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Effect of externally injected radiation on amplified spontaneous emission in CO

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Abstract. The effect of externally injected radiation on the two-photon laser-induced amplified spontaneous emission (TP-LIASE) is reported. The wave generated via the same LIASE process in a seeder cell acts as a seeder field for the inverted medium created in a main cell. A nearly tenfold gain is achieved in the $B\,^1\Sigma^+ \rightarrow A\,^1\Pi\,(0, 3)$ transition of the CO molecule. We demonstrate that the single rotational transition in the $B\,^1\Sigma^+ \rightarrow A\,^1\Pi\,(0, 4)$ band is selectively amplified by injection of laser radiation. This pump and seed arrangement facilitates detection of molecular spectra by simply tuning the seed-laser frequency. The polarization effect of the input laser radiation is briefly discussed.

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Amplified spontaneous emission (ASE) refers to the highly collimated radiation generated by an extended medium with an inverted population of atomic and molecular systems in the absence of cavity mirrors [1]. Although detailed experimental and theoretical treatments of the ASE processes have been conducted in the 1970s, applications of ASE relaxation processes to chemical kinetics and molecular spectroscopy have not been performed until very recently. Alekseev and Setser proposed a simple method for the generation of $Xe(6s[3/2]_1)$ whose energy level falls in the vacuum ultraviolet (VUV) region [2]: this method involves two-photon excitation of the $Xe(6p[1/2]_0)$ level followed by ASE to the $Xe(6s[3/2]_1)$ level. The population in $Xe(6s[3/2]_1)$ is high enough to measure the accurate quenching cross-sections of this level, providing detailed information on the interaction between Xe* and collision partners. In 1998, we developed a novel laser spectroscopic method involving ASE in the NO molecule [3]: in this regime, the $D\,^2\Sigma^+$ Rydberg state located in the VUV region, populated by ASE from the $E\,^2\Sigma^+$ Rydberg state, was employed as the intermediate state from which the higher Rydberg series were further excited. In both experiments, the key was the instantaneous population transfer accompanied by the ASE transitions between excited electronic states. In particular, in order to investigate subsequent chemical processes, it is essential to obtain population densities as large as possible. In this respect, it is of practical importance to amplify the population transfer to the relevant lower levels. In addition, the state-selective population control is highly desirable because of the different chemical property of each rovibronic level.

Westblom et al. performed a detailed study of the two-photon-driven $B\,^1\Sigma^+ \rightarrow A\,^1\Pi$ ASE transition of the CO molecule [4]. They found a considerable increase in the ASE signal if a quartz plate was placed in front of the cell and aligned so that optical feedback of the ASE beam was achieved. The two-photon excitation with subnanosecond laser pulses enhanced the $B\,^1\Sigma^+ \rightarrow A\,^1\Pi$ ASE transitions to such an extent that the fluorescence decay no longer obeyed a single exponential fit [5]. Though these experiments demonstrated the amplified population flow in molecular systems, any quantum-state selectivity has not been taken into consideration.

The purpose of the current study is the selective enhancement of the specific ASE channel by the injection of external radiation. Two schemes were investigated: the first method is the use of ASE as the seeder radiation. The influence of the ASE seeder field on the two-photon laser-induced ASE (TP-LIASE) is presented for the $C\,^1\Sigma^+ \rightarrow B\,^1\Sigma^+$ as well as the $B\,^1\Sigma^+ \rightarrow A\,^1\Pi$ electronic transition of the CO molecule. This regime is universal because the simple two-cell arrangement described in Sect. 1 allows us to work at any wavelength region with no additional excitation light source. The second method is the use of weak laser radiation as seeder light. In addition to the rotationally selective amplification in the CO $B\,^1\Sigma^+ \rightarrow A\,^1\Pi$ band system, the simple pump and seed arrangement facilitates detection of the molecular spectra by scanning the seed-laser frequency.

