensity at the wavelengths of interest. (Argon was used as a check to insure that our data were independent of the spectral structure of the source.) The v-uv light is detected by a sodium salicylate converter. This transforms the v-uv light into visible light (near 4400 Å) which passes through a Mylar window into the vacuum space where it is detected by an EMI 9514X photomultiplier (PM) tube<sup>6</sup> cooled to 130°K.

To reduce the effect of electrical noise resulting from the discharge in the lamp, the output of the PM tube is fed into an integrating amplifier followed by a gated amplifier (PAR Model No. CW-1) which samples the integrated current af-

ter the discharge has ceased. The small sampling time of the detection system also reduces the sensitivity to PM-tube dark current. It is necessary to compensate for the effect of intensity variations of the source, both those due to its line structure and those due to fluctuations in time. Accordingly, the intensity of the source is monitored by a reference signal obtained by inserting a movable converter into the direct beam from the monochromator. Data are then taken by alternately measuring, at each wavelength, the light intensity emerging from the monochromator and that reflected from the liquid.

The helium sample for each experiment was obtained by letting helium gas, purified by passage through a charcoal trap at 77°K, condense into the sample chamber. This chamber is cooled indirectly by thermal contact with the main helium bath; it is not pumped except through the slit of the monochromator. Contamination of the sample space by Kr (or Ar) from the light source is prevented by differential pumping (provided both by the monochromator itself and by an extra chamber placed between the source and the monochromator). To prevent pump oil from contaminating the sample space and monochromator, all pumps are isolated by zeolite or liquid nitrogen traps.

Figure 2 displays our final results obtained for the absolute reflectance  $R$  of liquid helium in the

