C02-Doped Diamond: A Potential Solid-State CO_2 Laser Material?

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ABSTRACT

The recent identification of solid-phase CO_2 in a matrix of natural diamond suggests a possible candidate for a solid-state CO_2 laser medium possessing near ideal characteristics.

1. Introduction

Since very early in its history the intrinsic properties of the CO_2 laser mechanism have been conducive to the realization of oscillators in the 9-11 μm wavelength region with exceptional spectral purity and stability [1]. Such sources at-e very important as probes for high-resolution spectroscopy, or as reference (local) oscillators in coherent laser radar (1 idar) applications. However, to attain such frequency performance it is often necessary to resort to extraordinary engineering measures [I]. Ultimately, the limiting factors controlling the frequency stability of such systems arc primarily environment al in nature (e.g. extraneous vibration, microscale turbulence within the gaseous lasing medium, etc.).

'l'he purpose of this letter is to introduce a novel concept for a solid-state CO_2 laser medium which, by eschewing the gas-phase approach, may offer prospects for a compact, robust 9-11 pm coherent source, coupled with the potential] y superior frequency stability characteristics afforded by monolithic solid-state construction [2]. This suggestion has been prompted by the recent description of a particularly interesting natural diamond specimen [3]. 'l-he sample in question is noteworthy because it contains high concentrations of C02 trapped within the diamond matrix, apparently in the form of solid-phase submicroscopic inclusions. Infrared absorption spectra indicate several features which correlate with the presence of CO_2 molecules, but which are shifted in frequency to a degree commensurate with a formation pressure ~5 GPa[3], close to the lower limit of the pressure range for diamond stability. In

particular, there is a very strong absorption feature which corresponds to excitation of the $CO_2(00°1)$ vibrational state (i.e. the CO_2 upper laser level). This feature occurs close to a local minimum in the much broader two-phonon stimulation regime characteristic of diamond (as illustrated in Fig.1), and is therefore relatively uninfluenced by competition with two-phonon processes.

11, Energy level structure

Starling from the absolute frequency measurements given in Ref.3, it is straightforward to infer the lowest lying C02 vibrational state energies. There suiting energy level diagram is reconstructed in Fig. 2, which also depicts the $[00°1 - (10"0,02"0)_{1,1}]$ regular band laser transitions. We may readily note that because. of the differential pressure shifts suffered by each of the levels shown, the resulting nominal laser transition wavelengths are predicted to be significantly less than those obtained from a conventional gas-phase CO_2 laser. Table 1 compares the salient vibrational state energies and inferred band edge lasing wavelengths for these two benchmark cases.

The volumetric number 'density of CO_2 molecules in the diamond matrix was estimated in Ref. 3 to be ~0.048 mol cm^{-3}. This is more than a thousand-fold the molecular concentration of pure gaseous C02 at ambient temperature and pressure (-4 x 10-5 mol cm-3), so that it may be feasible to induce a population inversion in this material sufficient to overcome even the

strong re-absorption of resultant laser radiation by the broad absorption band evident at 900 - 1300 cm^{-1} in Fig. 1. This latter feature, which attains a peak absorption coefficient of about 12 cm^{-1}, essentially tracks the one-phonon spectrum of diamond, which has its cutoff at around 1332 cm^{-1}. In a perfect diamond lattice this feature would be optically inert, I lowever, the presence of lattice defects or substitutional impurities (in this case nitrogen) results in a finite dipole moment, thus permitting phonon/photon coupling [4]. This restriction (lots not apply in the case of interactions involving two or more phonons, in which second-order dipoles may be created [5]. Nitrogen-activated one-phonon infrared absorption is a defining characteristic of so-called type 1 diamonds; it is worth noting here that this absorption feature would be absent in a type 11 (nitrogen-deplete(l) diamond specimen, for which the bulk absorption coefficient drops to 0.035 cm^{-1} at 10.6 pm [6].

It therefore follows that type II diamond substrates would exhibit negligable re-absorption losses at the inferred laser wavelengths and should be preferred as a solid-state CO_2 laser medium.

111. Pumping st rat egics and relaxation mechanisms

One of the most fundamental factors which will govern whether a truly compact, rugged solid-state C02 laser device proves feasible will be the availability of suitable optical pump sources. The most commonplace approach in the solid-state laser arena, broadband incoherent pumping

by means of flashlamps, cannot be countenanced here because these sources emit at much shorter wavelengths than the mid-infrared region which incorporates the CO_2 pump bands. The resonant pumping alternative is similarly beset by a relative dearth of suitably powerful laser sources in the required spectral region. However, for the purposes of a laboratory testbed for the investigation of this unfamiliar material, there do exist potential coherent sources worthy of consideration.

