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Infrared Stimulated Emission of N₂O Trapped in Argon Matrices: Comparison with O₃ and CO₂

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N₂O molecules dispersed in argon matrices, at a concentration of 1/2000, are excited to their $\nu_3 = 1$ vibrational level by a laser pulse at 2218 cm⁻¹. Stimulated emission of the $\nu_3 - \nu_1$ transition is observed when the inversion population is large enough, i.e., when the energy absorbed from the laser pulse exceeds a threshold value. From the measured energy threshold, we derive a "loss coefficient" for the cavity-like polycrystalline excited argon sample (a disk about 200 μ m thick and 1.5 mm in diameter). Using this loss coefficient, on the basis of molecular spectroscopic parameters, we predict the inversion population threshold for stimulated emission on other N₂O transitions, and for other molecules in identical matrices. The prediction is remarkably consistent with our previous observations on O₃ and ¹³CO₂ for which the emitting level ($\nu_3 = 2$ and $\nu_2 = 3$ or 2, respectively) is populated via intramolecular nonradiative transfers.

I. Introduction

Recently, we reported¹ stimulated emission of the $2\nu_3 \rightarrow \nu_3$ transition of ozone trapped in low-temperature matrices, when excited by a laser pulse around 5 μ m to the $\nu_1 + \nu_3$ level, 60 cm⁻¹ above $2\nu_3$. Under very similar conditions, we have observed² stimulated cascades in the ν_2 manifold of ¹³C¹⁶O₂ in argon matrices after intramolecular transfer ($\Delta E \approx 400$ cm⁻¹) from the excited ν_3 mode. In the present paper, we describe identical experiments, performed on ¹⁴N₂¹⁶O, which yield a new result. Emission now comes from the excited level ν_3 of the molecule, so that threshold measurements, involving laser energy and absorption by the sample, give direct information concerning the onset of the stimulated process. We may then compare the behavior of three triatomic molecules in a similar environment, excited at 5 μ m with similar laser fluences. The discussion is focused on the molecular parameters.

II. Experimental Section

a. Setup. Details about the apparatus can be found in refs 1 and 2. We just recall here some characteristics of the experiment. Solid argon samples, about 200 μ m thick, are obtained by deposition of a gaseous mixture onto a gold plated copper mirror held at 18 K and then cooled to 5 K. The concentration, 1/2000 in the cases of ¹³CO₂ and N₂O, has been chosen to avoid the formation of dimers. It was 1/200 for O₃. The laser, focused on an area of 2×10^{-2} to 3×10^{-2} cm², impinges normally on the sample mirror. The detection angle, 45°, can only be varied by $\pm 8^\circ$. The stimulated light is emitted with low directionality out of the flat disk of the active medium. Scattering inside the polycrystalline sample, which increases the optical path length, is invoked to explain the efficiency of the process and the absence of directionality.¹

b. Absorption Spectroscopy. In a first step, absorption spectra of N₂O in argon have been recorded using a FTIR Bruker

IFS 113 V spectrometer (resolution = 0.03 cm⁻¹). In contrast with CO₂, which is trapped in two sites of different stabilities,³ only one trapping site is observed, in agreement with literature data.^{4,5} Calculations in progress, based on the model⁶ elaborated for O₃, show that this site is a double substitutional one, similar to the one termed "unstable" in the CO₂ case.⁷

Such a geometry explains the observed lifting of the ν_2 mode degeneracy (Figure 1); under the present deposition conditions, the ν_2 doublet exhibits line widths (fwhm) of 0.09 and 0.075 cm⁻¹, whereas that of ν_3 is 0.14 cm⁻¹. These data concern the unannealed samples which are studied in the present emission experiments.