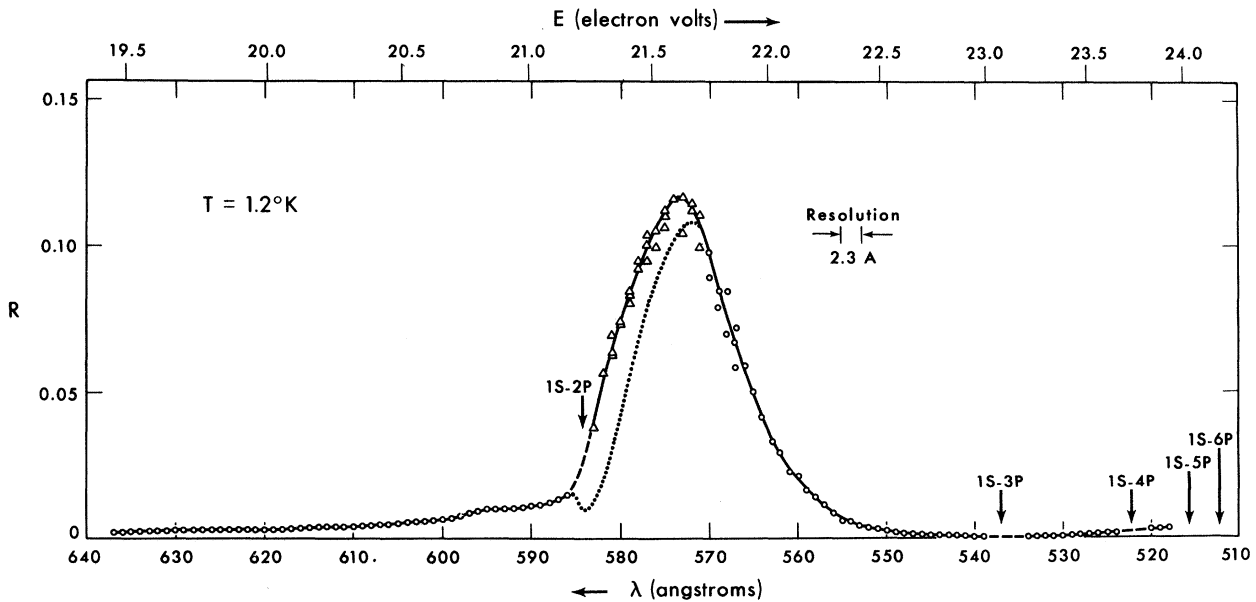


FIG. 2. Absolute reflectance  $R$  of liquid helium as a function of wavelength  $\lambda$ . The data are indicated by circles and triangles, the latter referring to data corrected for absorption in the vapor. (The dotted curve indicates uncorrected data corresponding to a vapor pressure of 0.6 Torr.) The solid curve represents the best fit to the data; the dashed portion indicates interpolations in regions of absorption or fluorescence in the He vapor. The positions of allowed atomic transitions ( $1^1S_0 \rightarrow n^1P_1$ ,  $n=2,3,\dots$ ) are indicated by arrows.

spectral range between 640 and 518 Å.<sup>7</sup> The main feature of the data is a peak at  $574 \pm 0.5$  Å (or 21.6 eV) with a full width (at half-maximum) of 15.5 Å (or 0.58 eV). The additional structure near 597 Å appears to be real. In the region between 584 and 571 Å it was necessary to correct for the strong absorption occurring in the helium vapor and caused by the  $1^1S_0 \rightarrow 2^1P_1$  transition of He atoms, inhomogeneously broadened by mutual collisions. As expected, this absorption is proportional to  $\rho^2$ , where  $\rho$  is the He atom density in the vapor. Corrections for this absorption were made by two distinct methods. One of these involved measuring the reflectances at several vapor pressures<sup>8</sup> and then extrapolating to zero pressure. The other method involved determining the absorption in the vapor by performing an independent measurement of the absorption of v-uv light reflected by a gold mirror in the presence of low-temperature helium gas. The two methods gave consistent results.<sup>9</sup> Finally, the presence of the vapor prevented obtaining data at certain wavelengths: either those corresponding to the higher atomic transition ( $1^1S_0 \rightarrow n^1P_1$ , for  $n > 2$ ) where fluorescence occurs in the vapor,<sup>10</sup> or those below 504 Å where the vapor absorbs because of photoionization.

We verified that the observed signal was due to v-uv light specularly reflected from the surface of liquid helium. This was done by observing that the intensity of the reflected light was greatly reduced when a mechanical impulse applied to the Dewar disturbed the liquid surface. The technique also revealed the existence of a small "background" signal which appeared only in the presence of the liquid, but was unaffected by disturbances of its surface. (This background, which is not present at wavelengths greater than 613 Å, may be due to v-uv fluorescence in the liquid.) Near the main reflectance peak, this background is negligible, so that all signal can be assumed to be specularly reflected from the liquid. By using a standard impulse applied to the Dewar, we could estimate that the background is everywhere less than 1% of the observed reflected signal at the main peak. This small background was subtracted from the raw data to give the final curve shown in Fig. 2.

To find the absolute reflectance  $R$  of the liquid, it is necessary to determine the scale factor  $s$  which relates  $R$  to the directly measured relative reflectance  $R' = sR$ . To this end, we measured  $R'$  at frequencies  $\omega$  below the lowest absorption in the liquid (i.e., between 977 and 637 Å)<sup>11</sup> and

extrapolated our data to a low frequency  $\omega_f$  where the absolute reflectance  $R(\omega_f)$  is known.<sup>12</sup> To achieve the extrapolation, we use the fact that the dielectric constant of the liquid in this low-frequency range should be given by  $\epsilon = 1 + \eta$ , where we can approximate  $\eta$  by the functional form

$$\eta \propto \frac{f_0}{\omega_0^2 - \omega^2} + \frac{f_1}{\omega_1^2 - \omega^2}. \quad (1)$$

