

tion for liquid helium of a constant *negative* differential specific heat  $(\partial C/\partial N)_T$  on starting to empty. Since on emptying, the free surface area increases, so should the heat capacity, which depends at low  $T$  on excitation of the ripplon modes (3) with  $a = a_m$ , the metastable radius. This increase more than compensates for the decreasing filled-pore term, since  $c_0(a_m) \ll s$ .

Finally, we note that if  $r_p$  is one of the two equal radii of curvature at the point  $P$  of Fig. 1(b), it follows from (8) and the assumption of equilibrium that

$$\ln[p(\infty)/p_0] = \beta[U(0) - 2v_l\sigma/r_p].$$

This and Eq. (8) are generalizations of the Kelvin equation of capillary condensation<sup>12</sup> to include substrate forces.

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<sup>1</sup>See J. Low Temp. Phys. **3**, 197 ff. (1970); D. C. Hickernell, E. O. McLean, and O. E. Vilches, J. Low Temp. Phys. **13**, 241 (1973).

<sup>2</sup>R. H. Tait, R. O. Pohl, and J. D. Reppy, in *Low Temperature Physics—LT13*, edited by W. J. O'Sullivan, K. D. Timmerhaus, and E. F. Hammel (Plenum, New York, 1973); R. H. Tait, private communication.

<sup>3</sup>F. D. M. Pobell, H. W. Chan, L. R. Corruccini, R. P. Henkel, S. W. Schwenterly, and J. D. Reppy, Phys. Rev. Lett. **28**, 542 (1972).

<sup>4</sup>T. C. Padmore, Phys. Rev. Lett. **28**, 1512 (1972); H. Haug, J. Low Temp. Phys. **12**, 479 (1972).

<sup>5</sup>S. A. Scott, E. Guyon, and I. Rudnick, J. Low Temp. Phys. **9**, 389 (1972); T. G. Wang and I. Rudnick, J. Low Temp. Phys. **9**, 425 (1972).

<sup>6</sup>M. Bretz, Phys. Rev. Lett. **31**, 1447 (1973).

<sup>7</sup>L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, London, 1959), Chap. 7.

<sup>8</sup>We assume  $\sigma$  to be constant. This is oversimplified, but the curvature and thickness dependences are probably small, except for very thin films or very small  $\alpha$ . See T. C. Padmore and M. W. Cole, Phys. Rev. A **9**, 802 (1974).

<sup>9</sup>I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Pitaevskii, Advan. Phys. **10**, 165 (1961).

<sup>10</sup>E. S. Sabisky and C. H. Anderson, Phys. Rev. A **7**, 790 (1973).  $\alpha$  for MgO should be similar to that for SiO<sub>2</sub>, the principal constituent of Vycor glass.

<sup>11</sup>We neglect the compressional energy of the liquid, which is smaller than  $U$  by a factor of pressure times compressibility. This factor is small near the interface, which is the only region important in determining the equilibrium configuration.

<sup>12</sup>S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area, and Porosity* (Academic, New York, 1967). An equation similar to (8) has been given by A. J. Symonds, thesis, University of Sussex, 1965 (unpublished). Unfortunately, the substrate potential was approximated by the result appropriate for a planar surface.

<sup>13</sup>Our numerical calculation of the adsorption isotherm for He in Vycor, to be published, is in good agreement with data of D. F. Brewer and D. C. Champeny, Proc. Phys. Soc., London **79**, 855 (1962).

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## Pressure Shifts and Quenching of Atomic and Molecular States Produced in Electron-Bombarded Liquid Helium\*

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The optical absorption and emission spectra of electron-bombarded liquid helium has been studied as a function of pressure between the saturated vapor pressure and 25 atm. The transitions of He\* and He<sub>2</sub>\* in the liquid shift toward the blue with increasing pressure. The observed line profile and pressure shift of the He(2<sup>3</sup>P) ← He(2<sup>3</sup>S) atomic absorption line are in good agreement with recent static line broadening calculations. We also report a strong pressure-dependent quenching of the excited atomic and molecular states in the liquid.

