

Near Infrared Emission of Highly Electronically Excited CO: A Sensitive Probe to Study the Interstellar Medium??

Murthy S. Gudipati^{1,2}

Institute of Physical Sciences and Technology, University of Maryland, College Park, MD

Abstract

Among the various spectroscopic features of the second most abundant molecule in the space, CO, "the triplet – triplet transitions involving the lowest triplet state $a^3\Pi$ and the higher-lying $a' ^3\Sigma^+$, $d ^3\Delta$, $e ^3\Sigma^-$ states spanning near-UV to mid-IR spectral range" have so far not been explored in astrophysical observations. The energies of these transitions are highly sensitive to the surroundings in which CO exists, i.e. gas-phase, polar or non-polar condensed phase. It is proposed here that these triplet-triplet emission / absorption bands can be used as a sensitive probe to investigate the local environments of CO, whether in the planetary atmosphere, stellar atmosphere or interstellar medium.

1. Introduction

Carbon monoxide (CO) is the second most abundant species in the Space. Due to its almost ubiquitous presence in stars, stellar objects and interstellar mater, CO has been one of the most extensively observed and tagged molecules as a remote-sensor of the local environments. Most commonly used spectroscopic signatures of CO are the vibrational fundamental at $4.7 \mu\text{m}$ (Boogert *et al.* 2002) and its overtones at 2.35 (Schreiber 2000) and $1.56 \mu\text{m}$ (Lançon and Wood 2000). Light emission or absorption due to electronic transitions in CO has also been utilized for remote-sensing purposes, for example in Red Rectangle and its central star HD 44179. The relevant electronic states of CO are given in Figure 1. Vacuum UV emission due to the fourth positive system of CO involving the $A^1\Pi - X^1\Sigma^+$ transition has been observed using GHRS on the HST (McMurphy and Jordan 2000; Glinski *et al.* 1997). Cameron emission from the $a^3\Pi$ state to the ground-state is also extensively used in astrophysical observations (Yan *et al.* 2000, for example). We may also note that CO is also a major constituent in the atmospheres of Satellites like Triton (Lellouch 1994; Tryka *et al.* 1993; Young *et al.* 2001) in our own solar system.

Given the importance of CO in astrophysical studies mentioned above, to our surprise, so far there has been no mention of other emission lines of CO in astrophysical literature (to the best of our knowledge) involving the triplet electronic states $a' ^3\Sigma^+$, $d ^3\Delta$, $e ^3\Sigma^-$, and $a^3\Pi$. Emission from the a' , d and e states to the a state, which is both spin and symmetry allowed, occurs when CO is electronically excited into the A -state or higher excited states (8 eV or above). The wavelength-region of this *triplet-triplet* emission can span between 0.3 to

¹Visiting Astrochemistry Laboratory, NASA Ames Research Center, Moffett Field, CA; Visiting Scientist at Molecular Physics Laboratory, SRI International, Menlo Park, CA E-mail:gudipati@ipst.umd.edu

²Also affiliated with Institute of Physical Chemistry, University of Cologne, Germany

3 μm . The only comprehensive compilation to date on the astrophysical relevance of the electronic states and the electronic spectra of CO (Morton and Noreau 1994) does not include the triplet-triplet transitions. As will be discussed below, NIR emission of CO can be used as a remote spectroscopic sensor that is sensitive for the local environments, wherever light with photon energies >8 eV (<0.16 μm) is present. We may also note that having a dedicated NIR monochromator (NICMOS) launched on the HST reflects the importance of NIR astrophysical observations and the complementary laboratory measurements.

2. Laboratory Studies

A few years ago we have discovered that NIR emission spectrum of CO isolated in Argon (Ar) matrices at 15 K (Gudipati and Kalb 1998) is entirely different compared to the gas-phase emission spectrum published in literature only once so far (Effantin *et al.* 1982). While the gas-phase spectrum is dominated by the $a' - a$ transition (Asundi system), in the condensed phase low-temperature Ar matrices, emission from all the three a' , d and e upper states to the a state has been observed. As mentioned earlier, the triplet-triplet emission from the a' , d and e states to the a state (Figure 1) spans 0.3 to 3 μm region and the intensity of these emission lines are stronger in the NIR region. A complete set of optical excitation and emission spectra of CO in low-temperature Ar matrices is also summarized in Figure 1. Spectra measured in the NIR region from CO in Ar matrices are expanded in Figure 2.