The $CO_2(00^o1$) upper laser level excitation feature apparent in Fig. 1 indicates a peak absorption coefficient of 28 cm^{-1} with an associated linewidth of -40 cm^{-1} FWHM. This is approximate] y twice the equivalent linewidth observed for this transition in pure solid CO_2 [7], presumably due to lattice broadening by the diamond two-phonon band. Ideally, it would be desirable to resonantly pump this transition with a diode laser operating around 4.21 µm. Such devices do exist in the form of tunable lead-salt diodes, but these must be operated at cryogenic temperatures with high controllability and even then are capable of delivering only ~10 mW multimode at best [8]. From the device point of view, therefore, these lasers are hardly more convenient a pump source than more conventional laser systems, which at least offer the possibility of high energy output and thus can be applied in a research context to drive the solid C02 medium into saturation to fully explore the performance envelope of this material, Extensive further development of these systems will be necessary before they can be realistically considered for the present application.

in gaseous CO_2 systems the $00°1$ state has been optically pumped using the $4P(6)[2\rightarrow 1]$ HBr laser line at 4.23 μm [9]. This pump frequency is offset by $\Delta v = -12$ cm^{-1} relative to the solid CO_2 absorption peak due to the v_3 pressure shift, However, the highly broadened nature of the solid $CO_2(00°1)$ state should nevertheless provide sufficient overlap with this line, although more optimal transfer efficiency could be achieved by pumping with the neighboring $4P(5)$ line near 4,20 μm ($\Delta v = +7$ cm^{-1}).

An alternative approach in this regard would be to pump the $CO_2(10°1,02°1)_{I,II}$ combination band with an 1 IF laser source [11]. Vibrational relaxation of this level then results in population of the $00°1$ upper laser level inter alia. in this way, high-pressure (up to 10 atm) CO_2 lasers have been optically pumped with remarkably high quantum efficiencies (-1496), apparently limited by gas dynamical effects [11], Although they are not shown here in Fig. 2, the authors of Ref. 3 did in fact report significant absorption which could be ascribed to excitation of the $CO_2(10°1,02°1)_{I,II}$ states appearing at 3752 cm^{-1} and 3620 cm^{-1}, corresponding to 2.66 pm and 2.76 μm, respectively. These wave.lengths are considerably shifted from the equivalent gas-phase values, but nevertheless remain accessible using the 2.67 μm 1'(5)[1→0] and 2.76 μm 1'(4) [2-)1] HF laser lines.

Ab initio estimation of the feasibility of laser action in the diamond sample described above is severely hampered by a lack of knowledge concerning the critical transition rate constants

for high-pressure solid-phase CO_2. However, one key decay process has been investigated in some detail, namely the decay of the Fermi doublet (10°0,0200)J,lp In high-pressure solid CO_2 the Fermi resonance is somewhat weaker than it is in gaseous CO_2 because the pressure dependences of the v_1 and $2v_2$ states are of opposing sense [12,13]0 Hence the resultant modified bound states more widely separated than in the gas phase. The Fermi diad in solid CO_2 relaxes by phonon excitation with a lifetime (at 4.4 GPa and 300K) of ~8ps [14,15], which is clearly much shorter than the microsecond-scale collisional deactivation lifetimes observed in gaseous CO_2 laser media. '1'here would appear to be an additional relaxation route via near-resonant excitation of phonons in the diamond lattice (note that the V_1:$2v_2$ Fermi diad is close in energy to the peak one-phonon density of states of diamond [10], as illustrated in Fig. 2), although the coupling efficiency of this process may be lowered by the fact that the solid $CO2$ is not present as a substitutional dopant, but rather as microcrystallite inclusions. Nevertheless, we may expect excess heat dissipation to be greatly facilitated by the extremely high thermal conductivity of diamond [16].

IV. Conclusion

The recent discovery of a natural diamond specimen containing solid-phase $CO2$ formed at high pressure suggests, it is argued, a means for fabricating a solid-state CO_2 laser device for the generation of spectrally robust radiation' in the 8-10 pm region. Although insufficient measurement data currently exist that would support theoretical confirmation of such a

plausibility, it should be possible to test this assertion directly with available technology in a laboratory setting.

