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Preferential excitation and enhanced emission of Pb atoms following detonation of lead azide

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Preferential excitation of the $^3P_1^\circ$ state of the lead atom and enhanced emission in the Pb($^3P_1^\circ \rightarrow {}^1D_2$) transition at 722.9 nm have been observed following the detonation of lead azide, $Pb(N_3)_2$. The detonation is initiated by a short laser pulse and the products are expanded through a supersonic nozzle. It is suggested that the enhanced emission is due to preferential excitation of Pb($^3P_1^\circ$) via energy transfer from electronically excited N_2 combined with the effect of self-trapping of the emission from $^3P_1^\circ$ to the $^3P_{0,1,2}$ states. The implications to short-wavelength chemical lasers are discussed.

The possibility of obtaining chemical laser oscillation in the visible region continues to intrigue the *Chemical Laser* community.[1–3] Thus, two recent papers in this journal reported on cw laser oscillation-like phenomena around 700 nm observed from a cavity containing chemically produced, electronically excited O_2.[2,3] In the present letter we report on experiments in a pulsed system aimed at achieving preferential population of specific electronic states of the lead atom. Our approach[4] is based on exploiting an energy-rich material where a potential lasant and an energetic fuel are "premixed". Premixing is essential for achieving chemical laser action from initially separated reagents since the reaction rate is limited by the diffusive mixing rate, which for reagents in many potential visible chemical lasers is slower than their quenching rates.

The primary explosive lead azide, $Pb(N_3)_2$, is a suitable energetic material where a potential lasant (Pb) and a fuel precursor (N_3) are inherently mixed. It yields Pb atoms and N_3 radicals in the first stage of decomposition; the N_3 readily dissociates to ground electronic state N_2 molecules and N atoms and the latter efficiently react with N_3 to produce electronically excited, triplet N_2.[5] Since all triplets decay collisionally or radiatively to N_2 in the metastable A state,[6,7] decomposition of $Pb(N_3)_2$ produces, eventually, $N_2(A)$. Recent investigations[8,9] have revealed that energy transfer from $N_2(A)$ to metal atoms can be both efficient and state selective, i.e. there is a preferential excitation of specific electronic states of the metal for which the transfer is approximately resonant, spin-allowed, and involves large $N_2(A,v'\text{-}X,v'')$ Franck–Condon factors.

The energy levels of Pb lying $< 50\,000$ cm^{-1} above its ground state, $^3P_0$, are presented in Fig. 1. Note that $N_2(A)$ lies $\sim 50\,000$ cm^{-1} above the ground state, $N_2(X)$, and that only the $v' = 0,1$ levels of $N_2(A)$ are significantly populated in the presence of $N_2(X)$.[9] Also, near-resonant excitation of Pb $^3P_0$ to $^3P_0^\circ$ and $^3P_1^\circ$ may be favored due to the large $N_2(A,v'=0-X,\ v''=6,7)$ Franck–Condon factors. Indeed, previous $Pb(N_3)_2$ detonation experiments[4(b)] have shown that about 80% of the photon yield from the products originates in the Pb states of Fig. 1 and the rest in $N_2(B)$ and in occasional impurities. The Pb population distribution is nonthermal with 1/3 of the yield of the Pb emission originating in the $^3P_1^\circ$ state and 1/8 in $^3P_0^\circ$.

The present experimental setup is depicted in Fig. 2. 2–20 mg of $Pb(N_3)_2$ powder were initiated by a short (~ 8 ns) Nd:YAG laser pulse focused to a 2-mm-diam spot; the pulse energy was ~ 20 mJ. The detonation products were expanded in an evacuated reaction cell[10] through an axisymmetric converging-diverging supersonic nozzle with area ratio of 1/16 and throat area of 0.2 cm^2. The use of the nozzle was essential in order to get a transparent gaseous medium. To monitor the transparency, the transmittance of a HeNe laser beam was recorded by a photodiode (PD). The ensuing chemiluminescence from the detonation products was measured near the nozzle exit using imaging optics. The emission was monitored in the 230–850 nm region by both a gated optical multichannel analyzer (OMA) controlled by a computer (PC), and photomultiplier tubes (PMTs). The wavelength response of the PMTs was calculated from their quoted characteristics.