Figure 1 shows that the third component, observed between the two doublet lines, does not belong to N₂O monomers as it grows irreversibly upon annealing.

c. Characteristics of the Observed Emission. Upon excitation at 5 μ m, as for O₃ and ¹³CO₂, a strong and short emission is observed for N₂O. Figure 2 shows an excitation spectrum of this emission (Figure 2C) compared to the transmission of the laser through the sample (Figure 2B) and to a FTIR absorption spectrum (Figure 2A) in the ν_3 region. The spectrum shown in Figure 2B will be used later to estimate the number of absorbed photons. It has been obtained by measuring the laser intensity after its reflection at 45° on the sample holder mirror, which increases the absorption length by a factor of $\sqrt{2}$ when compared to emission experiments. However, the thickness of this sample is only ~ 90 μ m so that the observed absorption percentage provides a lower limit for 180 μ m samples illuminated at zero incidence. Moreover, we have considered the possible saturation of the ν_3 transition, especially through the irradiated first layers; effectively, the transmission slightly increases (from 18% to 22%) when increasing the laser fluence by a factor of 2, as can be seen on the expanded part B' of Figure 2B. The maximum of the emission nicely correlates with the absorption one. However, the excitation spectrum is narrower.

The spectral range of the emission is studied by means of filters. N₂O being an unsymmetrical molecule, many transitions

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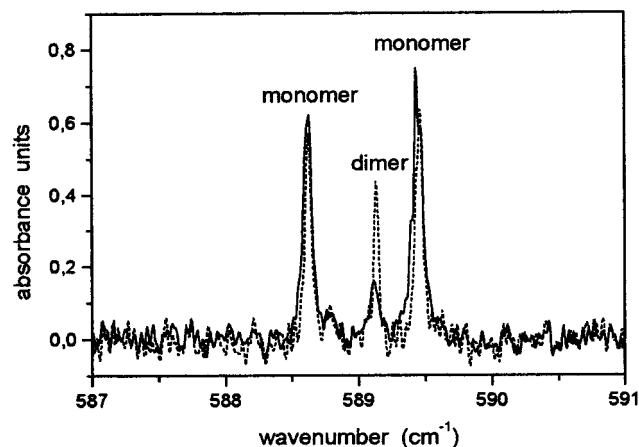


Figure 1. Spectroscopic study of $^{14}\text{N}_2^{16}\text{O}$ (ν_2 mode) in solid argon ($M/R = 2000$, $T = 5$ K, thickness ~ 160 μm , resolution = 0.03 cm^{-1}): (—) after deposition at $T = 18$ K; (---) after annealing at $T \approx 30$ K.

are allowed between vibrational levels below ν_3 . These transitions are schematically drawn on Figure 3 and some of their vibrational transition moments, taken from gas-phase literature data,^{8–11} are recalled. Using short wave cut off filters from Oriol ($\lambda_c = 8$ and 13.7 μm), we can assign the emission to the $\nu_3-\nu_1$ and/or $\nu_3-2\nu_2$ transition(s) at 10 μm . We carefully checked that the observed signal is not changed when replacing the 8 μm filter by a 5.7 μm one; this clearly rules out the ν_1 and $(\nu_1+\nu_2)-\nu_2$ transitions at 7.75 μm .

The dependence of the signal amplitude upon laser energy is presented on Figure 4 for three different experiments, concerning three samples of equal concentration ($1/2000$) but different thickness. In each case, an energy threshold is clearly found under which no signal can be detected. Above the threshold, the dependence upon laser energy seems linear in the studied range. As two MCT detectors with different sensitivity have been used, no information can be extracted from the vertical scale. The thresholds however can be compared; they obviously decrease when the thickness increases. Similar observations^{1,2} were made in the case of O_3 and CO_2 .

Considering the time response of the detection system (the fastest is a MCT detector from Belov-Technology, 38 ns rise time, ~ 300 ns decay time¹), no short-time measurements can be performed. Within experimental error, the signal reproduces the recorded laser pulse. This is not surprising since the emission directly starts from the level excited by the 5 ns laser pulse. Moreover, the emission being stimulated, its temporal behavior is not related to the vibrational lifetime of the ν_3 level.

We do not observe any long-lived weak-amplitude fluorescence, following the presently described short emission; this is obviously due to the limited dynamics of the detection.

III. Discussion

Except for the spectral range, the emission coming from N_2O , $^{13}\text{CO}_2$, and O_3 have very similar characteristics, in particular the existence of an energy threshold. Above the threshold, photons, spontaneously emitted on a given transition, are amplified by stimulated emission on their passage through the sample, thanks to the population inversion. This phenomenon is usually called amplified spontaneous emission (ASE).¹² We compare, at a semiquantitative level, the conditions for the onset of the stimulated process on different N_2O transitions, and on $^{13}\text{CO}_2$ and O_3 ones, considering only similar samples (concentration $\sim 1/2000$, thickness ~ 200 μm).