Here  $\omega_0$  is the frequency of the lowest absorption (corresponding to the reflectance peak at 574 Å) and  $f_0$  its associated oscillator strength; the remaining transitions in the liquid are then lumped into the second term, corresponding to an effective transition at the frequency  $\omega_1$  with an oscillator strength  $f_1 = 2 - f_0$ . Since  $\eta \ll 1$ , it follows that  $R^{1/2} \approx \frac{1}{4}\eta(1 - \frac{1}{2}\eta)$  or that  $R'$  has the functional form  $(R')^{-1/2} \approx b(\eta^{-1} + \frac{1}{2})$ . By fitting our low-frequency data with an assumed value of  $f_0$ , we can then determine the parameters  $b$  and  $\omega_1$ . Good fits can be obtained with physically reasonable values of  $\omega_1$  for values of  $f_0$  in the range  $0.2 \lesssim f_0 \lesssim 0.4$ . (For comparison, the oscillator strength of the lowest allowed transition in the He atom is  $f_0 = 0.28$ .)<sup>13</sup> Our extrapolation formula for  $(R')^{-1/2}$  can then be used to find  $R'(\omega_f)$  and hence the desired scale factor  $s = R'(\omega_f)/R(\omega_f)$ . This procedure leads to absolute reflectances having an estimated accuracy of  $\pm 10\%$ .

For purposes of theoretical interpretation, it is desirable to relate the observed reflectance to the dielectric properties of the liquid. A preliminary analysis was made by computing the strength, width, and position of an assumed Lorentzian absorption line which best reproduces the strength, width, and position of the observed peak in reflectance.<sup>14</sup> The result is an absorption line at 578.5 Å (or 21.4 eV) with a full width (at half-maximum) of 12 Å (or 0.43 eV). The fit with the experimental data is not sufficient to deduce a reliable value of the oscillator strength, but is consistent with values in the range  $0.1 < f_0 < 0.5$ . (This range of values is compatible with those which gave the best fit in the extrapolation procedure used in deducing the absolute reflectance; it is also consistent with the value of 0.28 for the atomic  $1^1S_0 \rightarrow 2^1P_1$  transition.<sup>13</sup>) Since the position of the absorption line is only shifted by about 1% from the corresponding atomic value of 584.3 Å, it seems reasonable to conclude that the main reflectance peak corresponds to the  $1^1S_0 \rightarrow 2^1P_1$  atomic transition.

Let us briefly comment on the possible origin

of the observed shift and width of the absorption line in the liquid compared with that of the isolated He atom. An atom in the liquid does not move appreciably during an optical transition. Its promotion to an excited state with a relatively large wave function can then give rise to a significant overlap of this wave function with that of a nearest-neighbor atom. The result is a repulsive interaction which tends to shift the atomic transition to higher frequencies.<sup>15</sup> Our data on helium gas<sup>9</sup> show, indeed, an absorption line having a pronounced high-frequency tail extending as much as 0.4 eV above the unshifted line. It is likely that this same interaction accounts in part for the observed shift of the line in the liquid and also for its width (by virtue of the statistical distribution of atomic nearest-neighbor separations).

The small structure shown by Fig. 2 near 597 Å is suggestive of one of the forbidden atomic transitions (probably the transition  $1^1S_0 \rightarrow 2^1S_0$ , at 602 Å in the atom). On the short-wavelength side of the main peak,  $R$  exhibits a long flat minimum followed by a slight rise (apparent near 518 Å); this behavior is probably due to the proximity of higher excited states or to the large oscillator strength in the photoionization continuum.<sup>16</sup> The low reflectance and lack of structure between the main peak and 518 Å suggests that the  $1^1S_0 \rightarrow 3^1P_1$  transition is either shifted to wavelengths less than 518 Å or excessively broadened,<sup>17</sup> probably because of the large size of the  $3P$  wave function and its consequent large interaction with surrounding atoms.

The shift of the lowest-frequency transition to higher energies is also observed in the rare-gas solids Kr and Ar.<sup>1</sup> These rare-gas substances, unlike liquid helium, exhibit doublet structure due to the appearance of the atomic  $1^1S_0 \rightarrow 3^1P_1$  transitions. The different behavior is presumably due to the fact that the much larger spin-orbit interaction in the heavier rare-gas atoms makes singlet-triplet transitions possible.

