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Review of the Absorption Spectra of Solid O_2 and N_2 as They Relate to Contamination of a Cooled Infrared Telescope

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ABSTRACT

With the inclusion of one unpublished spectrum, the literature reveals that the absorption spectrum of the solid oxygen molecule has been thoroughly studied from visible to millimeter wavelengths. Only two lines appear in the solid that do not also appear in the gas or liquid. A similar result is implied for the solid nitrogen molecule because it also is homonuclear. The observed infrared absorption lines result from lattice modes of the α phase of the solid, and disappear at the warmer temperatures of the β, γ, and liquid phases. They are not observed from polycrystalline forms of O_2, while strong scattering is. It is concluded that scattering rather than absorption is the principal natural contamination problem for cooled infrared telescopes in low Earth orbit.

INTRODUCTION

It is well known that gases and liquids composed of the homonuclear molecules O_2 and N_2 have no strong infrared absorption spectra because the molecules do not possess an electric dipole moment. However, during contamination studies for the Shuttle Infrared Telescope Facility (SIRTF), a liquid helium cooled space telescope, the question arose as to what the absorption spectrum of the solid state of these molecules would be, and particularly what laboratory measurements of the solid had been made in the infrared. This note is the result of a literature search to answer those questions.

The SIRTF is a large (about one meter diameter) liquid helium cooled telescope that will be flown on the Space Shuttle at altitudes near 300 km. The telescope surfaces will be cooled to between 5 and 20 K, where O_2 and N_2 condense as solids. Because of the photodissociation of O_2, the natural atmosphere at 300 km is principally atomic oxygen, with 5–15% molecular nitrogen the next most common constituent (CIRA 1972). All other natural constituents make up <3%. Although the orbital velocity at 300 km gives the natural atmosphere a very high kinetic temperature (100,000 K) relative to the Shuttle, equilibrium arguments indicate that the temperature of the ambient atmosphere which moves along with the spacecraft will be nearer 300 K. After several collisions within the cold telescope walls the ambient oxygen atoms will have cooled sufficiently to "stick" to the low temperature surfaces. Because of the high binding energy of the molecule, it is expected that once oxygen atoms have condensed on a surface they will quickly migrate to form molecules, and at these temperatures then form some type of solid state lattice. Conceivably, over a period of weeks, enough material could condense on the optical surfaces to seriously degrade or contaminate the transmission of the telescope. The spectral region in which the SIRTF telescope is expected to operate extends from 1 to 700 μm, and ambient absorption occurring in this region is of concern.

A review of molecular terminology is first appropriate. Classical electrodynamics predicts that radiation will be emitted or absorbed by any atomic system that undergoes a change of its dipole moment. According to Herzberg (1945), in free unsymmetric molecules (such as CO or HCN) the normal (or Eigen) frequencies of vibration always produce a change of the molecule's electric dipole moment, hence always result in radiation. Such motions are called "infrared active" and produce strong infrared absorption. Some particular vibrations of symmetric polyatomic molecules (CO_2, for example) do not result in a change of an existing dipole moment and do not affect radiation. These symmetric vibrations are called "infrared inactive." Often, a symmetric molecule will have both infrared active and inactive frequencies associated with its dipole moment.

A free diatomic homonuclear molecule (H_2, N_2, O_2) has two identical nuclei and such a high degree of symmetry that it lacks an electric dipole moment. Consequently, the gaseous and liquid states of homonuclear molecules have no permitted infrared spectra at all (Herzberg, 1950). However, these molecules may have magnetic dipole and/or electric quadrupole moments. Changes of those moments do produce radiation, but at efficiency levels about 10^{-5} (magnetic dipole) and 10^{-9} (electric quadrupole), that of an electric dipole. Hence, magnetic dipole radiation is most often observed from long paths through a low pressure gas. During collisions in the liquid and high pressure states of the gas, intermolecular forces may also induce a temporary electric dipole moment. However, the intermolecular forces are rather weak and collisions have no large scale order, so the induced bands are also weak.

In the solid state (Hadni, 1967), intermolecular forces become regular throughout large volumes and thus more effective than in the gas or liquid. In addition, other effects such as rotational hindrance and electron exchange result from the regularity and spacing of the solid. So a dipole moment, which does not exist in the other physical states, may occur in the solid. In such case, oscillatory modes of the crystal lattice may be superimposed on the normal vibration modes of the molecule. Such lattice modes are represented by phonons and magnons, somewhat abstract entities derived from the oscillatory energy levels of the lattice. They carry away the energy, momentum, and parity necessary to preserve those same conservation laws in the overall (lattice + molecule) transition. Thus energy levels from which transitions are forbidden in the gas may become active in the solid through the assistance of a phonon or magnon. Further, pure phonon or magnon resonance absorptions can also occur. These are generally found in the far infrared because the energy involved is small.