1 Experiment

The essential parts of the experiment are the two quartz cells standing in series as shown in Fig. 1a [6, 7]. The pump-laser light is split into two beams by a beam splitter (BS). The transmitted beam, referred to as pump I, is focused by a lens

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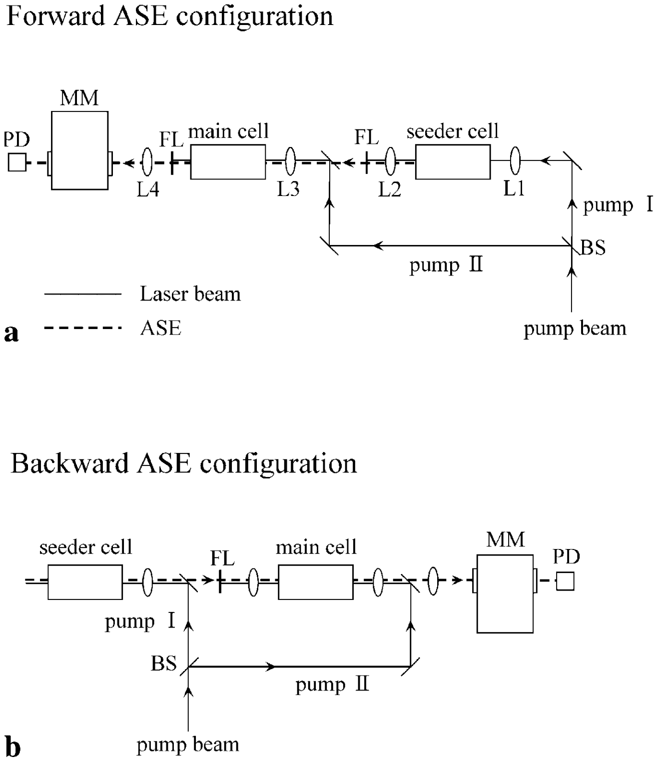

Fig. 1a,b. Experimental setup for the ASE seeding. Two-photon-driven ASE propagating in **a** forward and **b** backward directions serves as the seeder radiation for the main cell, respectively. L1, L2, L3, L4: lenses; BS: beam splitter; FL: filter; MM: monochromator; PD: photodetector

(L1; $f = 10\,\text{cm}$) into a seeder cell. The ASE propagating along the pump I laser beam is collimated by a lens (L2; $f = 8\,\text{cm}$). Only the seeder ASE field is transmitted by a dichroic mirror and is introduced into a main cell. The reflected beam, referred to as pump II, is focused by a lens (L3; $f = 12\,\text{cm}$) into the main cell. A He–Ne laser is used for the alignment of the two pump beams. The infra-red or visible output from the main cell, after being collimated by a lens (L4; $f = 80\,\text{cm}$) and separated from the laser radiation by optical filters, is detected with a Ge (Hamamatsu B1720-02), a PbS (Hamamatsu P2682) or a Si (Electro-Optics Technology ET-4000) detector through a monochromator (ARC SP401). In order to identify the emission in the VUV region, the VUV radiation propagating along the laser radiation was extracted by a 20-cm vacuum monochromator (ARC, VM-502) and detected by a solar blind photomultiplier (Hamamatsu R1459, CsI cathode). A stainless steel cell with a LiF exit window directly attached to the monochromator is evacuated below 10^{-5} Torr by a turbo pump.

The ultraviolet laser radiation around 215 nm needed for the two-photon excitation of the $C\,^1\Sigma^+(v = 0)$ state of CO is generated by frequency tripling [8] of the output of a dye laser (Continuum ND6000, DCM in methanol) pumped by a Nd:YAG laser (Continuum Surelite-II). The energy of the resulting sum frequency radiation is estimated to be about a few hundred μJ/pulse. The wavelength at 230 nm needed for the two-photon excitation of the $B\,^1\Sigma^+(v = 0)$ state is produced by frequency doubling by a BBO crystal (Fujian Castech Crystal).