A more difficult and lengthy analysis, based on the Kramers-Kronig relations, should permit use of our absolute reflectance data to deduce quantitatively the frequency-dependent complex dielectric constant of the liquid and, in particular, the shape and oscillator strength of the main absorption peak. Such an analysis is now in progress. It is hoped that the simplicity of liquid helium will permit exploitation of these optical data to achieve a more detailed theoretical understanding of the excited electronic states of the liquid.

We wish to acknowledge helpful discussions

with M. L. Cohen, P. Eisenberger, M. Iannuzzi, P. M. Platzman, and J. M. Stone. We would also like to thank J. M. Kahn, E. F. McLaughlin, and P. L. Richards for assistance in the implementation of the experiment.

\*Work supported in part by the U. S. Office of Naval Research.

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<sup>1</sup>See, for example, O. Schnepp and K. Dressler, *J. Chem. Phys.* **33**, 49 (1960); G. Baldini, *Phys. Rev.* **128**, 1562 (1962); D. Beaglehole, *Phys. Rev. Letters* **15**, 551 (1965); O. Bostanjoglo and L. Schmidt, *Phys. Letters* **22**, 130 (1966); and B. Raz and J. Jortner, *J. Chem. Phys.* **49**, 3318 (1968).

<sup>2</sup>C. M. Surko and F. Reif, *Phys. Rev. Letters* **20**, 582 (1968), and *Phys. Rev.* **175**, 229 (1968).

<sup>3</sup>A preliminary abstract of this work can be found in C. M. Surko, G. J. Dick, F. Reif, and W. C. Walker, *Bull. Am. Phys. Soc.* **14**, 854 (1969).

<sup>4</sup>See J. A. R. Samson, *Techniques of Vacuum Ultraviolet Spectroscopy* (John Wiley & Sons, Inc., New York, 1967).

<sup>5</sup>Since vacuum-tight windows are not available, a study of the transmission of radiation through the liquid would require maintaining, in the same vacuum space as the monochromator, a layer of liquid of very small, but constant, thickness while its vapor is being pumped off through the monochromator.

<sup>6</sup>This specially constructed PM tube has a thin SnO layer on the cathode to prevent degradation of its sensitivity at low temperatures.

<sup>7</sup>Data obtained from liquid He<sup>4</sup> containing a 1% concentration of He<sup>3</sup> show no observable differences (within  $\pm 10\%$ ).

<sup>8</sup>A temperature change as small as 0.2°K, produced by a heater on the sample space, is sufficient to produce a change in vapor pressure from 0.6 to 2.0 Torr.

<sup>9</sup>Our data on the frequency dependence of the absorption coefficient in He gas will be published elsewhere.

<sup>10</sup>This signal is probably due to gas fluorescence incident directly on the PM tube.

<sup>11</sup>These measurements do not rely on knowledge of the quantum efficiency of the sodium salicylate converter, since this efficiency is frequency independent in the region of interest (see Ref. 4, p. 215).

<sup>12</sup> $R(\omega_l)$  is determined from the index of refraction of liquid helium, measured at  $\lambda_l = 5465$  Å by M. H. Edwards, *Can. J. Phys.* **36**, 884 (1958).

<sup>13</sup>B. Schiff and C. L. Pekeris, *Phys. Rev.* **134**, A638 (1964).

<sup>14</sup>This analysis, based on a Lorentzian lineshape, is only a crude approximation. A more detailed analysis, using the Kramers-Kronig integral relations, is in progress.

<sup>15</sup>The effect of this interaction on a particular eigenstate has been calculated by J. C. Browne, *Phys. Rev.*

138, A9 (1965).

<sup>16</sup>The oscillator strengths in the photoionization continuum have been measured by J. A. R. Samson, J. Opt.

Soc. Am. 54, 876 (1964).

<sup>17</sup>This  $1^1S_0 \rightarrow 3^1P_1$  transition might not be observable if its width were significantly greater than 20 Å.

