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IR LASER-INDUCED UV-VISIBLE FLUORESCENCE IN MATRIX-ISOLATED CO

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Résumé - Sous l'effet d'une irradiation par un laser infrarouge à centres colorés, un film d'argon solide contenant 1 % de $^{13}\text{C}^{18}\text{O}$ émet une fluorescence dans la région UV-visible du spectre. La fréquence du laser infrarouge coïncide avec celle du centre de la raie d'absorption correspondant au premier harmonique de la vibration de CO. Le spectre d'émission est constitué d'un système complexe intense entre 650 et 800 nm et d'une progression simple plus faible qui s'étend de 320 à 640 nm. Ces deux bandes d'émission sont attribuées à des transitions électroniques de l'oxygène moléculaire. Le spectre d'émission infrarouge montre que les mécanismes de transfert V-V non resonnants peuplent des niveaux vibrationnels très élevés dans l'état électronique fondamental de CO. L'émission provenant des états excités $C^3\Delta_u$ et $b^1\Sigma_g^+$ de l'oxygène est l'évidence d'une conversion d'énergie vibrationnelle en énergie électronique.

Abstract - UV-visible fluorescence from a sample of solid argon containing 1 % of $^{13}\text{C}^{18}\text{O}$ is observed upon irradiation by a color-center laser whose frequency is coincident with the first overtone absorption band of CO. This emission consists of an intense complex system between 650 and 800 nm and of a weaker single progression extending from 320 to 640 nm. Both systems are assigned to electronic transitions of molecular oxygen. Infrared emission spectra indicate that high lying vibrational levels of the ground electronic state of CO (up to $v = 30$) are populated by anharmonic V-V pumping. The observation of subsequent emission from the $C^3\Delta_u$ and $b^1\Sigma_g^+$ excited electronic states of $\text{O}_2$ demonstrates that vibrational to electronic energy transfer occurs.

I - INTRODUCTION

In diatomic molecules, vibrational energy transfer tends to accumulate the vibrational energy in the high-lying levels. Such an excitation mechanism is known as the anharmonic V-V pumping and it occurs in gas phase ($^1\Sigma_g^+$) as well as in the solid phase ($^2\Sigma_g^+$). In gaseous CO ($^2\Sigma_g^+$) and NO ($^2\Pi$), irradiation with several watts of CW laser radiation results in UV or visible emission. In the present paper we report a similar experiment on matrix-isolated CO which is vibrationally excited to the $v = 2$ state by a low power color-center laser (CCL).

II - EXPERIMENTAL RESULTS

The CO molecules were optically pumped into the $v = 2$ state using a mechanically chopped CW CCL delivering $\sim 10$ mW at $\lambda = 2.47 \mu\text{m}$, the wavelength of the 0-2 overtone absorption band center of $^{13}\text{C}^{18}\text{O}$. The tuning range of our KCl:Li CCL extends from 2.45 to 2.9 $\mu\text{m}$. Therefore only the heaviest isotopic species of CO could be optically pumped with this source. Thin films of argon containing 1 % of $^{13}\text{C}^{18}\text{O}$ were

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obtained by depositing a gaseous mixture of Ar and CO at the desired ratio onto a gold-coated copper substrate held at liquid helium temperatures. IR emission spectra were recorded using a 1 m Sopra monochromator with an InSb or HgCdTe photodiode. UV-visible spectra were obtained with the aid of a HRS Jobin-Yvon spectrometer equipped with a RCA C31034 photomultiplier tube.

- Vibrational excitation of CO in solid argon

Overtone excitation of CO in solid Ar has revealed to be a very efficient way to produce strongly vibrationally excited CO molecules. The excitation mechanism has been studied in details using time resolved infrared spectroscopy (7). Due to the weakness of the 0→2 transition dipole moment, the v = 2 excitation is rather localized and migration aided energy transfer from v = 2 is inhibited. However overtone pumping produces a strong population inversion between level 2 and level 1 resulting in 2→1 stimulated emission. Actually evidence for stimulated emission has been obtained for CO in solid N₂ (8). Briefly, the excitation of high-lying v levels of CO in solid argon occurs in 4 steps:

1) direct optical pumping of v = 2
2) fast population transfer from v = 2 to v = 1 resulting from 2→1 stimulated emission
3) migration of the v = 1 excitation
4) non-resonant energy transfer through the well-known fusion process:
   CO(v) + CO(1) → CO(v+1) + CO(0) + ΔE.