In the cell configuration shown in Fig. 1b, the backward ASE from the seeder cell operates as the seeder field. For this configuration, the laser path length was arranged so that the backward ASE pulse overlapped with the pump II pulse in the main cell. The merit of the backward configuration is elimination of radiation generated by parametric four-wave mixing (PFWM); the phase-matching constraint permits the PFWM output waves to propagate only in the forward direction [9]. PFWM is distinct from ASE in that PFWM does not involve a population transfer and the molecular system remains in the ground state [10].

The experiment with the seed laser was undertaken with a single cell into which pump- and seed-laser beams are introduced collinearly. A Nd:YAG laser (Continuum Surelite-I)-pumped dye laser (Continuum ND-6000) was used as the seeder light. Two laser pulses are overlapped in time with a digital delay generator (SRI, DG-535). Throughout the experiment, the polarization direction of the UV pump laser was set horizontal. The polarization vector of the seed laser was changed by rotating a double Fresnel rhomb.

2 Results and discussion

2.1 Effect of the injected ASE on the $C\,^1\Sigma^+ \rightarrow B\,^1\Sigma^+$ (0, 0) band

We define the gain (G) as $G = I_{\text{total}}/(I_{\text{seed}} + I_{\text{main}})$. I_{seed} is the intensity of the ASE output from the seeder cell in the absence of the pump II beam. I_{main} is the intensity of the ASE output from the main cell in the absence of the pump I beam. I_{total} represents the total output intensity in the presence of both pumps I and II. Allen and Peters developed the theory of ASE and constructed a new approach which allows the effect of an external signal injected at one end of the inverted medium to be studied [11]. When the external signal is weak, the seeder field does not interact with the system.

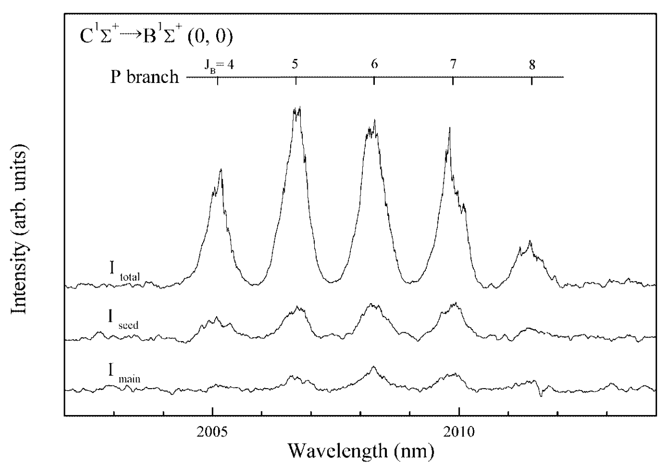

Fig. 2. Emission spectra corresponding to the $C\,^1\Sigma^+ \rightarrow B\,^1\Sigma^+(0,\,0)$ system of CO. The pump laser is fixed near the peak of the rotationally unresolved Q branch of the $C\,^1\Sigma^+ \leftarrow\leftarrow X\,^1\Sigma^+(0,\,0)$ two-photon transition. I_{seed}: intensity of the ASE output from the seeder cell in the absence of the pump II beam. I_{main}: intensity of the ASE output from the main cell in the absence of the pump I beam. I_{total}: total output intensity in the presence of both pumps I and II. CO pressure in the seed and main cells is 5 and 50 Torr, respectively

Above a certain threshold, the injected field is amplified in the medium while the ASE output decreases. In other words, the system is capable of producing ASE and yet is acting as an amplifier at the same time. Experimentally, however, these two contributions to I_{total}, i.e. ASE and amplifier intensities, can not be distinguished. The observable in the present experiment is thereby the sum of these two contributions. The value of G is unity if no amplification occurs.