However, successful operation of such a device is no guarantee of widespread practicality, which would be contingent on a ready supply of CO2-eloped type II diamond material - CO_2:C(II) - of sufficient size and optical quality. The diamond sample described in Ref. 3 was a "found" specimen whose site of origin could not be confirmed; it is therefore unknown whether or not the CO_2-bearing diamond (while certainly rare) is unique, Development of such devices beyond the state of "laboratory curiosity" would seem to depend on the ease with which artificial CO~,-bearing diamond specimens may be grown. Growth of synthetic gem-quality type II diamonds has been demonstrated up to sizes of ~6mm [17], although a means for introducing controlled amounts of CO_2 into the resulting crystal would also be necessary. High-quality diamond has also been synthesized using chemical vapor deposition from CO_2/mixed gas systems [18,19], which by introducing excess CO2 might conceivabl y provide a mechanism for creating a CO_2-enriched diamond substrate.

Assignment		Gaseous CO_2 (≤ 0.1 MPa)	Solid CO_2 (~ 5 GPa)
v , $(10^\circ 0)$ [cm^{-1}]		1388.3	1376
v_2 $(01^1 0)$ [cm^{-1}]		667.3	650
v_3 $(00^\circ 1)$ [cm^{-1}]		2349.3	*2376*
$2v_2$ $(02^\circ 0)$ [cm-']		1285.5	1244
$00^\circ 1$ - $(10^{\circ\circ}0, 02^\circ 0)$,	[pm] I	10.4	10.0
$00^\circ 1$- $(1\ 0^\circ 0, 02^\circ 0)_{II}$	[µm] I	9.4	8.8

J'able! **1.** Spectroscopic assignments and state energies of the low-lying molecular vibrational

levels involved in CO_2 laser action for gaseous and solid-state CO_2 at 5 GPa [3].

Also shown are the inferred nominal band edge laser wavelengths for both cases.

Figure Captions

Figure 1. Infrared absorption spectrum of the C02-bearing diamond (upper trace) compared with that of a type 11 diamond (lower trace). The systematic vertical offset is due to the inclusion of reflection losses ($\approx$ 2.9% [6]; equivalent absorbance $=$ *0.15)* at the parallel octahedral facets of the C02-bearing diamond, whereas the lower spectrum derives from bulk absorption losses only. (Adapted from Ref. 3.)

Figure 2. low-lying CO_2 vibrational state diagram of the C02-bearing diamond, showing the regular band laser transitions, Also shown is the one-phonon density of states for diamond [10].