Due to the fact that the transitions from the a' , d and e states to the a state are both spin and symmetry allowed, both emission and absorption involving the three upper a' , d and e states and the lower a state should have strong features that are purely dictated by the Franck-Condon factors (FCFs) in collision-free gas-phase very low-density conditions. If, on the other hand, collisions become important like in high-density molecular clouds or if CO exists in condensed phase, then it turns out that in addition to the FCFs, the energy gap between any given vibrational level of the a' , d and e states and the immediate energetically low-lying vibrational level of the a state is also crucial (Gudipati and Kalb 1998). Smaller the energy gap, faster will the nonradiative vibrational relaxation of the particular level of the a' , d and e states. When the energy gap turns out to be large, of the order of several hundred wavenumbers, these vibrational levels undergo radiative decay. Such electronic levels are known as *bottlenecks* and emission occurs from these vibrational levels.

The surrounding medium of CO also influences whether or not bottlenecks are formed at certain vibrational levels, because, the vibrational levels of the a' , d and e states shift energetically to different degree in different directions with respect to the a state based on the polarization and dipole moment of the surrounding medium. This happens because of the fact that each of the electronic states of CO has different inherent dipole moments, as for example, X (-0.12 D), A (0.15 D), a (0.84 D), a' (-2.49 D), and d (-2.31 D) (Lynch *et al.* 1982). Consequently, through shifting the sets of vibrational levels of different electronic states against each other, some bottlenecks disappear and others appear. Accordingly, the emission spectra change. As an example, the energy level diagram of the triplet states of CO in the gas-phase and in Ar matrices is shown in Figure 2. As a consequence, the transition energies and the corresponding

wavelengths change significantly between gas-phase and Ar matrices. For example, a blue shift of the 1.05 μm band by $\sim 200\text{ cm}^{-1}$ (Figure 2) is an enormous magnitude, compared to the changes in the ground-state vibrational frequencies of CO under similar circumstances ranging only less than 10 cm^{-1} (Elsila *et al.* 1997).

The ground-based or satellite-based NIR spectroscopic measurements on CO need to be carried out along with detailed laboratory investigations on the spectroscopic nature of CO in different environments. These studies may lead to a better understanding of the ISM containing CO. The objects that emit VUV and UV light due to $A \rightarrow X$ and Cameron emission of CO should also show the NIR absorption / emission features.

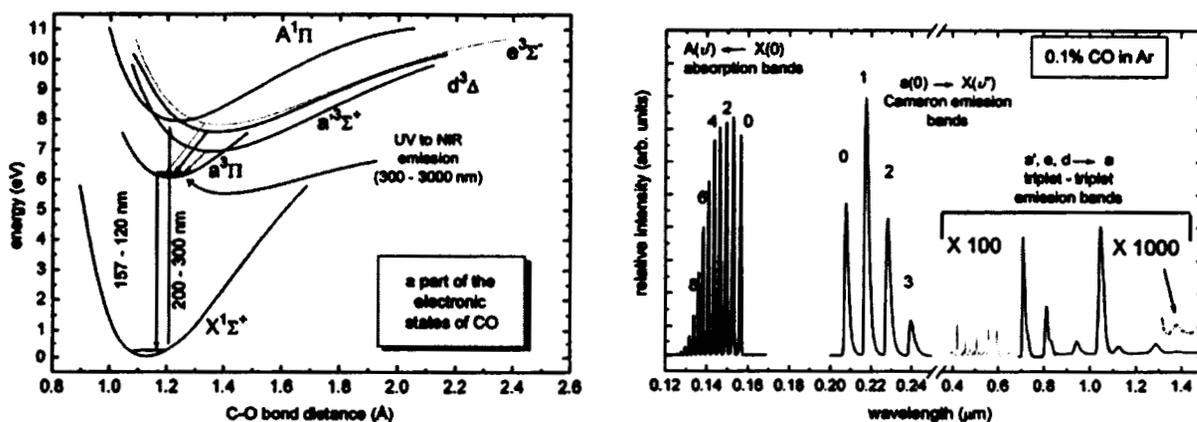


Fig. 1.— A part of the electronic states (left) and electronic spectra (right) of CO. The energies are given in eV (left). Vibrational levels of the final states are numbered accordingly (right).

