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M. E. Himbert, A. Lezama, J. Dupont-Roc. Laser excitation of Ba⁺ ions in liquid helium. Journal de Physique, 1985, 46 (11), pp.2009-2014. 10.1051/jphys:0198500460110200900 . jpa-00210149

HAL Id: jpa-00210149

<https://hal.science/jpa-00210149>

Submitted on 1 Jan 1985

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Classification
 Physics Abstracts
 32.50

Laser excitation of Ba^+ ions in liquid helium

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(Reçu le 6 mai 1985, révisé le 3 juillet, accepté le 5 juillet 1985)

Résumé. — En utilisant une technique de vaporisation par laser pulsé, des ions baryum ont été introduits dans l'hélium liquide à 0,5 K. Il a été possible de réaliser une excitation par faisceau laser de la transition de résonance 6s-6p à 455 nm des ions piégés dans le liquide : la raie d'absorption observée n'est pas déplacée, et présente une largeur de l'ordre de 5 nm.

Abstract. — Using a laser vaporization technique, barium ions have been injected in liquid helium at 0.5 K. Laser excitation of their resonance 6s-6p transition at 455 nm have been performed in the liquid. The observed absorption line shows no shift and a 5 nm width.

1. Introduction.

Pair potentials between helium atoms and alkali atoms in the ground state are characterized by a weak Van der Waals long range attraction, and a repulsive part, which begins at rather large distance, typically 6 Å for Na atoms [1, 2]. Hence, when immersed in liquid helium, such an atom excludes helium atoms from a rather large sphere. Typically, the space occupied by a Na atom is 12 Å in diameter and its surface involves more than 25 helium atoms.

Furthermore, the well depth of the ^4He -alkali potential, when the latter is in the ground state, is only a few kelvins, much smaller than the kinetic and potential energy of a helium atom in the bulk liquid (respectively +14 K and -21 K). Thus, it makes some sense to examine the properties of liquid helium around the alkali atom from a macroscopic point of view, and to describe its structure and its motion using hydrostatics and hydrodynamics. The system « alkali + helium atoms around it » would have specific properties, such as vibration modes, and could eventually provide a new microscopic probe of liquid helium, similar to positive or negative ions [3, 4]. In that respect, the optical spectrum of the immersed atoms could be a valuable source of information.

Similar properties are also true for metastable 2^3S_1 helium atoms or alkali-earth ions such as Ba^+ . Alkali earth ions are different in that respect from alkali ions. Because of their complete electron shell, the latter are of small size and show deeper potential wells for helium atoms. This results in the so-called « snow ball » structure around these ions in liquid helium. The 6s outer electron prevents the formation of such a solid layer around Ba^+ [15].

One may also consider the preceding system as an atom in a rare-gas matrix of extreme plasticity, and comparison with the spectroscopy of impurities in solid matrices is appropriate [5]. The efficient theoretical descriptions of liquid helium already known could allow a good modelization of such a system, whereas such a program is still underway for matrix isolated atoms.

Molecular or atomic impurities in liquid helium have been optically observed previously in various circumstances. Molecular emission bands of O_2 and N_2 were detected from helium bombarded with alpha particles [6]. High energy neutral excitations in liquid helium [7] were shown to be He_2^* (a $^3\Sigma$) metastable molecules through analysis of emission and absorption spectra [8, 9]. Metastable 2^3S_1 and more excited levels of helium atoms were also observed in the liquid [9] and a theoretical model has been set up to account for their spectral properties [11]. More recently, fluorescence from nitrogen atoms trapped in superfluid helium were observed, as well as electronic spin resonances of these species [12, 13].

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Although their special properties make alkali atoms particularly attractive, their study in liquid helium is not easy. The main experimental problem is the production of a sufficient number of impurities in liquid helium. Thus, it is appropriate to choose the impurity according to experimental considerations. The interaction potential of alkali-earth ions Ba^+ with helium displays the same general features as Na-He . Ba^+ have in addition two advantages compared to neutral alkali atoms. First, the attractive Van der Waals part of the $\text{Ba}^+\text{-He}$ potential has a $1/r^4$ long range behaviour because of the charge-dipole interaction, compared to $1/r^6$ for alkali (dipole-dipole). One thus expects a larger negative contribution to the energy of the impurity in helium and a better solubility of Ba^+ in liquid helium. Secondly, the charge of Ba^+ makes it possible to control the ion motion with electric fields, for example to force them into the liquid. Furthermore, Ba^+ ions in helium have already been used in mobility measurements [14], and their structure has been investigated theoretically [15].