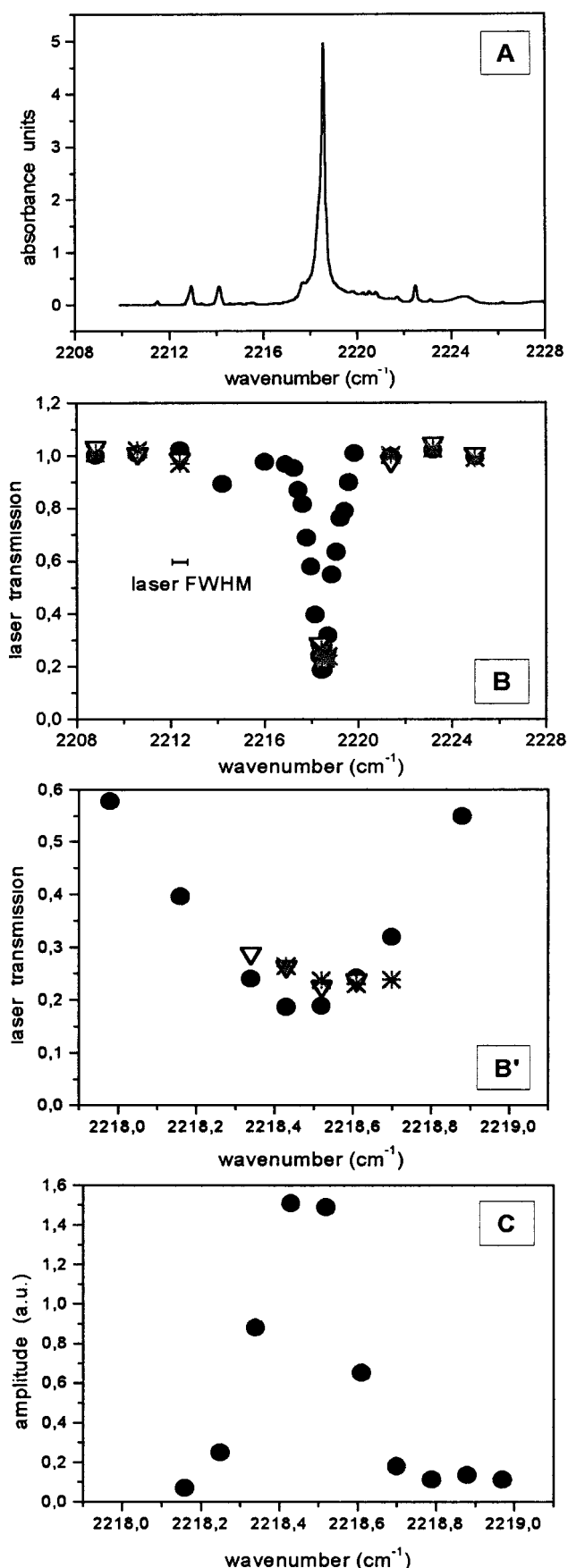


Figure 2. Absorption and excitation spectra of $^{14}\text{N}_2^{16}\text{O}$ in solid argon ($M/R = 2000$, thickness ≈ 90 μm , $T = 5$ K): (A) FTIR absorption spectrum in the ν_3 region, resolution = 0.1 cm^{-1} ; (B) transmission of the laser pulse through the sample after reflection on the sample holder mirror at incidence 45° ; (B') zoom of Figure 2B; (C) excitation spectrum of the 16 μm emission.