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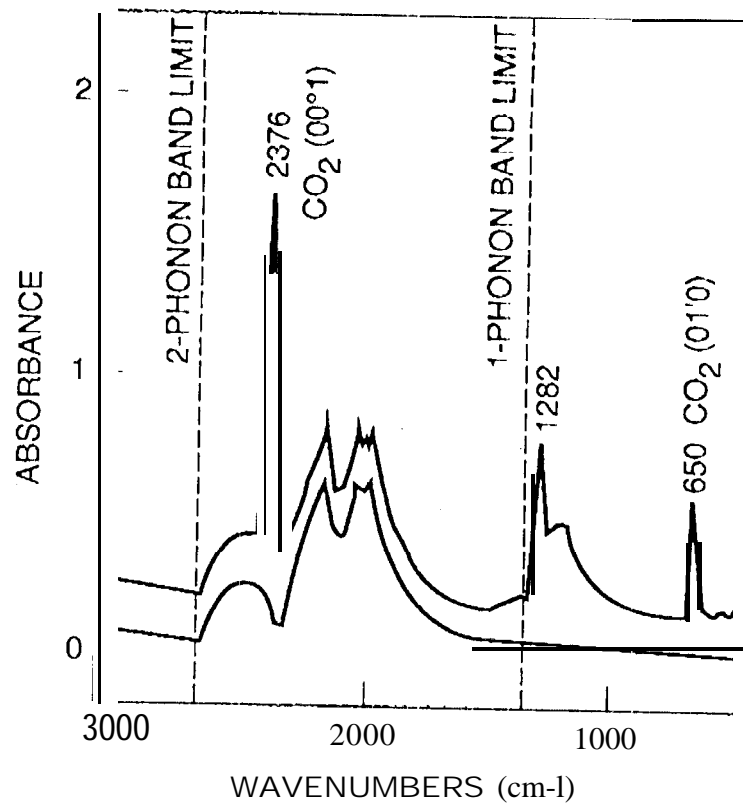
Figure 1. Infrared absorption spectrum of the CO2-bearing diamond (upper trace) compared with that of a type II diamond (lower trace), The systematic vertical offset is due to the inclusion of reflection losses ($\approx$ 29% [6]; equivalent absorbance = O. 15) at the parallel octahedral facets of the CO2-bearing diamond, whereas the lower spectrum derives from bulk absorption losses only. (Adapted from Ref. 3.)
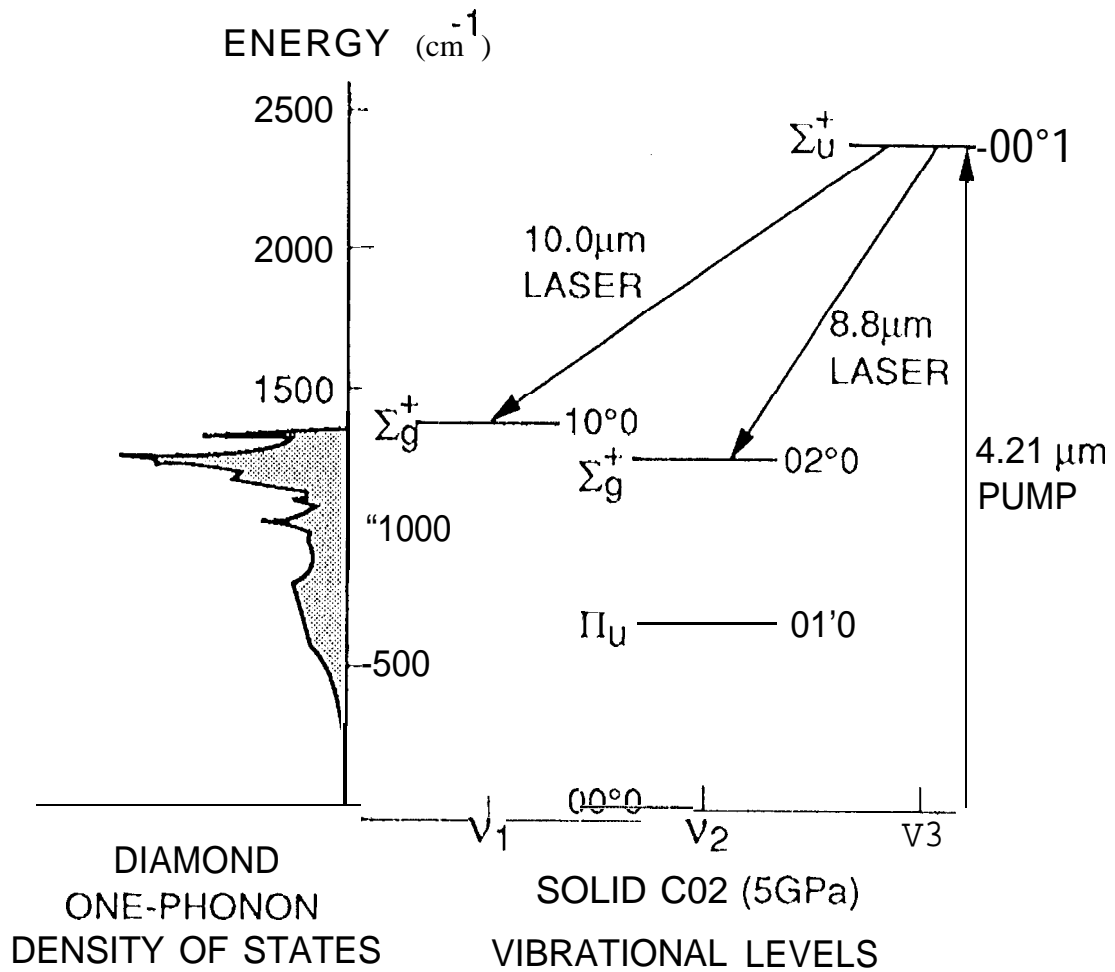
ENERGY (cm^{-1})

2500

2000

Σ_u^+ —————— -00°1

1500

10.0μm
LASER

8.8μm
LASER

4.21 μm
PUMP

Σ_g^+ ——— 10°0

Σ_g^+ ——— 02°0

"1000

Π_u ——————— 01'0

-500

00°0

V_1 V_2 V_3

DIAMOND
ONE-PHONON
DENSITY OF STATES

SOLID C02 (5GPa)
VIBRATIONAL LEVELS

Figure 2. Low-lying C02 vibrational state diagram of the C02,-bearing diamond, showing the regular band laser transitions. Also shown is the one-phonon density of states for diamond [10].