We describe in the present paper the experimental procedure followed and the results obtained in an attempt to study optically Ba^+ trapped in superfluid ^4He [16].

2. Experimental procedure.

2.1 BARIUM ION PRODUCTION METHOD. — The ions are extracted from a laser generated plasma [17]. The principle of the experiment is explained in figure 1, which shows the low temperature part of the apparatus. A bit of barium metal is held above the surface of the liquid ^4He . The beam of a pulsed nitrogen laser L_1 is focused on the metal surface by a UV lens. The pulse peak power is sufficient to vaporize and ionize a small amount of Ba. This appears as a bright spark at the surface, produced by each laser pulse. The very hot and dense plasma produced in that way expands

Fig. 1. — Principle of the low temperature part of the experimental arrangement. Total height $h \simeq 15$ mm. B : bit of metallic barium. D : metallic diaphragm (potential $V_D = 0$ V). S : liquid helium surface. G : grid (typical potential $V_G = -500$ V). P : collecting plate (typical potential $V_P = -800$ V). L_1 : vaporizing pulsed laser beam ($\lambda \simeq 330$ nm). L_2 : delayed dye laser beam ($\lambda \simeq 455$ nm).

rapidly. It contains barium atoms and ions, and presumably clusters. A loosely collimated beam is selected by a diaphragm D and reaches the helium surface, making its way through the low density helium vapour in equilibrium with the liquid (the temperature T is around 0.6 K, so that the vapour pressure is of the order of 10^{-3} torr).

A pulsed dye laser L_2 , pumped by another nitrogen laser, is used to excite the Ba^+ ions on the $6^2\text{S}-6^2\text{P}$ resonance transitions. The relevant energy levels of Ba^+ are shown in figure 2. The subsequent fluorescence is detected either on the same transition, or using the $6^2\text{P}-5^2\text{D}$ red fluorescence. The delay between the vaporizing laser L_1 and the laser L_2 , used for the detection can be varied from 0.1 μs up to 0.1 s. The life time of the excited state being very short (6 ns) [18], the fluorescence of the ions takes place at the same point where they have been excited by L_2 . Repeated shots with different delays and various positions of L_2 above the surface of the liquid reveal the cloud of Ba^+ ions at various stages of its expansion. From the intensity of the fluorescence light the number of ions produced by the pulses can also be estimated. It was found that each pulse produces a large amount of fast Ba^+ ions, typically 10^8 - 10^9 . Their velocity is of the order of 10^4 ms^{-1} , which corresponds to a temperature of 10^6 K (100 eV). This is a typical spark temperature [17, 19].

The overall heating produced by this method is quite low. The vaporizing pulse has a typical energy of 1 mJ. At the repetition rate of 1 Hz, the power dissipated is well met by the ^3He refrigerator, which cools the ^4He sample at an averaged temperature of 0.6 K. But transient heating up to 0.8 K is likely to take place after each pulse.

The ions reach the liquid surface in a few microseconds and are stopped here. A grid G, negatively polarized, immersed in liquid helium, attracts them into the liquid. The ions which have travelled up to G are then collected on a plate P, and the corresponding current is measured by a picoammeter.

Crossing the liquid surface is likely to be the most difficult part of the travel of the ions. As a matter of fact, there is certainly above the surface a large amount of electrons produced by the initial laser pulse and which are excluded from the liquid by the 1 eV pseudo-potential seen by an electron in liquid helium [20].

Fig. 2. — Relevant energy levels and transitions of the Ba^+ ion. Wavelengths are in nm.

They tend to keep the ions at the surface and to recombine with them there. This process is revealed by a fluorescence located *at the surface* which lasts about 1 ms. Its spectrum exhibits lines of neutral barium. More precisely, we have compared the spectrum of the light emitted by the plasma during its expansion above the surface and that of the light coming later from the surface itself. In the last one, the lines corresponding to the recombination of Ba⁺ with an electron are increased, especially the 6s 6p ¹P → 6s² ¹S line. None of the spectral lines of He were found in the light coming from the spark or from the surface. This indicates that He⁺ ions are not numerous, and that the ion current is mainly due to Ba⁺ ions [21].