The optical fluorescence of liquid systems has been a subject of long-standing scientific interest. However, the excited states of most liquids are difficult to study because the surrounding fluid

usually causes rapid nonradiative de-excitation of the excited states.<sup>1</sup> In contrast to the usual situation, recent spectroscopic studies of electron-beam-bombarded superfluid helium have

shown that excited liquid helium offers a particularly unique opportunity to investigate a variety of excited atomic and molecular states that are in constant interaction with a dense surrounding medium.<sup>2-5</sup> Recent studies of liquid helium at saturated vapor pressure (SVP) have detected wavelength shifts between corresponding absorption and emission bands of the liquid as well as shifts with respect to transitions of the free atom or molecule.<sup>6</sup> The shifts observed in the case of the atomic transitions  $\text{He}(2^3P) \rightarrow \text{He}(2^3S)$  have been interpreted in terms of a "bubble model" which suggests that the excitations reside within small voids in the liquid.<sup>7</sup> In order to study further the nature of the interaction between the ground-state liquid and the atomic and molecular excitations, we investigated the absorption and emission spectra of electron-bombarded liquid helium as a function of pressure between SVP and 25 atm.

The details of the experimental apparatus including the electron accelerator, beam steering and pulsing, the cryogenic system, and the optical arrangement used to obtain absorption and emission spectra have been described elsewhere.<sup>3,4</sup> For these experiments the sample liquid is contained in a copper chamber that is submerged in a liquid helium bath. The bath temperature is regulated by pumping under fixed vapor pressure conditions. The sample pressure is measured and regulated to within about  $\pm 2$  lb/in.<sup>2</sup> by a pressure regulating system which consists of a helium gas bottle at high pressure, a precision Bourdon-tube gauge, and a pressure regulator equipped with a downstream relief valve. The optical signals produced by the pulsed 0.1- to 2.0- $\mu\text{A}$  beam of 160-keV electrons incident on the liquid are detected through sapphire windows in the chamber and recorded using conventional phase-sensitive techniques.

The measured wavelength shifts as a function of pressure for several atomic and molecular emissions of the liquid are shown in Fig. 1(a). All the atomic and molecular emission bands that we studied exhibited shifts of roughly  $3.2 \text{ \AA}/\text{atm}$ ; for clarity not all of our results are included in Fig. 1(a). The atomic and molecular absorption bands, on the other hand, shift at markedly different rates as indicated by curves 1, 2, and 3 in Fig. 1(b) for the  $(0-0)c^3\Sigma \rightarrow a^3\Sigma$ ,  $(0-0)b^3\Pi \rightarrow a^3\Sigma$ , and  $2^3P \rightarrow 2^3S$  transitions, respectively. Measurements of the  $2^3P \rightarrow 2^3S$  atomic absorption line require special experimental consideration because of overlapping and relatively intense molecular

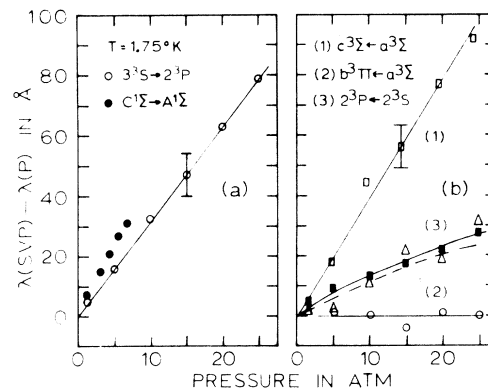


FIG. 1. (a) Pressure shifts for the  $3^3S \rightarrow 2^3P$  (7060  $\text{\AA}$ ) and  $(0-0)C^1\Sigma \rightarrow A^1\Sigma$  (9128  $\text{\AA}$ ) emission bands of electron-excited liquid helium. Although not shown, the  $(4-3)C^1\Sigma \rightarrow A^1\Sigma$  (8641  $\text{\AA}$ ),  $(0-0)D^1\Sigma \rightarrow B^1\Pi$  (6586  $\text{\AA}$ ),  $(0-0)d^3\Sigma \rightarrow b^3\Pi$  (6396  $\text{\AA}$ ),  $(0-0)c^3\Sigma \rightarrow a^3\Sigma$  (9173  $\text{\AA}$ ), and  $2^3P \rightarrow 2^3S$  (10910  $\text{\AA}$ ) bands exhibit shifts represented by the line in the figure. The band maxima at SVP are indicated in parentheses. (b) Pressure shifts of the  $(0-0)c^3\Sigma \rightarrow a^3\Sigma$ ,  $(0-0)b^3\Pi \rightarrow a^3\Sigma$ , and  $2^3P \rightarrow 2^3S$  absorption bands. The molecular bands were observed at  $T=1.75^\circ\text{K}$ ; the atomic band for  $T=1.98^\circ\text{K}$  (solid square) and  $T=1.4^\circ\text{K}$  (open triangle). Curve 3 also indicates the shifts predicted by the "bubble model" (solid line) and by static line broadening theory (dashed line) for the  $2^3P \rightarrow 2^3S$  absorption band (Ref. 8).