ASE from the $C\,^1\Sigma^+$ Rydberg state of CO was first observed by Hasegawa and Tsukiyama [12]. Figure 2 displays the effect of the seeder field for the P branch of the $C\,^1\Sigma^+ \rightarrow B\,^1\Sigma^+(0,\,0)$ ASE system with the same vertical scale. The R branch exhibits a similar response. Because the two-photon excitation spectrum corresponding to the $C\,^1\Sigma^+ \leftarrow\leftarrow X\,^1\Sigma^+(0,0)$ system consists of an unresolved Q branch, several rotational levels are populated in the $C\,^1\Sigma^+(v=0)$ manifold simultaneously. The gain is approximately 3. Values of G larger than unity correspond to the role of the main cell as the amplifier, namely, enhanced population transfer from $C\,^1\Sigma^+$ to $B\,^1\Sigma^+$ by the seeder field. The fairly large transition probability between $B\,^1\Sigma^+$ and $X\,^1\Sigma^+$ may generate the phase-matched infra-red radiation driven by PFWM [13]. However, the fact that a similar gain was obtained under the backward configuration as well as the forward configuration strongly suggests a major role of ASE as the seeder field.

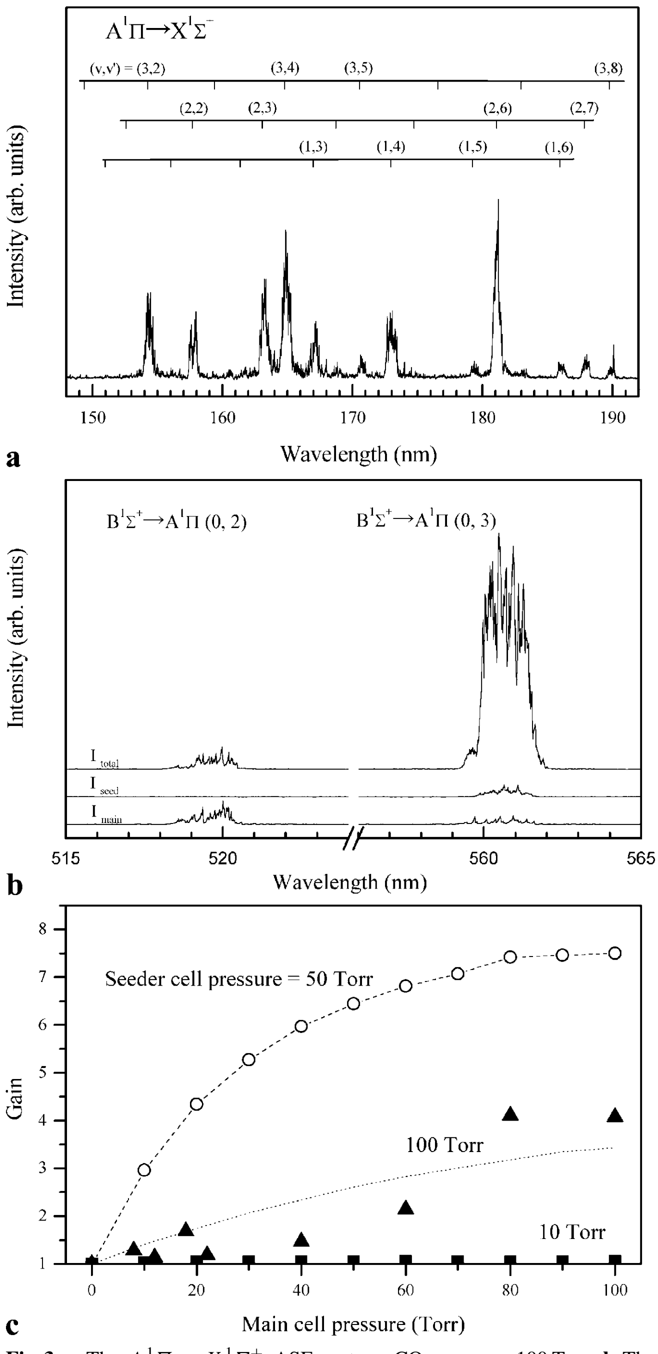

Fig. 3. **a** The $A\,^1\Pi \rightarrow X\,^1\Sigma^+$ ASE system. CO pressure: 100 Torr. **b** The $B\,^1\Sigma^+(v=0) \rightarrow A\,^1\Pi\ (v=2$ and $3)$ ASE transitions. The CO pressure in the seed and main cells is 50 and 100 Torr, respectively. I_{main}, I_{seed} and I_{total} are the same as those in the caption of Fig. 2. **c** The pressure dependence of gain for the $B\,^1\Sigma^+ \rightarrow A\,^1\Pi\,(0,3)$ band. CO pressure: 100 Torr

2.2 Selective enhancement of the $B\,^1\Sigma^+ \rightarrow A\,^1\Pi$ (0, 3) vibronic ASE band

The two-photon-driven ASE from the $B\,^1\Sigma^+$ Rydberg state of CO was studied in detail by Westblom et al. [4]. Because the lower electronic state, $A\,^1\Pi$, is a valence state, the transition intensities are distributed to several rovibronic transitions. ASE occurs mainly on those transitions with the largest Franck–Condon factors, i.e. the $B\,^1\Sigma^+ \rightarrow A\,^1\Pi$ (0, 3) band around 560 nm and (0, 2) around 519 nm. The intensities of the (0, 1) and (0, 4) ASE bands at 480 and 607 nm are less than 1/50 of the strongest (0, 