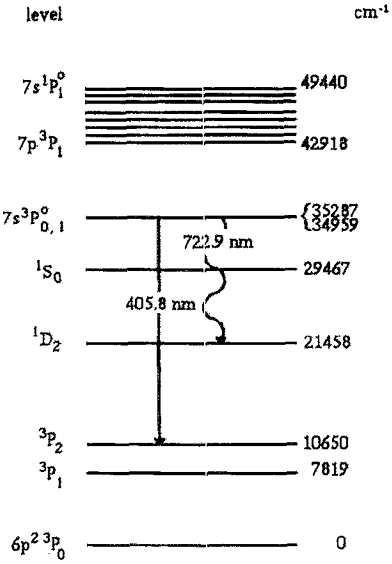

FIG. 1. Pb energy levels below 50 000 cm^{-1}. The levels between 42 918 and 49 440 cm^{-1} which are not marked in the figure are $7p\,^3P_0$, $7p\,^3D_{1,2}$, $6d\,^3F_2^\circ$, $6d\,^3D_{2,1}^\circ$, $6d\,^3F_3^\circ$, $7s\,^3P_2^\circ$, and $8s\,^3P_{1,0}^\circ$, respectively. The emissions from $^3P_1^\circ$ which are presented in Fig. 4 are marked here for reference. The $^3P_1^\circ \rightarrow {}^1D_2$ line at 722.9 nm is a potential lasing transition as explained in the text.

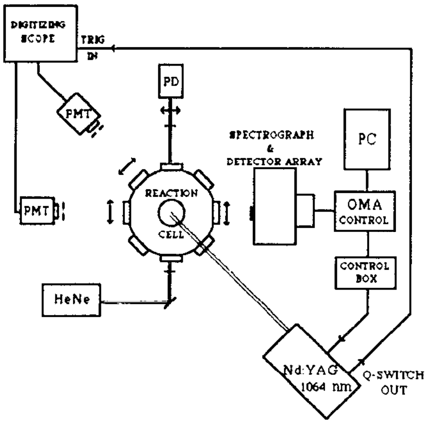

FIG. 2. Experimental setup.

An example of chemiluminescence spectra monitored near the nozzle exit by the OMA is given in Fig. 3, where the Pb transitions are marked. A striking feature of these spectra is the increase with time of the emission intensity of all lines terminating in the $^1D_2$ state. This increase was also observed for the $^3P_1^\circ \rightarrow {}^1D_2$ transition at 722.9 nm, which is outside the spectral range shown in Fig. 3. Moreover, the intensity of the transitions to the states that lie below $^1D_2$, $^3P_{0,1,2}$ decreases with time.

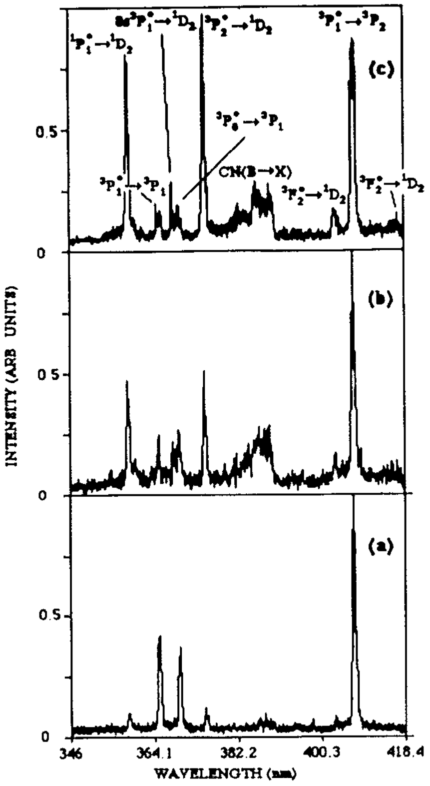

FIG. 3. Example of chemiluminescence spectra monitored ~1 mm downstream from the nozzle exit by the OMA in the blue wavelength region following detonation of 8 mg of $Pb(N_3)_2$. (a) 6–7 μs, (b) 9–10 μs, and (c) 13–14 μs after initiation. The spectra are not corrected for the wavelength response of the detection system and the gain of the recording system in (a) is two times lower than in (b) and (c). The CN emission is due to reactions of nitrogen with carbon-containing impurities.

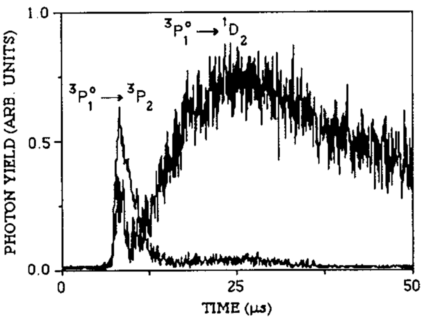

FIG. 4. Time sequential behavior of the $^3P_1^\circ \rightarrow {}^3P_2$ transition at 405.8 nm and $^3P_1^\circ \rightarrow {}^1D_2$ at 722.9 nm recorded simultaneously 10 mm downstream from the nozzle exit by two PMTs following initiation of 3 mg of $Pb(N_3)_2$ at $t = 0$. The photon yields are corrected for the wavelength response of the detection system.