The thorough review by Wachtel and Wheeler (1971) has been used in the following description of the free molecule and solid states of N_2 and O_2. Nitrogen is a homonuclear diatomic molecule with no unpaired electrons; hence, it has neither an electric nor a magnetic dipole moment. Its ground state is $^1\Sigma$. Although also homonuclear, O_2 has two unpaired electrons (one from the 2p shell of each of its atoms) whose orbital angular momenta cancel in the ground state, but whose spins add. This results in the molecule having a magnetic dipole moment which gives it a triplet ground state ($^3\Sigma$) and some interesting forbidden transitions.

In the solid state O_2 and N_2 form molecular crystals, that is, crystals in which the molecule retains its identity. Such crystals have temperature-dependent phases, each with a different crystal structure. O_2 has three solid phases. The α phase ($T < 23.8$ K) is monoclinic, of space group C_2h^3, with two molecules per unit cell. The β phase ($23.8 \text{ K} \leq T < 43.76$ K) is rhombohedral, D_3d^5, with one molecule per unit cell. The γ phase of O_2 ($43.76 \text{ K} \leq T < 54.39$ K = melting point) has eight molecules per unit cell, space group $O_h{}^3$, and a high degree of rotational disorder prior to transition to the liquid. N_2 has two solid phases described by St. Louis and Schnepp (1969). The α phase ($T < 35.6$ K) is face-centered cubic, of space group $P2_13(T^4)$, with four molecules per unit cell. The β phase of N_2 ($35.6 \text{ K} \leq T < 63.1$ K = melting point) is a hexagonal close-packed structure D_{6h}, with two molecules per unit cell and some disorder of the molecular axes relative to the crystal axis.

SOLID O_2 AND N_2: LITERATURE SEARCH, REVIEW, AND CONCLUSION

From the point of view of optical or infrared contamination it is particularly important that the observed absorption spectrum of solid O_2 be carefully studied because it is very difficult to predict which transitions will become active in the solid, even when molecular and crystal structures are quite well known. Subsequently, theoretical considerations may be used to evaluate what observational gaps exist.

Two literature search computer programs were used during June of 1976 and updated in September 1977. "DIALOGUE," a commercial program developed by Lockheed Missiles and Space Company, was utilized to search the general literature by indexing Chemical Abstracts, Science Abstracts, and the National Technical Information Service. "RECON," a program developed within the NASA library system, was used to search NASA's internal report base by indexing International Aerospace Abstracts and "STAR" (Science and Technology Aerospace Reports). Of many search headings employed, the most effective was intersection of the two sets "solid molecular oxygen" (or nitrogen) and "infrared absorption spectra." Critical reviews of the emission and absorption of O_2 by Krupenie (1972), and of N_2 by Lofthus and Krupenie (1977) were very helpful with the gas and liquid states. In addition, the Berkeley Newsletter of the University of California Physics and Astronomy Departments (edited by S. P. Davis and J. G. Phillips) was searched for the period from 1969 through mid-1977.

Because a null result is seldom reported, it was fortunate for this search that solid oxygen has some sufficiently unusual forbidden transitions to have generated a moderate infrared literature. In particular, we refer to two null spectral searches reported only in the footnotes and bibliographies of other papers. One, by P. N. Noble (1965), covered the range from 6.7 to 40 μm in search of an O_4 complex and was reported in the paper by Cairns and Pimentel (1965) as their reference 17. According to them, Noble deposited 26 millimoles (about 1/2 mm) of oxygen at 20 K without observing any absorption.

The other null search, by Anderson and Leroi (1965), covered the range from 25 to 400 μm in search of translational lattice modes in αO_2, and was mentioned in the paper by Laufer and Leroi (1971). According to a personal communication from Anderson and Leroi, they used an RIIC FS520 interferometer and did not observe any absorption from a deposit approximately 0.1 to 0.5 mm thick. They note that the large (~90%) scattering loss in the deposit produced noisy interferograms where "weak features could easily have been missed."

The principal results of this literature search are the observed absorption spectra of solid O_2 and N_2 shown in figures 1 and 2. Figure 1 shows that with the exception of a small gap from 1.25 to 3 μm, the spectrum of solid O_2 has been completely studied from 0.33 to 2500 μm. The study of solid N_2 (fig. 2) is not as complete. