

New near infrared emission bands of CO: a highly sensitive spectroscopic property of CO to probe the interstellar matter

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Abstract. Several new near infrared (NIR) emission bands between 7000 and 16000 cm^{-1} of CO isolated in Ar matrices at 20 K have been observed that are due to radiative deactivation of the $e^3\Sigma^-$, $d^3\Delta$ and $a'^3\Sigma^+$ states to the $a^3\Pi$ state. The corresponding excitation spectra are due to the fourth positive system of CO, namely, the $A^1\Pi(v') \leftarrow X^1\Sigma^+(v'' = 0)$ transition. The environment around CO, i.e., whether it is in the gas-phase or imbedded in a condensed environment, influences strongly which radiative channels get active or not and their transition energies. It is proposed that this behaviour can be taken to advantage to probe the environment of the interstellar matter.

Key words: molecular data – molecular processes – infrared: general; ISM: lines and bands – methods: laboratory

1. Introduction

Carbon monoxide is one of the major constituents of stellar and interstellar media. The near infrared emission of CO due to the ground-state vibrational transitions at 4.67 μm ($1 \rightarrow 0$) and 2.3 μm ($2 \rightarrow 0$) are used as markers to study the evolution and ages of several stars (for example Greene & Lada 1996, Brooke et al. 1996) and the 4.67 μm absorption band is used to investigate the composition of interstellar matter, especially the low temperature grains and ice analogues (Elsila et al. 1997). Rotational lines of CO in the microwave region are commonly used in astronomy (for example George et al. 1994). The vacuum ultraviolet (VUV) features of CO have been observed with *International Ultraviolet Explorer (IUE)* followed by *Hubble Space Telescope (HST)* using Goddard High-Resolution Spectrograph (GHRS) (for example Lambert et al. 1994). The dark sunspot umbral spectrum also shows strong absorption bands due to several vibrational transitions in the ground-state ($X^1\Sigma^+$) of CO (Wallace & Livingston). On the other hand, the spectroscopic features of CO in the near infrared region (NIR) between .9 and 2 μm involving the electronically excited states have not yet been explored in astrophysical observations, presumably due to the lack of sensitive detectors that cover the NIR region. Only recently,

due to the development of highly sensitive NIR detectors, the NIR region became accessible for astronomers (Wallace & Livingston, Greene et al. 1993, Kelly & Latter 1995). A compilation of electronic transitions in CO and their relevance for astronomy is published by Morton & Noreau (1994). However, in this review the NIR region mentioned above is not taken into account. There are several important spectroscopic characteristics of CO in the region between 0.9 and 1.6 μm , which could be useful to understand more about the composition of the interstellar matter.

Spectroscopic data of CO in the gas-phase at shorter wavelengths than 0.86 μm is compiled by Krupenie (1966) and Tillford & Simmons (1972). In the NIR region between 0.75 and 3.0 μm relatively few studies are available in the literature (Efantin et al. 1982, Amoit & Islami 1986, Momona et al. 1993), of which only the first two articles reported the triplet-triplet NIR emission bands of CO in the gas-phase. We report here several new NIR emission bands of CO isolated in Ar matrices at 20 K and discuss their astrophysical implications.

There exist four triplet electronic states of CO that lie between the ground-state ($X^1\Sigma^+$) and the first optically allowed excited singlet state ($A^1\Pi$). These triplet states with increasing energy are: $a^3\Pi$, $a'^3\Sigma^+$, $d^3\Delta$ and $e^3\Sigma^-$, respectively. The a-state of CO, which lies at 6.01 eV above the ground-state, is a metastable state with a lifetime of several ms, an estimated value of 94 ms in an unperturbed environment, 90 ms in Ne matrices and 7.2 ms in Ar matrices (Fournier et al. 1980). For this reason, the $e \leftrightarrow a$, $d \leftrightarrow a$ and $a' \leftrightarrow a$ transitions that range from UV to NIR region are important for the processes occurring in both stellar and interstellar environment, where the abundance of CO is significant. The a-state of CO is populated subsequent to the $A \leftarrow X$ excitation between 1570 and 1200 Å. Bahrtdt et al. (1987) studied in detail the spectroscopic properties of CO in rare-gas matrices except for the NIR emission. These studies will be referred in the following.

