STIMULATED INFRARED EMISSION FROM TRIVALENT URANIUM

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Schawlow and Townes[1] have proposed the extension of maser techniques to generate coherent light in the visible and infrared regions of the electromagnetic spectrum. Recently Maiman[2] and Collins et al.[3] obtained stimulated emission of radiation in chromium-doped Al_2O_3 in the R_1 transition from the ^2E metastable state to the ground state. The oscillation was achieved by inverting the population of the metastable state relative to the ground state by a sufficient amount to overcome the losses in the optical cavity. Since this required approximately 10^{18} - 10^{19} ions in the metastable state, very high optical pumping power was necessary to achieve inversion.

This Letter describes the characteristics of stimulated emission from trivalent uranium ions substituted for divalent calcium ions in calcium fluoride. The crystals were grown by a technique similar to that described by Galkin and Feofilov.[4] In contrast to the case of the ruby optical maser, the oscillation takes place in a transition from a metastable state to a level approximately 515 cm^{-1} above the ground state. At low temperatures this state is depopulated by at least a factor of 10^{10} relative to the ground state. The general condition for stimulated emission is that the number of excited ions in the metastable state must exceed the number of ions in the lower state by a certain amount Δn sufficient to overcome the cavity losses. In trivalent uranium this condition will be achieved at low temperatures when the population of the metastable state is approximately equal to Δn since the population of the lower state is negligible. The value Δn may be generally much less than the number of ions in the ground state. It was indeed observed that the pumping power necessary to achieve stimulated emission was lower by about a factor of 500 compared to ruby.

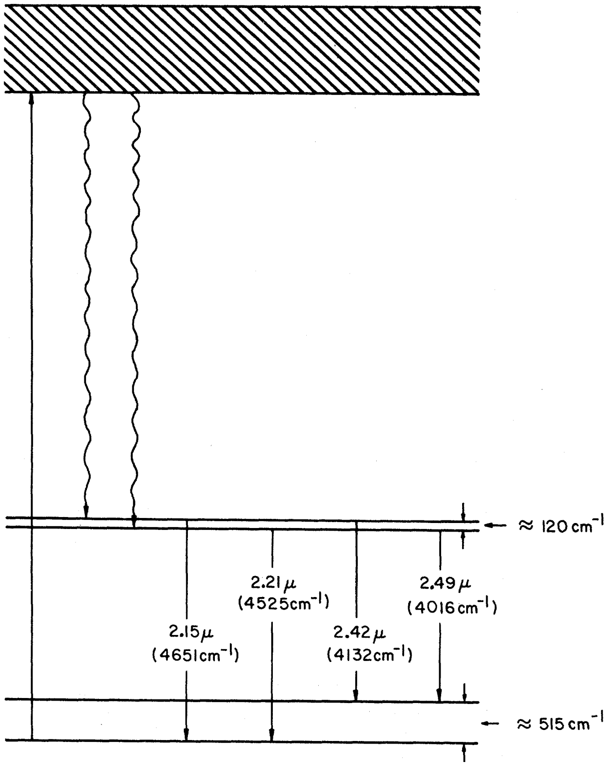

FIG. 1. Energy level diagram of trivalent uranium in calcium fluoride based on the paper by Galkin and Feofilov. Broad-band pumping light applied in the blue and green visible spectrum causes transitions to excited bands, one of which is depicted in the figure. These pumping transitions are followed by rapid, nonradiative transitions to the two metastable levels shown.

Figure 1 shows the pertinent energy levels of the trivalent uranium ion when substituted for calcium in the CaF_2 lattice.[4] The ion has several strong absorption bands in the visible and near infrared wavelength regions. The strongest absorption bands are in the green and blue, and as a result the crystals have a pale to deep red color and thus show a striking resemblance to ruby. Very strong fluorescence is observed in the infrared region between 2.0 and 2.6 microns when exciting radiation is applied in the range of the absorption bands. The room temperature fluorescence spectrum consists of four peaks. The two shorter wavelength peaks coincide with the absorption peaks and therefore are resonance lines. The two longer wavelength peaks represent emissions to a state located approximately 515 cm^{-1} above the ground state. The longest wavelength emission occurs from the lower metastable state and is the transition in which the maser oscillations are observed.

