

³C. M. Surko and F. Reif, *Phys. Rev.* **175**, 229 (1968).

⁴The present authors wish to acknowledge that we are aware of the fact that C. M. Surko and F. Reif have carried out a similar investigation which is based on a different method of excitation. C. M. Surko and F. Reif (private communication); see C. M. Surko, R. E. Packard, G. J. Dick, and F. Reif, *Phys. Rev. Letters* **24**, 657 (1970) (this issue).

⁵Y. Tanaka, A. S. Jursa, and F. J. LeBlanc, *J. Opt. Soc. Am.* **48**, 304 (1958).

⁶A. L. Smith, *J. Chem. Phys.* **49**, 4817 (1968).

⁷R. Allison, J. Burns, and A. J. Tuzzolino, *J. Opt. Soc. Am.* **54**, 747 (1964).

⁸J. Jortner, L. Meyer, S. A. Rice, and E. G. Wilson, *Phys. Rev. Letters* **12**, 415 (1964).

⁹HAVAR foil, manufactured by the Hamilton Watch Company, Lancaster, Pa.

¹⁰R. E. Huffman, Y. Tanaka, and J. C. Larrabee, *Appl. Opt.* **2**, 617 (1963).

¹¹This result differs from the observations of M. R. Fischbach, H. A. Roberts, and F. L. Hereford, *Phys. Rev. Letters* **23**, 462 (1969). These authors used a Po^{210} α -particle source for the excitation and reported a 15% decrease in the total scintillation intensity between T_λ and 0.9°K.

¹²C. M. Surko, G. J. Dick, F. Reif, and W. C. Walker, *Phys. Rev. Letters* **23**, 842 (1969).

¹³The appearance of these bands depends upon the discharge conditions, and, as shown in Fig. 2(b), they do not appear in a condensed helium discharge.

SPECTROSCOPIC STUDY OF THE LUMINESCENCE OF LIQUID HELIUM IN THE VACUUM ULTRAVIOLET*

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The spectral distribution of luminescence excited in liquid helium by fast electrons was measured in the region between 500 and 3000 Å. The spectrum shows transitions of the He_2 molecule and is sensitive to the presence of impurities such as N_2 .

The luminescence produced in liquid helium by energetic charged particles has been the subject of several experimental investigations.¹⁻⁵ These have provided evidence for the existence of metastable states in the liquid and have given information about optical transitions between excited states of the liquid. An investigation of the direct luminescent decay of the liquid to the ground state is more difficult since it requires measurements in the vacuum ultraviolet. We have undertaken such an investigation by studying the luminescent spectrum in the wavelength range between 500 and 3000 Å.

In our experimental arrangement the liquid helium (condensed after passing through a liquid- N_2 -cooled charcoal trap) is excited by a 1-Ci tritiated-titanium β emitter immersed approximately 1 cm below the surface of the liquid. (In the liquid, the β particles have a range less than 0.05 mm.) The light produced in the region near the source travels vertically upward, passes through a monochromator,⁶ and then impinges on a sodium salicylate converter. To prevent absorption of the uv radiation, no windows are used between the liquid and converter. The visible and near-ultraviolet light produced at the converter is detected by a cooled EMI 9514X photomultiplier tube. The output of the photomultiplier

tube is fed into a discriminator (to discriminate against low-level noise and spurious large pulses due to cosmic rays) followed by either a scaler for a digital output, or an integrator for an analog output. Most data were taken digitally, setting the grating for a particular wavelength and pulse counting for up to four minutes.

The luminescence from the liquid is shown in Fig. 1(a) (solid circles) in the region between 580 and 1080 Å.⁷ The spectrum is characterized by a broad peak near 780 Å and by a narrower peak near 600 Å. No luminescence is observed at wavelengths between 1200 and 3000 Å, or below 600 Å. (No intensity should be observable below 500 Å since the He vapor above the liquid absorbs strongly in this region.) The spectral distribution is independent of temperature between 2.7 and 1.2°K, while the intensity increases by about 10% when the temperature is lowered from 2.7 to 1.2°K. (No sudden change is observed as the temperature is varied through the lambda transition at 2.2°K.) As shown in Fig. 1(b), the leading edge of the spectral distribution near 600 Å varies with liquid level, indicating that the liquid absorbs the radiation in this region.