These observations strongly suggest that the emission to the $^3P_{0,1,2}$ states is self-trapped and that trapping is increased with time due to accumulation of population in these states resulting from quenching of higher states. On the other hand, any population that might be formed in the $^1D_2$ state might, in turn, be quenched by the increasing number of Pb atoms in lower states. The suggested role of quenching processes in the time sequential behavior of the emission is supported by the dependence of the emission on the density of the detonation products.[4(b)] The intensity of the emission of the $^3P_{0,1,2}$ states decreased relative to that to $^1D_2$ when the density was raised by increasing the amount of explosive or confining the explosion volume. Although we do not have direct evidence for the particular quenching channels, it is worth noting that the process

$$\mathrm{Pb}(^1D_2) + \mathrm{Pb}(^3P_0) \rightarrow 2\mathrm{Pb}(^3P_2) \qquad (1)$$

has an energy mismatch of only 158 cm^{-1}.

Direct evidence for self-trapping was obtained from experiments where the density of the Pb atoms was high (i.e., when the density of the detonation products was raised):[4(b)] extreme line broadening and appearance of dips in the line center were observed for the Pb transitions terminating in the $^3P_{0,1,2}$ states. But the most convincing evidence for the suggested excitation and quenching mechanisms and the most significant result in the context of our goal was obtained from the present experiments which compared the time sequential behavior of two transitions originating from the *same* Pb state, $^3P_1^\circ \rightarrow {}^3P_2$ at 405.8 nm and $^3P_1^\circ \rightarrow {}^1D_2$ at 722.9 nm.

In these experiments two PMTs were placed at equivalent locations with regard to the reaction cell to monitor simultaneously the two transitions. The PMTs were equipped with 10 nm bandpass filters, one centered at 405 nm and the other at 720 nm. To check the validity of the measurements, the locations of the PMTs were interchanged in some experiments. Figure 4 presents an example of the time sequential behavior of the two lines. It clearly shows that the 405.8 nm line peaks 8 μs after the initiation of detonation and then rapidly decays whereas the 722.9 nm line, which initially follows the same pattern, starts to grow again 10 μs after the initiation. Note that the photon yield for the 722.9 nm line is higher than that for the 405.8 nm line most of the time, whereas from the corresponding transition probabilities for the $^3P^\circ_1 \rightarrow {}^1D_2$, $^3P_2$ emissions the latter should have been stronger by two orders of magnitude.

The important conclusion from these experiments is that once the self-trapping process is effective (when population accumulates in the $^3P_{0,1,2}$ states) it serves as a mechanism for storing population in the radiatively short-lived $^3P^\circ_1$ state which is continuously fed by energy transfer from the metastable $N_2(A)$ and thus can recover after its initial fast decay. The combination of these processes with the efficient quenching of $^1D_2$ results in enhanced emission of the $^3P^\circ_1 \rightarrow {}^1D_2$ line.

Our observations indicate that a lasing scheme based on the $^3P^\circ_1 \rightarrow {}^1D_2$ transition is feasibile (see Fig. 1). The above-mentioned processes: preferential population of the $^3P^\circ_1$ state, its self-trapping, and quenching of the $^1D_2$ state, seem to be essential for this scheme. The population of the upper potential lasing level, $^3P^\circ_1$, can be evaluated from the measurements of the emission intensity. A lower limit for the population is obtained from the intensity of the $^3P^\circ_1 \rightarrow {}^1D_2$ emission assuming that self-trapping by $^1D_2$ is negligible. For example, it is found that for the conditions of Fig. 4 the population of $^3P^\circ_1$ 12 μs after initiation is 7×10^{11} cm^{-3}. The population of the nonemitting $^1D_2$ state is more difficult to evaluate, but a rough estimate can be obtained assuming a Bolzmann-like distribution among the four low lying states of Pb (see Fig. 1). From fluid dynamics calculations it is found that at 12 μs after initiation the temperature at the nozzle exit plane for the conditions of Fig. 4 is around 2000 K and the population of $^1D_2$ is 2×10^9 cm^{-3}. For these conditions a population inversion in the $^3P^\circ_1 \rightarrow {}^1D_2$ transition is clearly established; the calculated small signal gain coefficient reaches 0.2 cm^{-1} (assuming Doppler line shape).

In summary, it was shown that it is possible to exploit a primary explosive as a source of premixed, potential chemical laser reagents. Storage of population in a preferentially excited potential lasing state can be assisted by self-trapping and draining of the lower state by efficient quenching. In order to obtain lasing in such a system, detonation in a laser cavity, producing a transparent, homogeneous medium has to be carried out. Experiments are in progress in our laboratory to achieve this goal.

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