A single crystal of calcium fluoride with 0.05 mole percent uranium was cut into a cylindrical shape 3/8 in. in diameter and $1\frac{1}{2}$ in. long. The ends were polished flat to one-twentieth of a sodium wavelength and parallel to fifteen seconds of arc. Silver films were evaporated on both ends, with one end left completely opaque and the other end left with a 1.5% transmission. A protective SiO coating was applied over the silver to prevent oxidation. The sample was placed in a specially constructed liquid helium Dewar and was cooled without being in actual contact with the liquid helium. A pulsed xenon discharge lamp excited the vertically positioned sample through a side port in the Dewar. The infrared radiation generated in the sample was coupled out through the 1.5% transmitting end face and was detected by a lead sulfide detector through a top port. Either a 2.5-micron interference filter or a Perkin-Elmer monochromator was used to isolate the infrared radiation from the lamp background. The response time of the detector was approximately 40 microseconds for decaying radiation.

Figure 2 shows typical oscilloscope traces of the detector response to the intense monochromatic stimulated emission when the pump power is set above the threshold value. The signal during the first 450 microseconds of Fig. 2(a) is due primarily to the scattered light from the xenon flash lamp plus a small but undetermined amount of spontaneous radiation. Oscillation begins where the rapidly rising, almost vertical, trace is observed and always occurs when the pumping power reaches the same critical level. Fig. 2(b) shows the same detector output with reduced gain and expanded time scale. The ratio between the stimulated emission and the background light was measured to be in excess of 1000, which means that the spontaneous emission is less than the stimulated emission by a factor of several thousand. This ratio is larger than that observed for the ruby maser, which conforms to the expectation of smaller spontaneous emission in the infrared as compared with the visible spectral region. The spectral width of the maser pulse was substantially less than the resolving power of the monochromator. The beam was confined to an angle of approximately

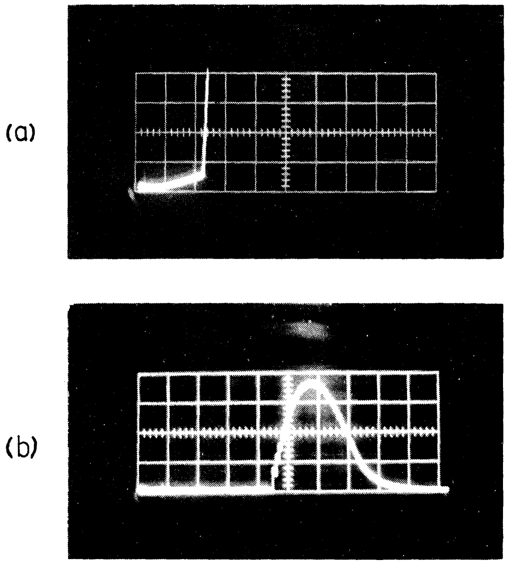

Fig. 2. (a) Detector response above threshold showing the onset of oscillation after 450 μsec. A filter with a bandwidth of 0.1 micron and centered at 2.5 microns is inserted before the detector. The sweep speed is 200 μsec/division. (b) Detector response with the conditions as in 2(a) except that the oscilloscope gain is reduced by a factor of 500 and the sweep speed is 100 μsec/division.