In order to examine the behavior of a potentially simpler system, we measured the luminescence from He gas at 4.2°K at pressures between

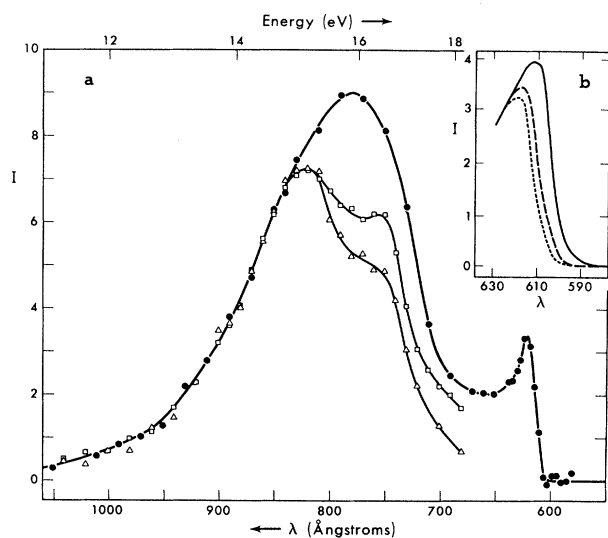


FIG. 1. Luminescent intensity I , in arbitrary units, as a function of wavelength λ . (a) Solid circles: no impurities (12-Å resolution). Squares: 0.2% N_2 impurities (20-Å resolution). Triangles: 0.6% N_2 impurities (20-Å resolution). (Vertical scales are adjusted so that the curves coincide at long wavelengths.) (b) Intensity I as a function of λ for various heights h of the liquid level above the source (12-Å resolution). Solid curve: $h=2$ mm. Dashed curve: $h=5$ mm. Dotted curve: $h=13$ mm.

1 and 300 Torr. A broad peak was observed at about 680 Å and a sharper peak at 600 Å. In spectra produced by electrical discharges in helium gas, the peak at 680 Å has previously been identified⁸ as the He_2 molecular transition $D^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$. The line near 600 Å has been attributed⁹ to transitions from weakly or nearly bound states of the He_2 molecule produced by the atomic reaction $He(2^1S) + He \rightarrow He_2(A^1\Sigma_u^+)$. (The atomic transition $2^1S \rightarrow 1^1S$, forbidden for an isolated He atom, would occur at 601.4 Å.) We find that, as the pressure of the gas is increased, the position of the peak near 600 Å shifts to longer wavelengths and the peak intensity decreases. (At gas pressures of 100-300 Torr, when the light traverses about 10 cm of He gas at 4°K, the luminescent spectrum of the gas near 610 Å appears similar to that of the liquid.) Thus it appears that the peak near 610 Å in the liquid is the wing of an emission line, centered at 600 Å, which is absorbed strongly by the liquid.

In the wavelength region above 1200 Å, previous work has shown that the total luminescent intensity is affected by the addition of O_2 or N_2 impurities (presumed to be in colloidal form).³ We find that in the vacuum-ultraviolet region both

the intensity and detailed spectral distribution are affected by N_2 impurities as shown in Fig. 1(a).¹⁰ The intensity at each wavelength decreases monotonically with impurity concentration.¹¹ (Thus the observed change cannot be due to emission from the impurities.) Furthermore, the spectral distribution does not change appreciably for impurity concentrations greater than those shown in Fig. 1(a). (Thus the observed change cannot be due to absorption by the N_2 impurities.)

The effect of the impurities can be explained by assuming that the spectral distribution near 780 Å consists of two peaks, one at 825 Å and one at about 755 Å, the latter being more sensitive to impurity concentration. In particular, if the excitation responsible for the 755-Å transition has a longer lifetime, it would have a greater probability of being quenched by the N_2 impurities as it diffuses through the liquid. In the case of electrical discharges in helium gas, various experiments suggest the existence of a broad emission peak in the region between 790 and 825 Å.¹² This peak has been identified as the helium molecular transition $A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$.⁸ In the liquid, population of the $A^1\Sigma_u^+(v=0)$ state has been observed previously.² It therefore appears quite likely that the peak at 825 Å is the molecular transition $A^1\Sigma_u^+(v=0) \rightarrow X^1\Sigma_g^+$. The origin of the peak at 755 Å seems less clear. Considering singlet states of the He_2 molecule, the singlet-singlet transitions $B \rightarrow X$ and $C \rightarrow X$ are forbidden by parity, while the $D \rightarrow X$ transition occurs at 675 Å. Furthermore, the triplet-singlet transition $a \rightarrow X$ would occur at an estimated wavelength about 12 Å shorter than the $A \rightarrow X$ transition, too close to account for the splitting we observe experimentally.¹³ One conceivable possibility is that the transition $B \rightarrow A$ takes place so slowly (because of the small energy difference between B and A) that the transition $B \rightarrow X$ occurs by some higher-order process. The $B \rightarrow X$ transition would then occur at a wavelength approximately 45 Å shorter than the $A \rightarrow X$ transition¹³ (as compared with our experimental peak at 755 Å which is 70 Å below the presumed $A \rightarrow X$ transition).