## EXCITON-PHONON INTERACTION IN ALKALI HALIDES

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(Received 5 September 1969)

High-resolution optical studies of alkali halides at liquid-helium temperature have revealed complex structures associated with the exciton peaks. A sideband picture which involves the emission either of localized vibrations or of crystal phonons, depending upon the exciton radius, is proposed.

The fine structure of the exciton lines, which has been detected in some alkali halides,<sup>1,2</sup> casts new light on the role of the exciton-phonon interaction in these crystals. Until recently the exciton-phonon interaction in the alkali halides was assumed to cause only a broadening of the exciton lines.<sup>3</sup> In fact, according to the large values of the linewidths as obtained from thin-film absorption data, phonon effects could not be observed directly. However, the linewidths as obtained from Kramers-Kronig analysis of reflectivity data on single crystals are much narrower than those measured on thin films, and as a primary consequence fine structured excitons have been observed in several alkali halides.<sup>2,4</sup>

One can observe the structures which accompany the excitons in some alkali halides in Figs. 1-3, where we report the reflectivity spectra of NaBr, KI, and LiI cleaved *in situ* at about 6°K. The  $n=1$  exciton is clearly split in NaBr, Fig. 1, while it appeared only as a shoulder at 55°K<sup>2</sup>; the magnitude of the splitting is  $39 \pm 3$  meV. In KI, Fig. 2, the  $n=1$  exciton shows a shoulder on the high-energy side, separated by  $35 \pm 5$  meV, while only a slight asymmetry was visible at 55°K.<sup>2</sup> It is to be noted that in both cases the energy splittings of the  $n=1$  exciton are well above the maximum phonon energy of the perfect crystal, which is 28 meV in NaBr and 18 meV in KI.<sup>5</sup> More striking is the shape of the  $n=2$  exciton in KI, which shows a well-defined structure, composed of four or five peaks, with a separation of  $16.5 \pm 1$  meV. A similar situation has been observed at 6°K also in RbI, with a splitting of 12 meV.<sup>4</sup> Several peaks are found also in the  $n=1$  exciton of LiI as shown in Fig. 3. Their average separation is  $39 \pm 3$  meV while the maximum phonon frequency of the crystal corresponds to 45

meV.<sup>6</sup> Multiple structure is observed also in NaI at liquid-helium temperature.<sup>4</sup>

According to the present data, it is found that the exciton-phonon interaction in the alkali halides appears more explicitly than expected and therefore the problem deserves further attention. There are essentially two mechanisms which describe this interaction: (1) Jahn-Teller instability when the exciton transitions take place between degenerate states; (2) phonon emission (or absorption) as found, e.g., for rare-earth ions.<sup>7</sup> The former model has been tentatively invoked in Ref. 1 in order to justify the doublet found in

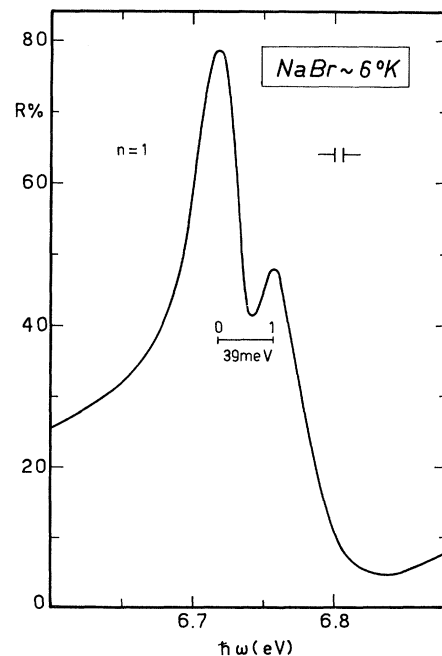


FIG. 1. Reflectivity spectrum of the lowest exciton peak ( $n=1$ ) of NaBr (the separation between the 0-phonon and 1-phonon lines is indicated).