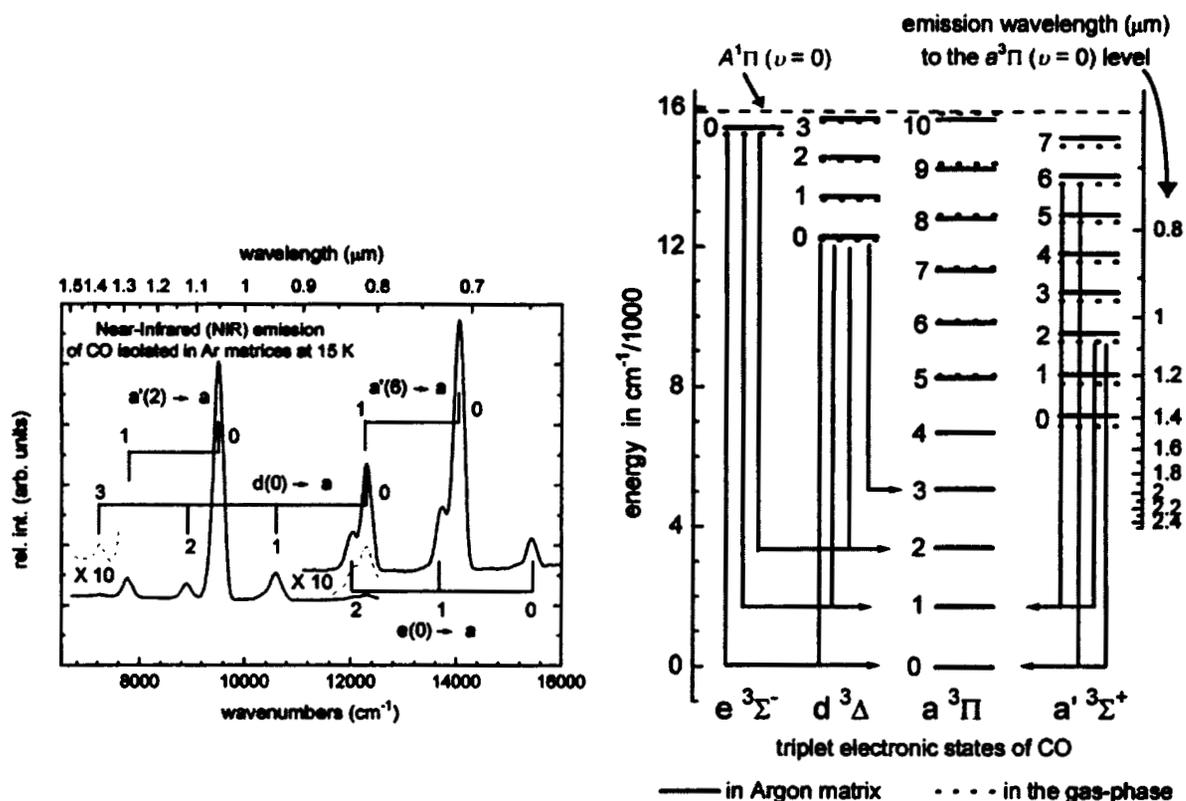


Fig. 2.— Near infrared emission from CO in Ar matrices (left) and shifts in the energies of the vibronic levels of the triplet states from the gas-phase to Ar-matrices (right).

Acknowledgments

I thank the financial support of NSF (Grant No. 9910914) and NASA (Grant No. UMD CP1131).

REFERENCES

- Boogert, A. C. A., Hogerheijde, M. R., and Blake, G. A. 2002, *ApJ*, **568**, 761-770.
- Elsila, J., Allamandola, L. J., and Sandford, S. A. 1997, *ApJ*, **479**, 818-838.
- Effantin, C., Michaud, F., Roux, F., D'Incan, J., and Verges, J. 1982, *J. Mol. Spectr.*, **92**, 349-362.
- Gudipati, M. S., and Kalb, M. 1998, *A&A*, **329**, 375-379.
- Glinski, R. J., Lauroesch, J. T., Reese, M. D., and Sitko, M. L. 1997, *ApJ*, **490**, 826-834.
- Lançon, A., and Wood, P. R. 2000, *A&AS*, **14**, 217-249.
- Lellouch, E. 1994, *ICARUS*, **108**, 255-265.
- Lynch, D., Herman, M. F., and Yeager, D. L. 1982, *Chem. Phys.*, **64**, 69-81.
- McMurry, A. E., and Jordan, C. 2000, *MNRAS*, **313**, 423-432.
- Morton, D. C., and Noreau, L. 1994, *ApJS*, **95**, 301-343.
- Schreiber, N. M. F. 2000, *ApJ*, **120**, 2089-2100.
- Tryka, K. A., Brown, R. H., Anicich, V., Cruikshank, D. P., and Owen, T. C. 1993, *Science*, **261**, 751-754.
- Yan, M., Dalgarno, A., Klemperer, W., and Miller, A. E. S. 2000, *MNRAS*, **103**, L17-L18.
- Young, L. A., Cook, J. C., Yelle, R. V., and Young, E. F. 2001, *ICARUS*, **153**, 148-156.