absorption bands. The overlapping molecular absorptions can be eliminated by pulsing the electron beam rapidly, such as 50  $\mu\text{sec}$  on and 50  $\mu\text{sec}$  off, because the concentration of metastable molecules does not vary appreciably on this time scale and thus the molecular absorption signal is not detected.<sup>3</sup> The pressure shifts for the  $2^3P \rightarrow 2^3S$  absorption line measured at the temperatures of 1.4 and 1.98 $^\circ\text{K}$ , shown in Fig. 1(b), indicate essentially no appreciable temperature dependence of the observed shift. The shifts for the  $2^3P \rightarrow 2^3S$  atomic absorption line have been calculated on the basis of the "bubble model" [solid curve in Fig. 1(b)] by Hickman and Lane,<sup>3</sup> and also by Steets, Hickman, and Lane using static line-broadening theory (dashed curve).<sup>8</sup> It should be noted that at 1.98 $^\circ\text{K}$  and for pressures in excess of 15 atm the liquid helium is no longer superfluid but is normal liquid helium because of the decrease in the  $\lambda$  transition temperature with pressure.<sup>9</sup> We have not made an exhaustive study comparing all the atomic and molecular transitions above and below the  $\lambda$  line, but in the many cases studied we have not detected any change in the intensity, spectral width, spectral

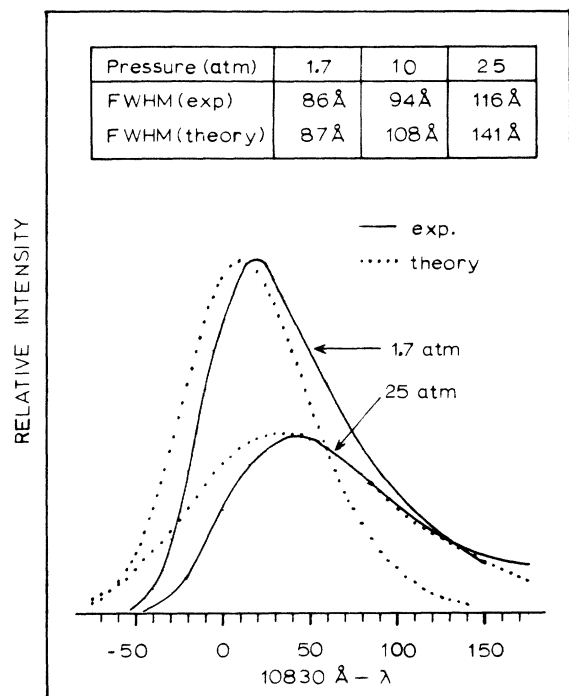


FIG. 2. The shift and asymmetry of the  $\text{He}(2^3P) \leftarrow \text{He}(2^3S)$  absorption line measured at 1.7 and 25 atm is compared with the static line-broadening analysis of Ref. 8. As shown, the intensity of this absorption decreases slightly with increasing pressure. The line-widths (full width at half-maximum) measured at other pressures are compared with theoretical values in the table. The calculated profiles and widths include the 39-Å instrumental bandpass of the experiment.

shift, or relative vibrational or rotational state populations upon the change of phase provided the pressure is sufficiently high so that the electron beam does not induce boiling of the normal fluid. (Pressures in excess of 10 atm are sufficient to prevent boiling of the normal fluid with 1  $\mu\text{A}$  of incident beam current.)