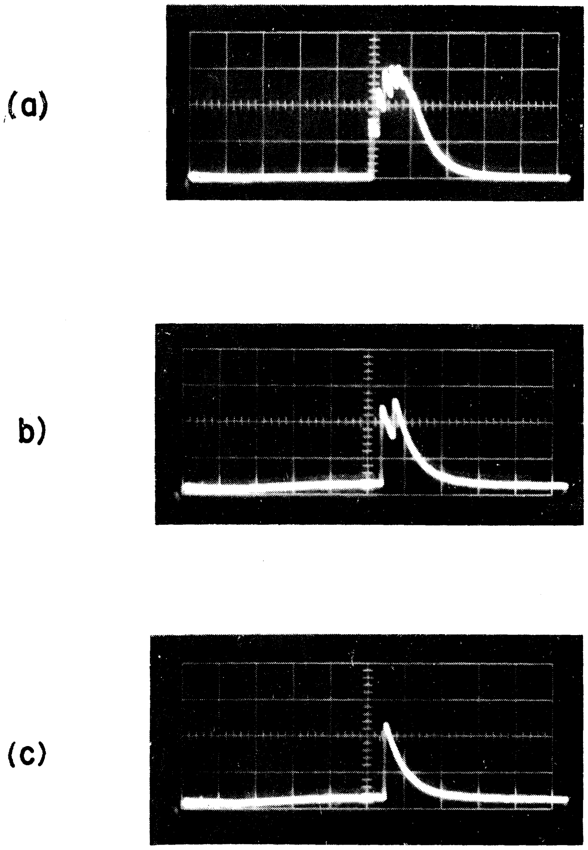

FIG. 3. Relaxation oscillations at varying pump power levels. The time scale is 100 μsec/division. Trace (a) shows the maser output with pump power about 1.5% above threshold. Traces (b) and (c) are taken at powers barely above threshold.

0.01 radian.

An interesting feature of the maser output shown in Fig. 2(b) is the presence of relaxation oscillations, previously also observed in less detail by Collins et al. in ruby. The number of observed spikes decreases rapidly as the power input into the exciting xenon lamp is lowered towards the threshold value until at barely above threshold only a single spike oscillation occurs. Figure 3 illustrates this phenomenon. The single spike takes place at exactly the peak of the pulse output of the xenon lamp, while the multiple spikes begin earlier because the exciting power reaches the threshold value at an earlier point. The spacing between the oscillations increases as the xenon lamp input power is brought closer to threshold. These features seem consistent with the explanation offered by Collins et al. for the relaxation oscillations in the ruby optical maser, perhaps complicated by contributions from several frequency modes within the inhomogeneously broadened line as suggested by G. J. Lasher of this laboratory.

The favorable energy level structure of trivalent uranium as compared to ruby may result in a strong cw infrared source for research purposes in the near future.

We would like to thank J. Lankard for assistance with the experiments, W. V. Smith and A. H. Nethercot for their continued interest and encouragement, and other members of the laboratory for helpful discussions. Special thanks are due Walter Hargreaves of Optovac, Inc. for cooperating with us in growing the crystals.

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[3] R. J. Collins, D. F. Nelson, A. L. Schawlow, W. Bond, C. G. B. Garrett, and W. Kaiser, Phys. Rev. Letters 5, 303 (1960).

[4] L. N. Galkin and P. P. Feofilov, Doklady Akad. Nauk S.S.S.R. 114, 745 (1957) [translation: Soviet Phys. – Doklady 2, 255 (1957)].

MOBILITY OF HYDROGEN IONS*

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Experimental measurements of the drift velocity or mobility of hydrogen ions in the parent gas indicate only a single type of ion, which has consistently been assumed to be H_2^+.[1-3] Rarely, a second ion has been reported,[4,5] but it has always been difficult to observe so that a cloud of suspicion as to its reality has prevailed. Identification of the ion as H^+ seems to be justifiable. The theory of ionic mobilities has been applied by Mason and Vanderslice[6] to hydrogen, and it supports the identification of the ions described above. It predicts also that H_3^+ should be found with a mobility considerably higher than that of either H^+ or H_2^+ or of any observed values reported in references 1-5.

Meanwhile, Stevenson[7] has published some properties of the H_3^+ ion which are listed here:

(1) H_3^+ is formed by the reaction $H_2^+ + H_2 = H_3^+ + H$.