2) band. Figure 3a depicts the cascading ASE bands in the vacuum ultraviolet region, which mainly consist of the vibrational progression from the $A\,^1\Pi$ ($v=1,2$ and 3) states to the vibrationally excited $X\,^1\Sigma^+$ state. No significant emission peaks below 150 nm, namely, the absence of the $A\,^1\Pi$ ($v=1,2$ and 3) $-\,X\,^1\Sigma^+$ ($v''=0$) bands, suggests the negligible contribution of PFWM. We can assume therefore that photons in the visible region are created solely by the ASE decay process. This is consistent with the observation by Westblom et al. that the intensities in the forward and backward visible ASE were approximately equal [4].

We performed selective enhancement of two competing ASE channels. By putting a glass filter (HOYA, O-56) between the seed and main cells in the backward configuration, only 560-nm radiation is introduced into the main cell as seeder field. Without the seeder radiation, the $B\,^1\Sigma^+ \rightarrow A\,^1\Pi\,(0,3)$ as well as the (0, 2) band can be observed, with the latter band being stronger than the former band as shown in the bottom trace in Fig. 3b. The instrumental resolution is not narrow enough to resolve any rotational structures. The 520-nm radiation is blocked by the color filter as shown in the middle trace. With 560-nm seeder radiation, the (0, 3)-band intensity is enhanced by nearly ten times, while no amplification is seen for the (0, 2) band as illustrated in the top trace. When an interference filter transmitting only 520-nm photons was used, we found that the (0, 2) band was amplified by a factor of ~ 4 without enhancement of the (0, 3) band. The higher gain for the weaker ASE band was also observed in a feedback experiment: Westblom et al. reported a pronounced enhancement of the (0, 3) transition relative to the strongest (0, 2) transition when a quartz plate was introduced prior to the cell and aligned so that optical feedback of the ASE beam was achieved [4]. The gain of the $B\,^1\Sigma^+ \rightarrow A\,^1\Pi\,(0, 3)$ band depends strongly on the seeder-cell pressure as depicted in Fig. 3c. The smaller gain at 100 Torr than 50 Torr implies a saturation effect. No detectable seeder radiation is produced at 10 Torr, resulting in no measurable gain.