When compared with the results of previous experiments,¹⁴ our data indicate that the liquid is transparent at wavelengths greater than about 605 Å. This observation is consistent with reflectance data on liquid helium since the reflectance peak of longest wavelength occurs near 597 Å.¹⁵ However, although the 2^3S state has previously been shown to be populated,² we find no evidence of the forbidden transition $2^3S \rightarrow 1^1S$ which

would occur at 626 Å.

In general, the present experiments¹⁶ indicate that the luminescence of liquid helium in the vacuum ultraviolet reveals well-defined spectral features and that, in transitions to the ground state as well as in those previously observed² between excited states, distinct He₂ molecular transitions can be identified.

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¹M. R. Fischbach, H. A. Roberts, and F. L. Hereford, *Phys. Rev. Letters* **23**, 462 (1969), and references therein; J. R. Kane, R. T. Siegel, and A. Suzuki, *Phys. Letters* **6**, 256 (1963).

²W. S. Dennis, E. Durbin, W. A. Fitzsimmons, O. Heybey, and G. K. Walters, *Phys. Rev. Letters* **23**, 1083 (1969).

³The spectrum from liquid helium containing impurities was studied by J. Jortner, L. Meyer, S. A. Rice, and E. G. Wilson, *Phys. Rev. Letters* **12**, 415 (1964).

⁴For a study of the luminescent spectra of other rare-gas liquids, see J. Jortner, L. Meyer, S. A. Rice, and E. G. Wilson, *J. Chem. Phys.* **42**, 4250 (1965); for a review of spectroscopy of rare-gas liquids, see M. B. Robin, in *Simple Dense Fluids*, edited by H. L. Frisch and Z. W. Salsburg (Academic, New York, 1968), pp. 215-250.

⁵For related work in He gas see W. R. Bennett, Jr., *Ann. Phys.* **18**, 367 (1962), and references therein.

⁶McPherson, Model No. 235, equipped with a 1200-

line/mm platinum-coated reflection grating blazed at 700 Å.

⁷With the addition of about 5% He³ to the He⁴, the intensity is decreased by about 50% while the spectral distribution is left unchanged (to within an accuracy of 10%).

⁸A. L. Smith and J. W. Meriwether, *J. Chem. Phys.* **42**, 2984 (1965).

⁹Y. Tanaka and K. Yoshino, *J. Chem. Phys.* **50**, 3087 (1969); A. L. Smith, *J. Chem. Phys.* **49**, 4817 (1968).

¹⁰The temperature dependence of the luminescence is also affected by impurities. With impurities present, the intensity increases by about 100% as the temperature *T* decreases from 2 to 1.3°K, then decreases as *T* decreases from 1.3 to 1.2°K. The luminescent intensity at 1.2°K is about 15% greater than that at 2°K.

¹¹The indicated concentrations are upper bounds since it is not known what fraction of the added N₂ actually enters the liquid in colloidal form.

¹²See for example Y. Tanaka, A. S. Jursa, and F. J. LeBlanc, *J. Opt. Soc. Am.* **48**, 304 (1958) or D. Villarejo, R. R. Herm, and M. G. Inghram, *J. Opt. Soc. Am.* **56**, 1574 (1966). Detailed comparison of spectra obtained by different investigators is difficult because of the wavelength dependence of the reflectivity of gratings usable in the vacuum ultraviolet. See E. M. Reeves and W. H. Parkinson, *J. Opt. Soc. Am.* **53**, 941 (1963).

¹³The relative positions of transitions to the ground state may be estimated from the energies and equilibrium internuclear separations of the excited states (see Ref. 8).

¹⁴It is difficult to compare the temperature dependence of the luminescent intensity with that measured previously because this temperature dependence appears to depend not only upon the type of radioactive source used, but also upon the presence of impurities.

¹⁵C. M. Surko, G. J. Dick, F. Reif, and W. C. Walker, *Phys. Rev. Letters* **23**, 842 (1969).

¹⁶Near the end of these experiments, we became aware of work along parallel lines by W. A. Fitzsimmons and co-workers at the University of Wisconsin. Their results, however, have not been available to us. See M. Stockton, J. W. Keto, and W. A. Fitzsimmons, *Phys. Rev. Letters* **24**, 654 (1970) (this issue).