2. Experimental

The experiments were carried out at the synchrotron radiation facility, BESSY, in Berlin using a 3m normal incidence

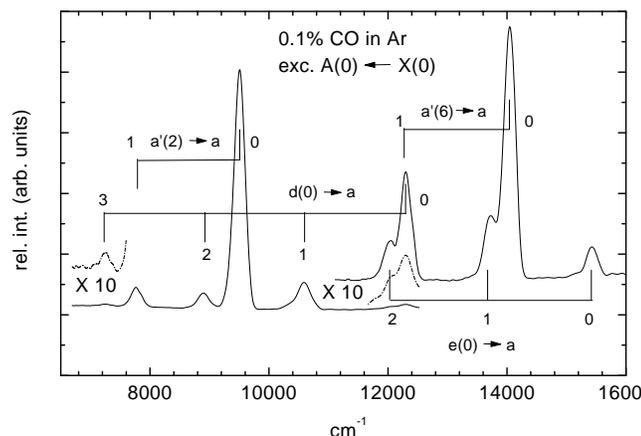


Fig. 1. NIR emission spectra of 0.1% CO in Ar matrices. Excitation at 63938.6 cm^{-1} into the $A^1\Pi(v' = 0) \leftarrow X^1\Sigma^+(v'' = 0)$ transition.

monochromator (3m-NIM-1). The apparatus used for these experiments is described in an earlier publication (Gudipati 1995). The emission was passed through a 0.5 m monochromator (Acton Research) and detected with either a liquid N_2 cooled InGaAs photodiode equipped with a preamplifier (Electro-Optical Systems, spectral region 0.8 to $1.5 \mu\text{m}$) or a GaAs photomultiplier (Hamamatsu, R943-02; spectral region 0.18 to $0.9 \mu\text{m}$). Ar (99.999%) and CO (99.995%) from Linde were used for preparing the matrices. Matrix ration was typically 1:1000 (CO:Ar).

3. Spectroscopic results

In order to retain the linearity of the energy scale we use wavenumbers (cm^{-1}) rather than wavelengths to present the results. The NIR emission spectra recorded during excitation of CO at 63938.6 cm^{-1} into the $A(0) \leftarrow X(0)$ transition is shown in Fig. 1. The emission spectrum between 16000 and 11000 cm^{-1} was recorded with the photomultiplier and the spectrum between 12500 and 6650 cm^{-1} was recorded with the photodiode. Due to different spectral responses of the photomultiplier and the photodiode, we did not attempt to normalise the spectra with each other. The excitation spectra measured by monitoring the emission at 14050 and 12311 cm^{-1} have been presented in an earlier publication (Gudipati 1997) and the excitation spectra recorded by monitoring the other strong emission bands at 10588, 9506, 8897 and 7770 cm^{-1} are collected in Fig. 2. Energy levels of the triplet states and the singlet $A^1\Pi(v'=0)$ state with respect to the zero vibrational level of the a-state are sketched in Fig. 3. For comparison gas-phase energies derived from the spectroscopic constants given in the paper of Bahrdt et al. (1987) are also included in Fig. 3.

It is obvious from the spectra presented in Figs. 1 & 2 that the emission results from CO. The emission bands could not be assigned as being due to a single upper electronic state. On the other hand, the gas-phase NIR emission bands are exclusively due to the $a' \rightarrow a$ transition (Effantin et al. 1982, Amoit & Islami 1986).

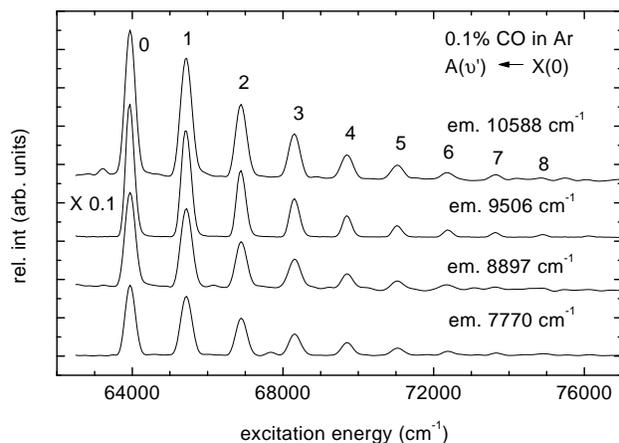


Fig. 2. Excitation spectra due to the $A^1\Pi(v') \leftarrow X^1\Sigma^+(v'' = 0)$ transitions by monitoring the NIR emission bands shown in Fig. 1. v' values are numbered on the top spectrum.