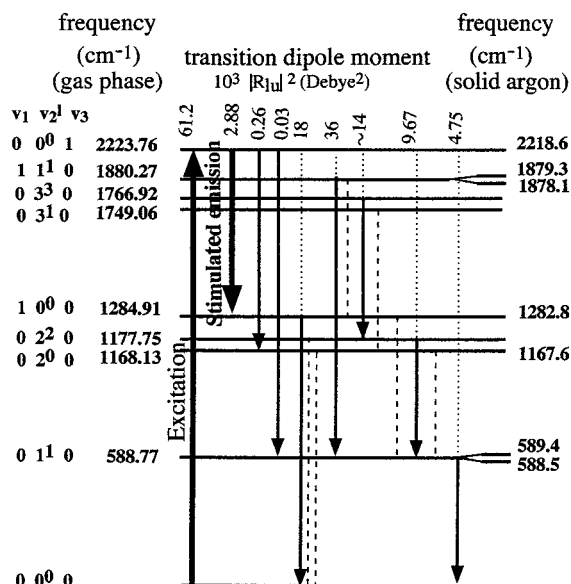


Figure 3. Vibrational energy levels of $^{14}\text{N}_2^{16}\text{O}$ in solid argon up to 2218 cm^{-1} . Most probable transitions are shown by a full arrow, and their gas-phase transition dipole moments are given (refs 8–11). Other transitions are only recalled by dashed lines.

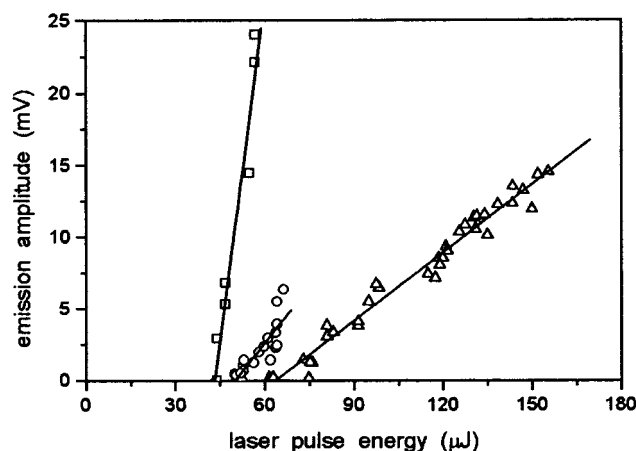


Figure 4. Dependence of the emission amplitude upon the laser pulse energy; existence of a threshold. Sample thickness: (□) $260\text{ }\mu\text{m}$; (○) $180\text{ }\mu\text{m}$; (△) $90\text{ }\mu\text{m}$.

The cross section for stimulated emission, σ_{ul} , between the upper level “u” and the lower level “l”, for Gaussian lines, is expressed as

$$\sigma_{ul} = \frac{c^2 A_{ul}}{8\pi \nu_{lu}^2 n^2 \gamma_{lu}} = \frac{8\pi^3 \nu_{lu}}{3hc \gamma_{lu}} |R_{lu}|^2 \frac{1}{n} \left(\frac{n^2 + 2}{3} \right)^2 \quad (1)$$

where R_{lu} is the matrix element of the dipole moment, related to Einstein’s coefficient A_{ul} , ν_{lu} and γ_{lu} are the wavenumber and the width at half-maximum of the transition, and n is the refractive index of the matrix. For argon matrices with $n = 1.27$, one gets

$$\sigma_{ul} = 4.74 \times 10^{-19} \frac{\nu_{lu}}{\gamma_{lu}} |R_{lu}|^2 \quad (2)$$

if R_{lu} is expressed in Debye unit.

Table 1 assembles the values of $|R_{lu}|^2$, ν_{lu} , and γ_{lu} which will be used to calculate σ_{ul} from formula 2.

(i) The gas-phase values of $|R_{lu}|^2$ are taken from the literature.^{8–11,13–15} For N_2O , it was checked¹⁶ that the integrated intensity ratio $I(\nu_2)/I(\nu_3)$ is consistent with the gas-phase value of $|R_{02}|^2/|R_{03}|^2$. Surprisingly, in the $^{13}\text{CO}_2$ case, the intensity ratio seems larger by a factor of 2 in the double site, compared to the single one. Either this is a real but unexplained effect and we have to increase $|R_{02}|^2$ by a factor of 2 (Table 1), or there is an artifact in the intensity measurement of the ν_3 line for thin samples ($\sim 2\text{ }\mu\text{m}$ thick), in which case the relative abundance of the two sites should be changed. In the ν_2 region, 42% of the absorption is due to the double site, 46% to the single one, and 12% probably to a dimer. The corresponding values in the ν_3 region are 25%, 65%, and 10% respectively.