From the above analysis, it would seem that the electric field E between G and the surface is essential to counteract the influence of the electrons and to force some Ba⁺ ions into the liquid. Another mechanism may also help as well. The helium surface is strongly heated by the plasma and a strong « wind » of elementary excitations is likely to flow from the surface to the bulk liquid. This flow of normal liquid could carry away the ions from the surface quite efficiently.

2.2 OBSERVED ION CURRENT.— A typical current pulse following a L₁ laser pulse is shown in figure 3. It belongs to a recurrent series taken with a repetition rate of 1 Hz. We noticed that first few current pulses of a series are much weaker and have different shapes. We attribute this phenomenon to the helium film which covers the barium, and which evaporates after a few laser pulses. The barium bit is held by thin wires, in order to minimize the helium film flow coming from the bulk liquid.

The initial spike, which lasts about 0.2 ms, is attributed to charges induced on the electrodes during the establishment of the plasma. It is also present (with a reversed sign) for opposite polarization of the electrodes and its delay is independent of the helium thickness. Later, the current decreases from a typical value of 30 nA to zero within 2 ms. It is higher and decreases faster for higher grid voltage. The corresponding density of ions, ρ_i , can be evaluated as follows : according to mobility measurements [14], drift velocities of posi-

tive ions in superfluid helium in an electric field of 2 kV cm⁻¹ are found between 10 and 30 ms⁻¹. The effective area of the grid G attracting the ions is of the order of 0.1 cm², which leads to $\rho_i \simeq 10^9$ cm⁻³. Since the spacing is 2 or 3 mm between G and the surface S, and 2 mm between G and P, transit times in the liquid are typically 0.1 ms. The number of charges collected by P during the whole pulse is of the order of 10⁸-10⁹. We also observed a current, although weaker and lasting 0.5 ms, when V_G was at the ground potential. This may be evidence for ions carried by the normal fluid flow discussed previously.

2.3 LASER EXCITATION AND FLUORESCENCE DETECTION OF THE IONS IN THE LIQUID.— The detection laser L₂ is focussed in liquid helium, between the surface S and the electrode G. Its diameter in this region is 0.5 mm, its peak power is 10 kW and its line width is 2 cm⁻¹. From the ion density ρ_i , it is inferred that 10⁶ ions can be excited for each pulse (this is a crude estimation). The fluorescence light is observed at right angle. Special care was taken to get rid of stray light. A spatial filter takes only the light coming from the illuminated region under the surface (1 mm × 3 mm). The intense stray UV light produced by the nitrogen laser beam in the cell, is rejected by a dichroic UV mirror, followed by a thick lucite plate which absorbs the remaining transmitted part. Two coloured filters eliminate the blue light scattered from the L₂ beam. As a result, we monitor the fluorescence light in a band from 560 nm to 900 nm. The total detection efficiency has been estimated taking into account the collection of light, the transmission of the filters and the quantum efficiency of the photomultiplier (Hamamatsu R666) : it is about 2×10^{-4} at 600 nm.

The fluorescence signal is recorded alternately with and without ion production. In the latter case, we have only the remaining stray light from L₂. Occasionally, the stray signal coming from L₁ alone is also measured. Since the fluorescence pulse is recorded using a sampling system triggered by L₂, the stray signal from L₁ is generally not detected, except for short delays between L₁ and L₂ (in that case, a tail originating from the L₁ pulse is detected and causes a background to the fluorescence signal).

3. Experimental results.

Figure 4 shows a typical fluorescence signal as a function of the wavelength of the exciting laser L₂. The delay between L₁ and L₂ was 0.24 ms. Subtracting L₂ stray light background, and normalizing to a constant L₂ intensity over the entire line scanning gives the optical resonance lines such as the one displayed in figure 5. The number of detected fluorescence photons corresponding to the signal of figure 5 is typically 500, which correspond to 2×10^5 emitted photons in the observed volume. This order of magnitude is consistent with the estimated number of ions in this region given above.

Fig. 3. — Current between G and P versus time t . $t = 0$ is taken at the L₁ laser pulse. Detection time constant is 0.1 ms. The initial spike is direct effect of the plasma on the detection system. $V_G = -500$ V, $V_P = -800$ V.