The infrared emission spectrum of 1 % $^{13}\text{C}^{18}\text{O}$ in solid argon corresponding to the successive Δv = 2 vibrational transitions is shown in Fig. 1. Fluorescence occurs from high-lying vibrational levels. Its intensity distribution reaches a maximum at v = 13, decreases smoothly up to v = 27 then breaks down beyond v = 28. The vibrational ener-
Energy of the topmost detected state \( v = 30 \) is fairly high (\( \sim 6 \text{ eV} \)). It roughly corresponds to 60% of the CO dissociation energy and matches that of the lowest electronic state \( \text{a}^3\Pi \).

**Ultraviolet and visible fluorescence**

The preceding observations on the IR spectrum suggest that intersystem crossing may occur in CO. However, the search for phosphorescence Cameron bands remained unsuccessful, in spite of the fact that a detection apparatus very sensitive in the 200 nm region was used. Instead we observed near UV and visible fluorescence from the sample area irradiated with the CCL. A typical emission spectrum is shown in Fig. 2. It consists of an intense complex system in the 680-800 nm region and of a weaker single progression extending from 320 to 640 nm.

![Fluorescence intensity](image)

*Figure 2*

Near UV-visible emission spectrum of solid argon doped with 1% \({}^{13}\text{C}^{18}\text{O}\) at \( T = 2.6 \text{ K} \) upon IR laser irradiation. The line at 6471 Å originates from the scattered light of the krypton laser used for optical pumping of the CCL.

![Fluorescence intensity](image)

*Figure 3*

Excitation spectra of the overall infrared CO fluorescence and of the most intense red and violet emission lines.
energy of the $0 \to 2$ overtone transition of CO centered at 4054.4 cm$^{-1}$.

The time evolution of the intensity of the two strongest fluorescence lines is shown in Fig. 4. The onset of the fluorescence at $\lambda = 4214$ Å is delayed with respect to the IR laser radiation by 3 ms. The fluorescence intensity then reaches a steady state value and disappears rapidly ($\sim 1$ ms) after the IR radiation is switched off. On the contrary, the red fluorescence at 7630 Å is not delayed, but grows at a rate slower than that of the IR fluorescence coming from the most populated CO levels and decays slowly ($\sim 100$ ms).

![Figure 4](image)

Time evolution of the intensity of the $^{13}\text{C}^{18}\text{O}$ infrared emission and of the red and violet emission bands.

The single progression extending throughout the UV-visible region is unambiguously identified with the Herzberg system of molecular oxygen. This emission spectrum has been observed previously by several authors and is now assigned to the $C^3\Delta_u \to X^3\Sigma^-$ transition of $^{16}\text{O}_2$ in solid argon (6). The dominant emission does not seem to have been reported in the literature and therefore its assignment is less certain. However the nine most intense lines are satisfactorily assigned to $b^1\Sigma^+ \leftrightarrow v' \to X^3\Sigma^-$, $v'' = v' - 1$ transitions of $^{16}\text{O}_2$ in solid argon, with $v' = 0, 1, 2, 3, 4$. Several lines can also be assigned to $b^1\Sigma^+ \leftrightarrow v' \to X^3\Sigma^-$, $v'' = v' - 1$ of $^{18}\text{O}_2$. However their intensity is 20 to 30 times weaker than that of the corresponding $^{18}\text{O}_2$ lines. It should be noted that the occurrence of this UV-visible emission is critically dependent upon the CO vibrational excitation and consequently upon the CO concentration. At 0.2 % of $^{13}\text{C}^{18}\text{O}$ in solid argon no visible emission is observed. Since oxygen was not intentionally added in our samples, it is most likely an impurity.

III - DISCUSSION :

- Vibrational to electronic energy transfer from CO to O$_2$

The observation of fluorescence from molecular oxygen induced by IR excitation of carbon monoxide demonstrates that energy transfer must occur from the CO vibrational ladder to the electronic energy levels of O$_2$. The sensitivity of this emission to a strong CO vibrational excitation indicates that energy transfer occurs from high lying vibrational levels. The time delay between the rise of the violet signal and the rise of IR fluorescence suggests that the $C^3\Delta_u$ state of $^{16}\text{O}_2$ is fed from $^{13}\text{C}^{18}\text{O}$ vibrational levels with $v > 25$. Besides the fact that the b-X and C-X emissions originate mostly from different isotopic species of O$_2$ they have also quite different properties.
Therefore energy transfer probably occurs via two distinct channels.