2.3 Rotationally selective amplification in the $B\,^1\Sigma^+ \rightarrow A\,^1\Pi$ (0, 4) system by the externally injected laser radiation

When two ASE decay channels are competing and the corresponding wavelengths are sufficiently apart, selective enhancement between the two is feasible as mentioned in Sect. 2.2. It is difficult to separate two rotational transitions belonging to the same vibronic band by optical filtering. In general, consequently, it would be practically impossible to amplify a single rotational line by ASE seeding. This difficulty can be solved by injecting the laser radiation instead of ASE. In addition, in case the gain induced by the external laser is sufficiently high, a sensitive probe of the rotationally resolved ASE transitions will be achieved by scanning the seed-laser frequency.

Prior to the laser seed experiment, we measured the polarization character of the 607-nm ASE corresponding to the $B\,^1\Sigma^+ \rightarrow A\,^1\Pi\,(0, 4)$ band. The electric vector of the ASE was found to be strongly polarized parallel to that of the UV pump laser as shown in Fig. 4. Tjossem and Smyth reported that the two-photon $B\,^1\Sigma^+ \leftarrow\leftarrow X\,^1\Sigma^+$ transition proceeds via the nearest resonant intermediate $A\,^1\Pi$ state with some contribution from states with Σ symmetry, such as the $C\,^1\Sigma^+$ state [14]. If we assume the virtual intermediate state of Π^+ and successive excitation by the $\Delta J = 0$ (Q-branch) transitions, the degree of polarization P, $(I_\parallel - I_\perp)/(I_\parallel + I_\perp)$ for the Q-branch emission starting at $X^1\Sigma^+$ ($J'' = 0$) is evaluated to be $+0.64$ [15]. Here $I_\parallel$ and $I_\perp$ denote the intensities of emission whose polarization vector is parallel and perpendicular to the linearly polarized pump-laser beam, respectively. The polarization of ASE is preferentially parallel to the pump-laser beam. On the other hand, for the P-branch emission following the same excitation path, the value of P is -0.36 [15]; the ASE is preferentially polarized perpendicular to the pump laser. The measured value of P, ~ 0.55, is well explained by the predominance of the Q branch in the emission. Both Q and (P, R) lines are allowed for the $B\,^1\Sigma^+ \rightarrow A\,^1\Pi$ system. The Hönl–London factors predict considerable P- and R-branch intensities, for example, $R(3) : Q(4) : P(5) = 0.75 : 2.25 : 1.50$. The intensity pattern of ASE, however, differs from that of spontaneous emission; the stronger transitions acquire more gain in the amplification process, resulting in a more accentuated contrast between stronger and weaker transitions than laser-induced fluorescence [4].