In order to analyse the present spectroscopic data and compare it with the data reported in the literature, it is necessary to consider the following aspects. In the present work isolated CO molecules are excited directly with electromagnetic radiation. On the other hand, excitation of CO in the gas-phase was achieved in a plasma generated through microwave or electric discharge. Under these experimental conditions collisions as well as recombination of C and O atoms generate the excited CO molecules. In spite of these differences, the spectroscopic data derived from the gas-phase experiments (Effantin et al. 1982, Amoit & Islami 1986) is accurate and reliable. For example, the $a'(2) \rightarrow a(0)$ transition at 9278.12 cm^{-1} measured by Effantin et al. (1982) is close to the value of 9282.28 cm^{-1} for the $a'(2) \leftarrow a(0)$ transition derived from the spectroscopic constants given by Huber & Herzberg (1979). Hence a comparison of the spectroscopic data from the present work with that of the gas-phase studies is justified.

The second aspect that needs to be considered is the dipole moment of CO in different electronic states. The dipole moments (μ) of the first five electronic states of CO are discussed in detail by Lynch et al. (1982), which are summarised here. A positive value of μ indicates positive charge on C and negative charge on O (C^+O^-). These are: in the $X^1\Sigma^+$ state, $\mu = -0.122 \text{ D (exp.)} \& -0.331 \text{ D (theory)}$; in the $a'^3\Sigma^+$ state, $\mu = -2.487 \text{ D (theory)}$; in the $d^3\Delta$ state, $\mu = -2.314 \text{ D (theory)}$; in the $a^3\Pi$ state, $\mu = 0.84 \text{ D (exp.)} \& 1.53 \text{ D (theory)}$ and finally in the $A^1\Pi$ state, $\mu = 0.15 \text{ D (exp.)} \& 0.539 \text{ D (theory)}$. Thus, based on the environment in which CO exists in the condensed phase, the electronic states X, a' and d which carry negative μ move energetically in the opposite direction (get energetically stabilised or destabilised) with respect to the electronic states a and A which carry positive μ . Keeping these aspects in mind we have analysed our emission spectra.

Using the spectroscopic constants (ν_{00} , ω_e and $\omega_e x_e$) of a, a' , d and e states of CO in Ar matrices obtained by Bahrdt et al. (1987), the energies of the vibrational states of the a' , d and e

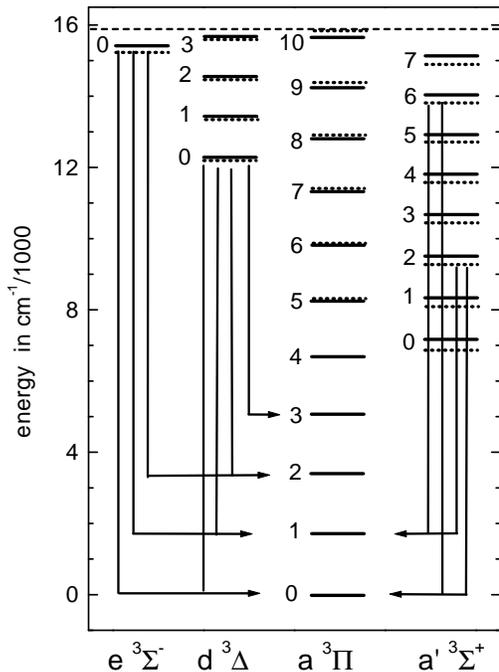


Fig. 3. Energies of the triplet states and their vibrational levels with respect to the $a^3\Pi(v'' = 0)$ level. The gas-phase energies are shown as dotted lines. The dashed line on top of the figure represents the $A^1\Pi(v' = 0)$ level. Vertical lines connected with horizontal arrowhead lines show the measured radiative transitions (compare to Fig. 1 and Table 1).

electronic states were independently calculated with respect to the $v''=0$ level of the a-state (Fig. 3). It was needed to shift the energies of the upper three electronic states (a' by -41 cm^{-1} , d by -183 cm^{-1} and e by -18 cm^{-1}) given by Bahrtd et al. (1987) in order to have a good agreement with the energies of vibronic states measured in the present study (Table 1). Due to the uncertainties in the ν_{00} values extrapolated and that only the gas-phase ω_e and $\omega_e x_e$ are available for the d and e states (Bahrtd et al. 1987), the above mentioned spectral shifts are acceptable. Possible second choice is also given for some of the bands in Table 1. It can clearly be seen that the choice of $d(0) \rightarrow a(1$ and $2)$ fits better with the bands at 10588 and 8897 cm^{-1} than the choice of $a'(6) \rightarrow a(2$ and $3)$. The band at 7244 cm^{-1} can be assigned to either or both the choices given in Table 1. All the other possible assignments resulted in more than 100 cm^{-1} difference between the observed and calculated energies.