(2) The cross section for this reaction is enormous, approximately 1×10^{-14} cm^2.

(3) The binding energy of H_3^+ is 97 kcal or 4.18 ev (private communication).

(4) H_3^+ ions passing through H_2 gas probably have an enormous charge-exchange cross section, of the same approximate size, 1×10^{-14} cm^2, as for the formation of H_3^+.

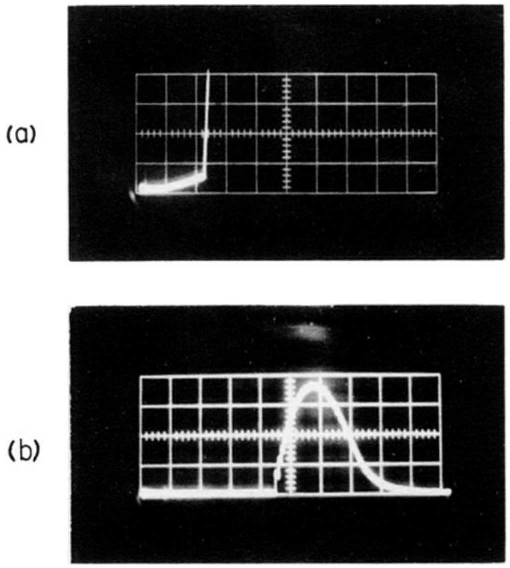
(5) The charge-exchange mechanism appears to be an exchange of a proton instead of the more usual exchange of an electron envisaged by the term "charge exchange."

If these findings are correct, and there is every reason to believe they are, then two changes must be made in the theory and interpretation of mobilities of ions in hydrogen.

(1) The H_2^+ ion is never observed in mobility experiments nor will it ever be observed.

(2) The H_3^+ ion has a lower mobility than predicted by Mason and Vanderslice, presumably having the value commonly observed.

The following justifications are offered: The chemical equlibrium constant for the formation reaction for H_3^+ given by Stevenson is so large that there is no possibility of shifting the equilibrium toward the H_2^+ side of the reaction within the bounds of swarm-type experiments, for ex-



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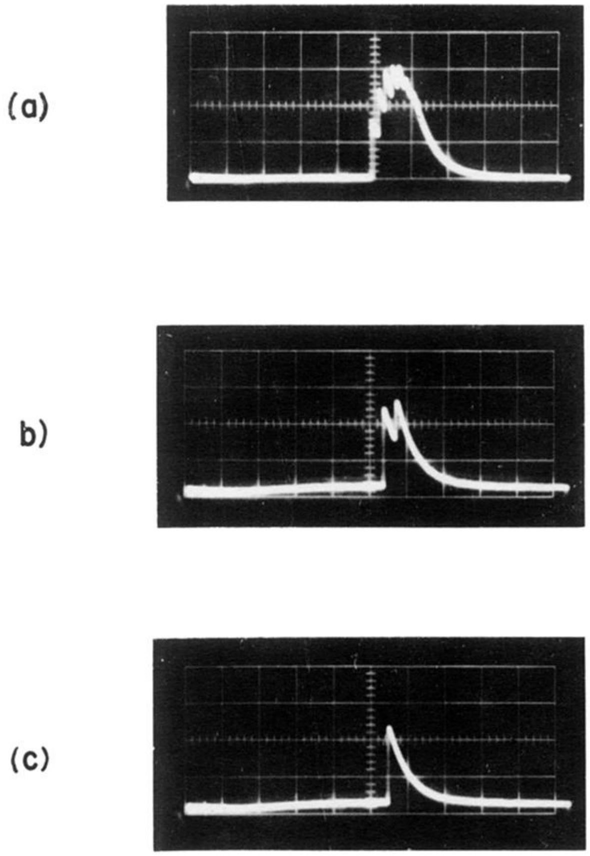

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