(ii) The values of ν_{lu} are derived whenever possible from the matrix position of the u and l levels, obtained from fundamental absorptions; otherwise, gas-phase values are retained.

(iii) For γ_{lu} , as the width of hot bands is not measurable in absorption at the matrix temperature, we tentatively use that of the corresponding fundamental. For combination bands such as $\nu_3 - \nu_1$ or $\nu_3 - 2\nu_2$, we use that of ν_3 .

We believe that these approximations are reasonable, if only orders of magnitude values are needed.

Absorbed energies, measured in the present study and described in section IIc, can be converted into initial population inversion, ΔN , which we suppose roughly homogeneous throughout the sample, because of the laser reflection on the sample holder mirror. Assuming distributed losses, α_L , the net gain G can be written as

$$G = \sigma_{ul} \Delta N - \alpha_L \quad (3)$$

so that the threshold condition for amplification is given by

$$\sigma_{ul} \Delta N_T = \alpha_L \quad (4)$$

Following Apkarian,¹⁷ who first pointed out the importance of stimulated processes in the vibrational relaxation of matrix trapped molecules and described the onset of ASE in such a medium, α_L can be interpreted as the reciprocal of the mean distance from the center of the illuminated disk to its boundaries, about 20 cm^{-1} in the present case.

Using the present threshold and transmission measurements ($50\text{ }\mu\text{J}$ pulse, absorption $> 82\%$, cf. section IIc), one gets a lower limit, $\Delta N_T > 0.28 \times 10^{19}\text{ molecules cm}^{-3}$.

We then derive $\alpha_L = \sigma_{ul} \Delta N_T > 26\text{ cm}^{-1}$, a coefficient which depends only on the characteristics of the matrix, not of its guest.

This value is fairly consistent with the geometrical coefficient proposed by Apkarian but, somewhat surprisingly, it leaves no place in the interpretation for optical scattering which was invoked to explain the absence of directionality of the emission.¹ Nevertheless, we will use this value to predict lower limits ΔN_T for the initial population inversion densities in the case of various other transitions. The results are presented in Table 1. The ratio of ΔN_T to the density of molecules (N_0 , cm^{-3}) is also included since it can be considered as a test of the feasibility of an ASE experiment. Whatever the experimental conditions, saturation of the absorption prohibits a $\Delta N_T/N_0$ value exceeding 50%.

Table 1 can now be used to check the consistency of our different experiments.

a. Other N_2O Transitions. First, at $10\text{ }\mu\text{m}$, ASE on the $\nu_3 - 2\nu_2$ transition is clearly ruled out, leaving $\nu_3 - \nu_1$ as the only transition responsible for the presently observed emission.

Second, we would predict ASE to be easier at 7.75 and $17\text{ }\mu\text{m}$, but this would imply an energy redistribution from the ν_3 level toward numerous levels. Increasing the absorbed energy

TABLE 1: Estimation of the Minimum Population Inversion ΔN_T Necessary for Stimulated Emission in a 180 μm Thick Argon Sample ($\Delta N_T/N_0$ Cannot Exceed 50%)

	(A) N ₂ O (Ar/N ₂ O = 2000)						(B) O ₃ (Ar/O ₃ = 200)			(C) CO ₂ (Ar/CO ₂ = 2000)					
	10 μm		7.75 μm		17 μm		10 μm		10 μm		16 μm		16 μm		
	$\nu_3-\nu_1$	$\nu_3-2\nu_2$	$\nu_1+\nu_2-\nu_2$	$3\nu_2^1-2\nu_2^0$	$3\nu_2^1-2\nu_2^2$	$2\nu_2^0-\nu_2^1$	$2\nu_3-\nu_3$		$\nu_3-\nu_1$	$\nu_3-2\nu_2$	$3\nu_2^1-2\nu_2^0$	$3\nu_2^1-2\nu_2^2$	$2\nu_2^0-\nu_2^1$		
	sing. site	doub. site	sing. site	doub. site	sing. site	doub. site	sing. site	doub. site	sing. site	doub. site	sing. site	doub. site	sing. site	doub. site	
ν_{lu} (cm ⁻¹)	938.5 ^a	1051 ^a	1290 ^a	581 ^b	571 ^b	579 ^b	1012 ^a	1011 ^a	913 ^b	913 ^b	1018 ^b	625 ^a	626 ^a	596 ^a	614 ^a 613.5 ^a
γ_{lu}^a (cm ⁻¹)	0.14	0.14	0.10	0.08	0.08	0.08	0.30	0.26	0.36	0.12	0.12	0.09	0.032	0.032	0.09 0.032
$10^3 \times R_{lu} ^2$ (D ²)	2.88	0.26	36	9.58	3.88	4.88	71	71	1.77	1.77	0.67	50.6	101	41	21.7 43
$10^{16} \times \sigma_{ul}^c$ (cm ²)	0.092	0.009	2.2	0.33	0.13	0.17	1.1	1.3	0.021	0.064	0.027	1.67	9.38	3.58	0.70 3.94
$10^{-16} \times \Delta N_T^e$ (cm ⁻³)	280 ^d	2900	12	80	200	150	24	20	1230	400	950	15	2.7	7	37 6.5
$\Delta N_T/N_0^e$ (%)	21 ^d	215	0.9	6	15	12	0.5	0.21	140	115	270	2	0.9	2.2	5 2