In contrast to the gas-phase, where the radiative or nonradiative processes are controlled by electronic coupling (A) and vibrational ($\langle v'|v'' \rangle$) Franck-Condon factors, in condensed environment, for example in the interstellar grain particles (rare-gas matrices in the present case), an additional factor plays a crucial role. This factor is due to the coupling of phonons with the vibronic levels ($\langle p'|o \rangle$). A detailed discussion can be found in the publication of Bahrtd & Schwentner (1988). It is sufficient to state here that the coupling constant V' for nonradiative relaxation, which can be expressed as a product of the above

three interactions: $V' = A \langle v'|v'' \rangle \langle p'|o \rangle$, is insignificantly small among a' , d and e states, but gets significant between a and a' , d or e states. The vibrational levels of any particular electronic state having small values of the coupling constant V' build so called *bottlenecks* where radiative relaxation competes with nonradiative relaxation. In general, it may be expected that the probability of emission to occur from a vibrational level of the a' , d and e states increases with increasing gap between this vibrational level and the vibrational levels of the a-state that lies immediately below. Consequently, the *bottlenecks* can be identified as $e(0)$, $a'(6)$, $d(0)$ and $a'(2)$ from Fig. 3. Bahrtd (1987) has observed from three of these upper states, namely the $e(0)$, $a'(6)$ and $a'(2)$ states, respectively, radiative transitions (in the VUV region) directly to the ground-state and our NIR spectra complement their observations.

4. Astrophysical implications

The NIR emission of CO presented here may have important astrophysical implications. The strongest emission band at 9506 cm^{-1} ($1.052\text{ }\mu\text{m}$) occurs in the highly transparent window between the telluric absorption regions due to water at 0.95 and $1.12\text{ }\mu\text{m}$ (Sommerville 1995) and thus should be relatively easy to detect. In fact the NIR region, especially between 0.9 and $1.5\text{ }\mu\text{m}$, is still largely unexplored by astronomers (Foing & Ehrenfreund 1995) and our spectroscopic data could be of use for future endeavours. It is an advantage that in the NIR region the continuum extinction is significantly smaller than in the visible region. A further advantage comes from the influence of the environment on the energies of the triplet states. The triplet-triplet transitions of CO occur among the higher excited states involving vibrationally excited electronic states. As mentioned in the previous section, the energy levels of these vibronic states are highly sensitive to the environment in which CO exists. Consequently some of the *bottlenecks* may disappear and new ones may appear.

For example, in Ne matrices, where the energy levels are least perturbed compared to the gas-phase (Fig. 3), the a' -state is stabilised with respect to the a-state when compared to the corresponding energy levels in Ar matrices. As a consequence, the $a'(5)$ is shifted to lower energy than the $a(8)$ (Fig. 3) in Ne matrices (Bahrtd & Schwentner 1988). This results in appearance of a *bottleneck* at $a'(5)$ in Ne matrices and a *bottleneck* at $a'(6)$ in Ar matrices. The positions of these NIR emission bands are also sensitive to the environment of CO. For example, the gas-phase energy of the $a'(2) \rightarrow a(0)$ transition at 9278 cm^{-1} (Effantin et al. 1982) is shifted to lower energy by 228 cm^{-1} compared to the energy in Ar matrices (amounting to a $0.0258\text{ }\mu\text{m}$ shift).

Kelly & Latter (1995) have studied the NIR emission spectra ($\lambda = 0.9 - 1.3\text{ }\mu\text{m}$) of several evolved stars. These authors reported some unidentified lines in addition to several identified ones. We find that three out of four unidentified emission lines from *HM Sge* lie close to the NIR emission bands of CO measured in Ar matrices in the present study. These are: 0.9495 (0.9445), 1.0447 (1.0520) and 1.2893 (1.2870) μm , the values

Table 1. Spectroscopic constants of the triplet states of CO in Argon matrices from Bahrtd et. al. (1987), the energies of the NIR triplet-triplet transitions calculated using these constants (calculated) and those measured in this work (measured). All values are given in cm^{-1} .