Fig. 4. — Typical fluorescence intensity *versus* the wavelength of the exciting laser beam L_2 . The L_1 laser producing the ions is alternately on (a) and off (b) during the scanning of L_2 . The delay between L_1 and L_2 was 0.24 ms.

Fig. 5. — Resonance signal obtained from fluorescence intensity (Fig. 4) by subtracting L_2 stray light and normalizing to a constant L_2 excitation (open circles). The points ∇ correspond to a different value of the delay τ between L_1 and L_2 pulses : $\tau = 0.84$ ms.

The signal was recorded for various delays between L_1 and L_2 . The shape of the line is time independent and its intensity decreases with increasing delay, in much the same way as the current does. For shorter delays a non-resonant background appears, the origin of which has not been clearly identified. In the narrow range explored (447–470 nm) we found only one absorption line, roughly symmetrical, 5 nm wide (300 cm^{-1}) and essentially unshifted. Although a detailed study was not performed the line does not seem to be saturated : decreasing L_2 intensity decreases the fluorescence signal.

This result is surprising, if compared with the spectra of matrix isolated atoms and ions. Absorption spectrum of Na atoms in Ne [22], exhibits an unshifted part (width 150 cm^{-1}) and a blue shifted band 1500 cm^{-1} further. According to Bondybey and English, changing from neutral atoms to isoelectronic ions lead to sharper lines [23]. On the other hand, heavier atoms are likely to give rise to larger perturbations [24]. So a blue shift of the mean value of the absorption line is expected.

For solid matrices, the crystal field anisotropy is generally invoked to explain multiplet band structure of the absorption spectrum by removal of the p state degeneracy [25, 26]. According to this explanation, a singlet line is expected for liquid helium, because of the spherical symmetry of the medium. However, this spherical symmetry is expected to hold only on the average. Instantaneous departure from this symmetry occurs certainly due to fluctuations. They would lead to instantaneous non degenerate transitions (Jahn-Teller effect). The case of a large fine structure was considered by Weinert *et al.* [27] and describes well the example of Ba^+ ($E_{p3/2} - E_{p1/2} \simeq 1700\text{ cm}^{-1}$). They suggest that the D_2 line ($6S_{1/2} \rightarrow 6P_{3/2}$) may be split in two by the Jahn-Teller effect. Thus it could be that the centre of the whole structure is about 447 nm and that another line may be found on the blue side of this centre.

Another possibility is that the environment of the trapped ion is grossly perturbed, either by the presence of vortices or by a large amount of thermal excitations, leading to a reduced density around the impurity, and consequently to a reduced shift. Anyway a much wider line scanning would have been interesting, in order to cover the entire fine structure of the line. The other fine structure component of the 6s-6p transition is expected to be simpler due to the

absence of second rank tensor perturbation of the $j = 1/2$ excited state [32]. Such a scanning was unfortunately not available to us.

A spectral analysis of the fluorescence light would also have been valuable. But the small number of detected photons would have required very long operating times, which we were unable to get, due to the window darkening by the deposit of metallic barium. We made only a rough estimate by changing the coloured filters in the detection system. The result is shown in table I. The main part of the detected fluorescence is emitted in the 530-565 nm range. This does not mean that none is emitted at shorter wavelengths, but it was rejected by the filters in the detection set up.

4. Conclusion.

We have described a first attempt to observe experimentally the excitation and the fluorescence of Ba⁺ impurities trapped in liquid helium. An unshifted absorption line was found. Further experiments [28]

Table I. — *Rough analysis of the fluorescence light above 530 nm.*

Spectral range (nm)	530/565	565/625	610/730	710/870
Number of detected fluorescence photons (%)	63	16	8	13

to complete this information are needed to allow a valuable comparison with theoretical models [32]. A geometrical arrangement in which all the windows would be protected by liquid helium to avoid the deposit of metallic barium would be a significant improvement. More efficient detection of the excited atoms is the clue for the access to higher excited states. In that respect, beams of liquid helium droplets [29] might be very useful : seeded with Ba⁺ ions, they would allow ionization detection techniques, which have been already used very efficiently for atomic spectroscopy [30, 31].

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