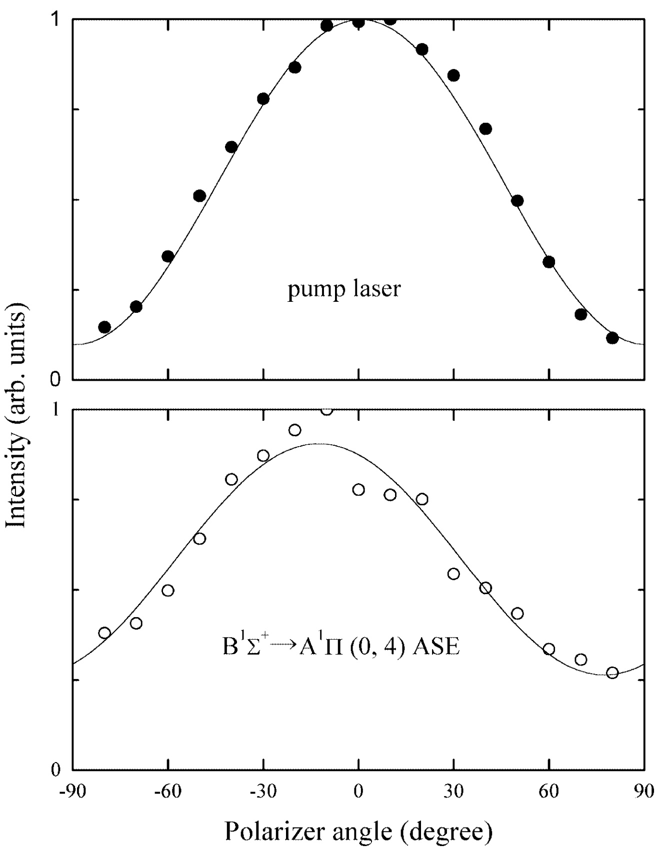

Fig. 4. Polarization properties of the pump laser *(upper part)* and ASE corresponding to the $B\,^1\Sigma^+ \rightarrow A\,^1\Pi\,(0, 4)$ band *(lower part)*. CO pressure: 100 Torr

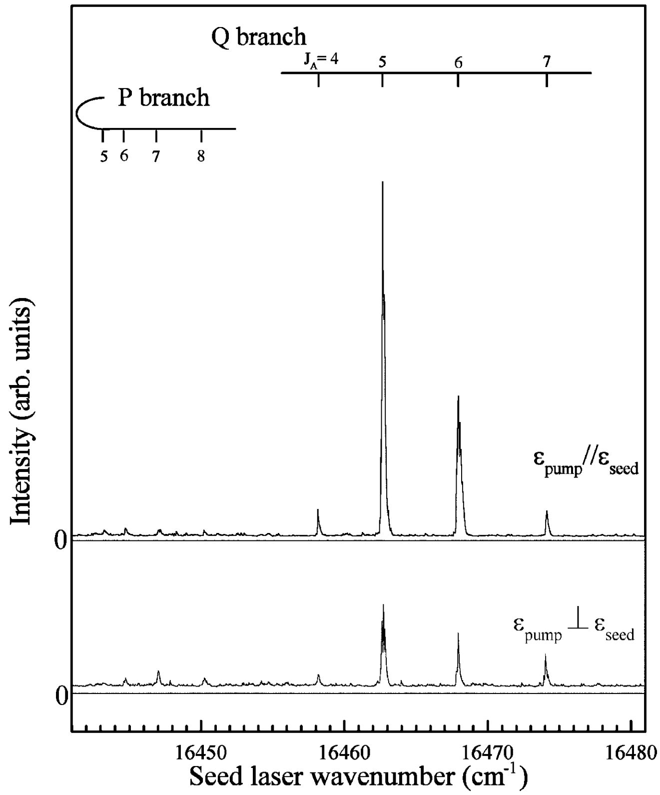

Fig. 5. Total output intensity as a function of the seed-laser wavenumber in the spectral region corresponding to the $B\,^1\Sigma^+ \rightarrow A\,^1\Pi$ (0, 4) band. The pump laser is fixed near the peak of the rotationally unresolved Q branch of the $B\,^1\Sigma^+ \leftarrow\leftarrow X\,^1\Sigma^+(0, 0)$ two-photon transition. Seed-laser energy: < 50 nJ/pulse. CO pressure: 100 Torr

Figure 5 corresponds to the gain spectra when the seed-laser frequency was scanned around the $B\,^1\Sigma^+ \rightarrow A\,^1\Pi\,(0, 4)$ band. The spectrum is taken with a collinear-beam configuration. The output is detected in the forward direction after the elimination of the UV pump radiation. A similar spectral trace is obtained with the counter-propagating beam configuration. The pump laser is fixed on the peak of the rotationally unresolved Q branch of the $B\,^1\Sigma^+ \leftarrow\leftarrow X\,^1\Sigma^+(0,0)$ excitation. Several rotational levels around $J = 5$ are thereby populated in the $B\,^1\Sigma^+$ $(v = 0)$ manifold simultaneously. The polarizations of the pump and seed lasers are set parallel (upper trace) and perpendicular (lower trace). The most prominent feature is the rotational selectivity effected by the external laser radiation. It should also be noted that the gain of the Q lines is considerably reduced under the perpendicular polarization. This marked polarization dependence suggests that the inverted medium is acting as an amplifier of the external signal while maintaining the polarization anisotropy driven by the two-photon excitation.