Spectroscopic constants:					
	$a^3\Pi$	$a'^3\Sigma^+$	$d^3\Delta$	$e^3\Sigma^-$	
ν_{00}^a	48046	55265(55224) ^b	60540(60357)	63492(63474)	
ω_e	1762	1202	1168 ^c	1116 ^c	
$\omega_e x_e$	17.74	8.07	9.68 ^c	9.76 ^c	
Energies of the transitions:					
transition	measured		calculated		difference (m-c)
	band maximum (m)	vibrational spacing ($\Delta v'' = 1$)	band maximum (c)	vibrational spacing ($\Delta v'' = 1$)	
e(0) - a(0)	15427		15427		0
e(0) - a(1)	13710	1717	13700	1727	10
e(0) - a(2)	12013	1697	12009	1691	4
a'(6) - a(0)	14050		14050		0
a'(6) - a(1)	12311 ^d	1739	12323	1727	-12
d(0) - a(0)	12311 ^d		12311		0
d(0) - a(1)	10588	1723	10584	1727	4
or			or	or	or
a'(6) - a(2)			10632	1691	-44
d(0) - a(2)	8897	1691	8893	1691	4
or			or	or	or
a'(6) - a(3)			8976	1656	-79
d(0) - a(3)	7244	1653	7237	1656	7
or			or		or
a'(0) - a(0)			7178		66
a'(2) - a(0)	9506		9533		-27
a'(2) - a(1)	7770	1736	7806	1727	-36

a) energy of the 0-0 transition from the ground-state ($X^1\Sigma^+$);

b) values in parentheses are obtained after shifting the energies as indicated in the text;

c) gas-phase values referred in Bahrtd et al. (1987);

d) overlapping bands.

in parentheses being from the present study. Though the differences can be attributed to matrix shifts, further investigations need to be carried out to positively identify these lines.

The interpretation and assignment of the diffuse interstellar absorption bands (DIBs) is still a puzzle in spite of the spectacular progress made in the recent years (see Herbig 1995 for a review). A variety of organic molecules and ions have already been proposed to be the carriers of some of these DIBs

(Foing & Ehrenfreund 1997, Ehrenfreund et al. 1997 and references therein). Multiphotonic processes in molecular hydrogen are also proposed to cause the appearance of some of the DIBs (Sorokin & Glowina 1996) and positively identified recently by Ubachs et al. (1997). CO is one of the most abundant molecules in space and its triplet-triplet transitions involving the $a^3\Pi$ state range between $0.3 \mu\text{m}$ and $3 \mu\text{m}$ (present work, Krupenie 1966, Effantin et al. 1982, Amoit & Islami 1986, Bahrtd & Schwent-

ner 1988). The $a^3\Pi$ state of CO, which is a metastable state, is populated after the $A \leftarrow X$ excitation at wavelengths between 1570 and 1200 Å. In this region several DIBs and the $A \leftarrow X$ absorption bands of CO have been measured (Cardelli 1995). Keeping in mind lifetimes of the $a^3\Pi$ state of CO (see Introduction), a significant population of this state can be achieved under the conditions existing in the interstellar clouds. Consequently, the triplet-triplet transitions may also result in some of the DIBs. We would like to propose, for example, that the infrared DIB observed by Joblin et al. (1990) at 1.3175 μm may be due to the $a'(2) \leftarrow a(1)$ transition in CO. The corresponding emission occurs at 1.3221 μm in the gas-phase (Effantin et al. 1982) and at 1.287 μm in Ar matrices. Similarly the DIB at 0.9577 μm whose carrier has been proposed to be C60^+ (Foing & Ehrenfreund 1994), lies close to the $a'(3) \rightarrow a(0)$ transition in CO, which occurs at 0.9575 μm in the gas-phase (Effantin et al. 1982). Further work is warranted to positively identify whether or not CO can be the carrier of these DIBs.