The CO(\(v\)) - \(O_2\) interaction is too weak to give rise to non resonant energy transfer involving a curve crossing mechanism. Resonant processes are more likely expected to be efficient in this case. A schematic diagram of the lowest vibronic energy levels of CO and \(O_2\) which may be involved in V-E transfer are shown in Fig. 5. Oxygen is unique in having two low-lying excited electronic states: \(a^3\Delta_g\) at 0.98 eV and \(b^1\Sigma_g^+\) at 1.63 eV relative to the ground state \(X^3\Sigma_g^-\). Such energies correspond to that of a small number of CO vibrational quanta. It should also be pointed out that CO\(X^3\Sigma_g^+, \ v > 19\) and \(O_2\)\(C^3\Delta_u, \ v\) have similar energies. The energy of CO\(X^3\Sigma_g^+, \ v > 29\) also matches that of CO\(a^3\Pi, \ v\). Therefore several nearly resonant V-E transfer processes may occur.

Quite generally speaking, the probability for V-E transfer is dependent upon three factors: one is the electronic coupling matrix element, the second is a Franck-Condon type factor taking into account the fact that the nuclei may not follow a change in the electronic configuration, and the third is an energy gap term coming from the fact that lattice phonons are emitted to compensate for the energy mismatch. Three kinds of mechanisms should be considered:

a) direct V-E transfer involving the conversion of many vibrational quanta of CO into a single quantum of electronic energy in \(O_2\). Such a process requires a rather strong intermolecular coupling and it is expected to take place among CO-\(O_2\) dimers. It is also expected to be efficient for populating the low-lying singlet levels of \(O_2\).

b) Intersystem crossing in CO (intramolecular V-E transfer) followed by intermolecular transfer of electronic excitation (E-E). This process could benefit from an eventual stronger intramolecular interaction. However its efficiency to populate electronic states of high energy will be limited by the smallness of the F-C factors.

c) Intermolecular V-V transfer from CO to \(O_2\) involving the exchange of one or several quanta between the two vibrational ladders then followed by intersystem crossing in \(O_2\).
Two possible explanations may account for the predominance of the b-X emission of $^{18}$O$_2$ with respect to that of $^{16}$O$_2$. Either $^{18}$O$_2$ is more abundant than $^{16}$O$_2$ or an isotopically selective transfer process occurs in favor of the more diluted $^{18}$O$_2$ species. $^{18}$O-enriched molecular oxygen could be contained in the isotopically enriched CO gas used for preparing the solid $^{13}$C$^{18}$O samples or it may result from the in-situ dissociation of $^{13}$C$^{18}$O induced by the IR laser radiation.

Let us assume for instance that $^{18}$O$_2$ is the most abundant species. The selective excitation of $^{16}$O$_2$ ($C^3\Delta_u$) could then result from migration of the triplet excitation among the most abundant $^{18}$O$_2$ molecules and trapping by the least abundant $^{18}$O$_2$ species. However such a mechanism would require a rather large $^{18}$O$_2$ concentration and the existence of an energy gap between the $C^3\Delta_u$ states of $^{18}$O$_2$ and $^{16}$O$_2$. In solid N$_2$, the energy of $^{16}$O$_2$ ($C^3\Delta_u$) has been found to be smaller than that of $^{18}$O$_2$ ($C^3\Delta_u$) by 12 cm$^{-1}$ $(^8)$. Even such a small difference is large enough to ensure energy trapping at low temperatures. On the contrary if $^{18}$O$_2$ is assumed to be more abundant than $^{16}$O$_2$, the selective excitation of $^{18}$O$_2$ (b$^1\Sigma^+$) would be due to migration of the vibrational excitation among $^{16}$O$_2$ and trapping on the heaviest isotopic species $^{18}$O$_2$.

IV - CONCLUSION

The observation of IR-induced UV-visible fluorescence is the evidence for V-E energy transfer from CO to O$_2$. The experimental observations suggest that the O$_2$ fluorescent electronic states are populated via two independent processes. Molecular oxygen is present in the samples as an impurity and both the concentration and the isotopic ratio are unknown. Although it is difficult to unambiguously identify the V-E transfer mechanisms, the following 2-channel scheme reasonably accounts for the experimental behaviour:

i) O$_2$($C^3\Delta_u$) is fed by intermolecular E-E transfer from CO to O$_2$ mediated through internal conversion $X^2\Sigma^+ \rightarrow a^3\Pi$ in CO.

ii) O$_2$($b^1\Sigma^+$) is populated either by direct V-E transfer or by intermolecular V-V transfer between CO and O$_2$ followed by internal conversion in O$_2$.

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