The pressure dependence of the  $2^3P - 2^3S$  line profile has been studied also. The observed asymmetric absorption line for the pressures of 1.7 and 25 atm and the full width at half-maximum measured at other pressures are compared in Fig. 2 with the theoretical predictions of Steets, Hickman, and Lane.<sup>8</sup> In order to compare with experiment the theoretical results have been convoluted with the 39-Å-wide instrumental profile of the monochromator used during these measurements.

During the measurements of the pressure shifts and line profiles, we found that the intensities of

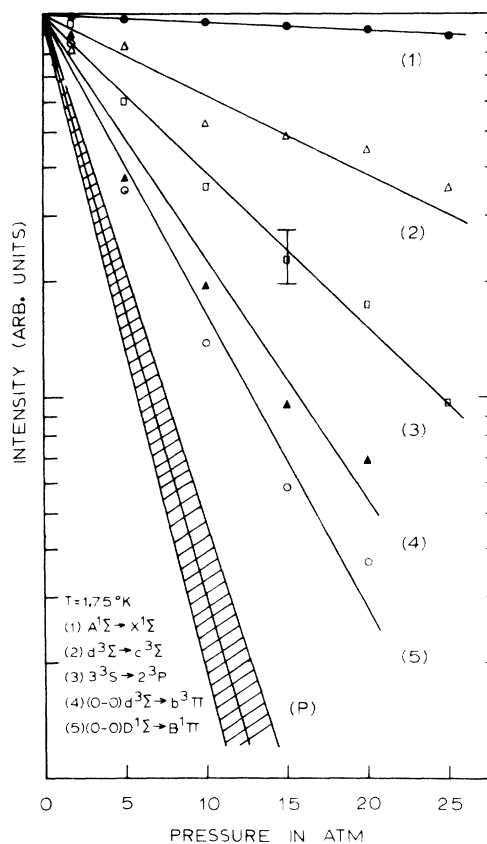


FIG. 3. Relative intensities of atomic and molecular emissions of excited liquid helium versus pressure. The hatched area (labeled P) indicates the quenching of the  $(0-0)c^3\Sigma \rightarrow a^3\Sigma$ ,  $(0-0)C^1\Sigma \rightarrow A^1\Sigma$ , and  $2^3P \rightarrow 2^3S$  bands all of which have a P-type-orbital excited electron in the upper state. The remaining curves refer to transitions for which the upper state can be characterized by an S-type-orbital electron.

the atomic and molecular emissions decreased exponentially with increasing pressure, in some cases decreasing by as much as several orders of magnitude between SVP and 25 atm. The observation is rather surprising, particularly in view of the fact that the density of the liquid changes by only 20% between SVP and 25 atm.<sup>9,10</sup> The measured pressure-dependent intensities are summarized in Fig. 3 where the intensity of each band has been normalized to unity at SVP. The sensitivity of the various atomic and molecular emissions to pressure quenching is apparently related to the type of the upper state involved in the transition. For example, the pressure-dependent intensities of the  $(0-0)c^3\Sigma \rightarrow a^3\Sigma$ ,  $(0-0)C^1\Sigma \rightarrow A^1\Sigma$ , and  $2^3P \rightarrow 2^3S$  transitions are all within the

band indicated in Fig. 3, and these transitions are all similar in that the upper state can be characterized by a  $P$ -type-orbital excited electron.<sup>11</sup> On the other hand, the remainder of the curves in Fig. 3, all of which have different slopes and are outside the  $P$ -type band, indicate the intensities of emission from  $S$ -type-orbital upper states. The intense 800-Å continuum due to the  $A^1\Sigma \rightarrow X^1\Sigma$  transition is least affected by pressure.<sup>4,10</sup> It should be noted also that the ratio of the intensities  $d^3 \rightarrow b^3$  and  $d^3 \rightarrow c^3$  (curves 4 and 2 in Fig. 3) is pressure dependent even though the upper state is the same for both transitions.