^a Matrix values. ^b Gas-phase values (refs 8–11 and 13–15). ^c Deduced from *a* and *b*. ^d Present experimental values. ^e Estimated from *c* and *d*.

only results in an immediate increase of the $\nu_3-\nu_1$ ASE. The absence of other emissions is then not surprising.

b. $2\nu_3-\nu_3$ Transition of O₃ at 10 μm . The present limit $\Delta N_T/N_0 > 0.21\%$ is too high but has the right order of magnitude in comparison with the value 0.13% obtained in ref 1 from absorption measurement at threshold. The very efficient transfer from $\nu_1+\nu_3$ to $2\nu_3$ is confirmed.

c. $^{13}\text{CO}_2$ at 10 μm . From Table 1, stimulated emission of the $\nu_3-\nu_1$ transition seems impossible at the concentration $C = 1/2000$. However, a decrease of $\Delta N_T/N_0$ below the critical value of 50% only requires an increase of the concentration by a factor of 2.5. Indeed, ASE has been observed recently at 10 μm at the concentration $C = 1/500$ and only for the double site. The thickness was about 400 μm and the threshold rather high, but qualitatively the prediction was valid. As for N₂O, the time shape of the emission reproduces the laser pulse seen by the detection.

d. $^{13}\text{CO}_2$ at 16 μm : ν_2 Manifold. In our previous paper,² we reported several ASE transitions observed for both sites in the ν_2 manifold. For example, to observe the $3\nu_2^1-2\nu_2^0$ transition at 625 cm⁻¹, we need to excite about 15% of the molecules to the $\nu_3 = 1$ level. This compares well with the present prediction, which requires 2% on the $\nu_2 = 3$ level (Table 1). The difference by a factor of 7.5 is not surprising because of the large energy gap between ν_3 and $3\nu_2$ which makes excitation transfer slower. Besides, the time shape of the emissions now differs from the laser one, allowing kinetic studies. These are presently in progress, with the hope of extracting nonradiative transfer rates from the temporal behavior of the emissions. We use a kinetic model largely inspired by Apkarian.¹⁷

IV. Conclusion

We have obtained with N₂O a new example where vibrational stimulated emission largely dominates over spontaneous emission, making detection easier but relaxation analysis more difficult. The present study, and previous work on O₃ and $^{13}\text{CO}_2$, reveal that the conditions for ASE are fairly often satisfied in matrixes. Population inversions are favored at low temperatures, and tunable laser sources bringing a few millijoule per cm² in one pulse are convenient. Nanosecond pulses about 1 cm⁻¹ broad are efficient enough.

The comparison of the molecular properties of these three species allows a rationalization of our previous experimental results. The ASE onset in similar argon disks is clearly related to transition moments and line widths. Weak transitions can be used for excitation provided that a high concentration may be chosen (O₃ case), when looking at a strong emission transition. Weak transitions are able to give ASE, when the pumping rate is high ($^{13}\text{CO}_2$ and N₂O cases). The semiquantitative considerations developed here may provide a predictive tool for stimulated processes to occur for other guests in similar samples.

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