As discussed in the previous section, the relative energy levels of the triplet states are strongly influenced by the environment of CO. For this reason, the gas-phase energies may be of use only if free CO is in consideration. The low temperature grains and ice analogues containing CO strongly influence its spectroscopic properties. Controlled laboratory experiments using synchrotron radiation as the source of excitation and low temperature ices having the composition similar to the interstellar ice particles are in progress. These studies and the astrophysical observations that complement each other should render precise information on the nature and composition of the interstellar matter.

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References

- Amoit, C., Islami, K. 1986, *J. Mol. Spectr.* 118,363
 Bahrtdt, J., Gürtler, P., Schwentner, N. 1987, *J. Chem. Phys.* 86,6108
 Bahrtdt, J. 1987, Doctoral Thesis; Freie Universität Berlin, Berlin, Germany.
 Bahrtdt, J., Schwentner, N. 1988, *J. Chem. Phys.* 88,2869
 Brooke, T.Y., Orten, G.S., Crisp, D., Friedson, A.J., Bjoraker, G.L. 1996, *Icarus* 121, 422
 Cardelli, J.A. 1995, in *The Diffuse Interstellar Bands*, eds. Tielens, A.G.G.M., Snow, T.P., Kluwer Academic Publishers, Dordrecht, p.53
 Effantin, C., Michaud, F., Roux, F., D'Incan, J., Verges, J. 1982, *J. Mol. Spectr.* 92,349
 Elsilá, J., Allamandola, L.J., Sandford, S.A. 1997, *ApJ* 479, 818
 Ehrenfreund, P., Cami, J., Dartois, E., Foing, B.H. 1997, *A & A Lett.* 318, L28
 Foing, B.H., Ehrenfreund, P. 1994, *Nature* 369, 296
 Foing, B.H., Ehrenfreund, P. 1995, in *The Diffuse Interstellar Bands*, eds. Tielens, A.G.G.M., Snow, T.P., Kluwer Academic Publishers, Dordrecht, p.65
 Foing, B.H., Ehrenfreund, P. 1997, *A & A Lett.* 317, L59
 Fournier, J., Mohammed, H.H., Deson, J., Vermeil, C., Schamps, J. 1980, *J. Chem. Phys.* 73,6039

- George, T., Urban, W., Le Floch, A. 1994, *J. Mol. Spectr.* 165, 500
 Greene, T.P., Tokunaga, A.T., Toomey, D.W., Carr, J.S. 1993, *Proc SPIE* 1946,313
 Greene, T.P., Lada, C.J. 1996, *ApJ* 461,345
 Gudipati, M.S. 1995, *Chem. Phys.* 201,451
 Gudipati, M.S. 1997, *J. Phys. Chem. A* 101,2003
 Herbig, G.H. 1995, *ARA&A* 33, 19
 Huber, K.P., Herzberg, G. 1979, *Molecular Spectra and Molecular Structure, Vol. 4. Constants of Diatomic Molecules*, Van Nostrand-Reinhold, New York.
 Joblin, C., Maillard, J.P., d'Hendecourt, L., Léger, A. 1990, *Nature* 346,729
 Kelly, D.M., Latter, W.B. 1995, *AJ* 109, 1320
 Krupenie, P.H. 1966, *The Band Spectrum of Carbon Monoxide*, NSRDS-NBS5, National Bureau of Standards, Washington D.C.
 Lambert, D.L., Sheffer, Y., Gilliland, R.L., Federman, S.R. 1994, *ApJ* 420, 756
 Lynch, D., Herman, M.F., Yeager, D.L. 1982, *Chem. Phys.* 64, 69
 Momona, M., Kanamori, H., Sakurai, K. 1993, *J. Mol. Spectr.* 159,1
 Morton, D.C., Noreau, L. 1994, *ApJSS* 95, 301
 Somerville, W.B. 1995, in *The Diffuse Interstellar Bands*, eds. Tielens, A.G.G.M., Snow, T.P., Kluwer Academic Publishers, Dordrecht, p.83
 Sorokin, P.P., Glowina, J.H. 1996, *ApJ* 473,900
 Tilford, S.G., Simmons, J.D. 1972, *J. Phys. Chem. Ref. Data* 1,147
 Ubachs, W., Hinnen, P.C., Reinhold, E. 1997, *ApJ Lett.* 476,L93
 Wallace, L., Livingston, W. *An Atlas of a Dark Sunspot Umbral Spectrum from 1970 to 8640 cm^{-1} (1.16 to 5.1 μm)*, NAO, P.O Box 26732, Tucson, AZ 85726, USA.