We interpret the results in Fig. 3 as evidence for pressure-induced destruction of the excited states. Our results indicate that the two lowest states  $A^1\Sigma$  and  $a^3\Sigma$  are populated at pressure-independent rates,<sup>12</sup> and previous work has shown that these rates are many orders of magnitude greater than those due to radiative cascade.<sup>4-6</sup> Thus the production of the two lowest states could be in part due to the nonradiative de-excitation of higher states. There is also direct evidence for the quenching of the  $c^3\Sigma$  and  $C^1\Sigma$  states: the  $c^3$  and  $C^1$  states can radiate only to the  $a^3$  and  $A^1$  states, respectively, and the measured decay times for these near-infrared bands are less than 20 nsec which is too short to be the radiative lifetime.<sup>13</sup> Furthermore, the pressure quenching of the  $c^3\Sigma$  state relative to the  $d^3\Sigma$  state is implied by the measured intensity ratio  $(d^3 - c^3)/(c^3 - a^3)$  which is about 1 at SVP, but is roughly 100 at 15 atm.

The strong pressure quenching of the excited states of liquid helium is an unexpected result. For example, the effects of pressure on the fluorescence of most liquids are due either to the changes in density or index of refraction (a small effect), or to the pressure dependence of the viscosity (or diffusion coefficient) which influences the excitation transfer rates between excited states and other solute molecules.<sup>14</sup> Neither of these processes could account for our results. We conclude that the quenching of the liquid fluorescence is related to the microscopic interaction between the excited states and the surrounding liquid. The quenching mechanism could involve the formation of a complex of atoms which ultimately dissociates into either the  $A^1\Sigma$  or  $a^3\Sigma$  states depending upon the spin quantum number

of the original state. In fact such a process has been invoked previously to account for the destruction of the  $2^1S$  and  $2^3S$  atomic metastable states in the liquid.<sup>1,5</sup> Additional experiments are required to establish the nature of this quenching phenomenon, and in particular the fluorescent decay times of the various transitions should be examined as a function of pressure and density in both the liquid and dense gas phases of helium.

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<sup>1</sup>See, for example, I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules* (Academic, New York, 1971), 2nd ed., and references therein.

<sup>2</sup>W. S. Dennis, E. Durbin, Jr., W. A. Fitzsimmons, U. Heybey, and G. K. Walters, *Phys. Rev. Lett.* **23**, 1083 (1969).

<sup>3</sup>For a recent review of this subject see W. A. Fitzsimmons, in *Atomic Physics 3*, edited by S. J. Smith and D. K. Walters (Plenum, New York, 1973).

<sup>4</sup>M. Stockton, J. W. Keto, and W. A. Fitzsimmons, *Phys. Rev. A* **5**, 372 (1971). See also C. M. Surko, R. E. Packard, G. J. Dick, and F. Reif, *Phys. Rev. Lett.* **24**, 657 (1970).

<sup>5</sup>J. W. Keto, M. Stockton, and W. A. Fitzsimmons, *Phys. Rev. Lett.* **28**, 792 (1972).

<sup>6</sup>J. C. Hill, O. Heybey, and G. K. Walters, *Phys. Rev. Lett.* **26**, 1213 (1971).

<sup>7</sup>A. P. Hickman and N. F. Lane, *Phys. Rev. Lett.* **26**, 1216 (1971).

<sup>8</sup>W. Steets, A. P. Hickman, and N. F. Lane, to be published.

<sup>9</sup>J. Wilks, *The Properties of Liquid and Solid Helium* (Clarendon Press, Oxford, England, 1967).

<sup>10</sup>The intensity of the 800-Å  $A \rightarrow X$  uv continuum has been found to increase slightly with pressure when the superfluid is subjected to  $\alpha$ -particle bombardment. See H. A. Roberts, W. D. Lee, and F. L. Hereford, *Phys. Rev. A* **4**, 2380 (1971).

<sup>11</sup>G. Herzberg, *Molecular Spectra and Molecular Structure: I. Spectra of Diatomic Molecules* (Van Nostrand, Princeton, N. J., 1950), 2nd ed.

<sup>12</sup>The concentration of  $a^3\Sigma$  metastable molecules in the superfluid actually increases with pressure, but this effect is due entirely to the pressure dependence of the roton energy gap  $\Delta$ . The results of this investigation will be published later.

<sup>13</sup>J. W. Keto, Ph.D. thesis, University of Wisconsin, 1972 (unpublished).

<sup>14</sup>See, for example, H. W. Offen and D. T. Phillips, *J. Chem. Phys.* **49**, 3995 (1968); A. H. Ewald, *J. Phys. Chem.* **67**, 1727 (1963).