Two factors contribute to the background level of the spectral trace in Fig. 5, namely, the ASE and the seed laser. The reduction of the pump- and seed-laser power to the minimum level is essential for a good signal-to-noise ratio. In particular, it is the key to a flat baseline to reduce the pump-laser power to the level at which ASE is almost undetectable. Because the gain saturates for the higher seeder energies as stated in Sect. 2.2, there is inherently no need of high seed-laser power. The line width of the Q lines in Fig. 5 is $\sim 0.2\,\mathrm{cm}^{-1}$ at $\sim 50\,\mathrm{nJ/pulse}$ of the seed laser. The width increases with input powers, reaching as large as $0.6\,\mathrm{cm}^{-1}$ at $3\,\mu\mathrm{J/pulse}$. At the same time, the ASE intensity of the (0, 2) band decreases by $\sim 20\%$ when the stronger seed laser resonant to the $Q(4)$ line of the (0, 4) band is injected, indicating that a part of the population transfer from $B\,^1\Sigma^+$ $(v = 0)$ to $A\,^1\Pi$ $(v = 2)$ is distributed to $A\,^1\Pi$ $(v = 4)$.

3 Summary

The present paper describes seeded enhancement of the population transfer involving the $A\,^1\Pi$, $B\,^1\Sigma^+$ and $C\,^1\Sigma^+$ states of CO.

1. ASE traveling collinearly with the pump-laser beam is amplified in the second inverted medium. The gain for the $C\,^1\Sigma^+ \rightarrow B\,^1\Sigma^+$ inter-Rydberg system is ~ 3. For the $B\,^1\Sigma^+ \rightarrow A\,^1\Pi\,(0, v)$ transitions, simple optical filtering leads to manipulation of the competing ASE relaxation channels; the gain for the $B\,^1\Sigma^+ \rightarrow A\,^1\Pi\,(0,3)$ band is as large as 10.
2. We demonstrated that the single rotational transition in the $B\,^1\Sigma^+ \rightarrow A\,^1\Pi\,(0,4)$ band was selectively amplified by injection of the laser radiation. By reducing the ASE output, a gain close to 100 was obtained.

Finally it is advantageous to mention a few spectroscopic applications of the laser-seeded amplification method. Two-photon ASE was extensively used in a variety of environments such as flames and gas discharges where laser-induced fluorescence is often hampered due to the strong background light. In general, one may not expect high ASE signal intensities because of the low concentrations of the reactive species. The laser injection, having a pronounced effect under the low ASE output, would bear a part in increasing detection efficiency. The wavelengths required for the downward transitions of important atoms, 656 nm for H [16], 870 nm for N [17] and 845 nm for O [18], can be covered by the fundamental output from the conventional pulsed dye laser.

The highly vibrationally excited levels in the electronic ground state of polyatomic molecules are the subjects of both experimental and theoretical research, because mutual interactions among these levels give rise to unusual vibronic structures. Stimulated-emission pumping (SEP) has been known as a unique spectroscopic technique for probing these levels which are forbidden from the $v'' = 0$ level. The small Franck–Condon factors between the laser-prepared level and high vibrational levels cause the higher threshold inversion density for ASE. These circumstances again seem to be appropriate for the laser injection. Furthermore, in most cases, the SEP transitions have been detected by reduction of the population in the upper level, i.e. the dip of fluorescence intensity [19]: a requisite for SEP is a large quantum yield of the upper level. On the other hand, ASE can be observed from weakly predissociative levels which are undetectable in ordinary fluorescence spectra [20], indicating that the inverted medium with the predissociative upper level can operate as an amplifier for the external signals [6]. We believe therefore that the current technique, as complementary to the fluorescence-dip scheme, may be extended to a number of important polyatomic molecules including SO_2 and NO_2, whose predissociative lifetimes of the electronically excited states fall in the subnanosecond time scale.

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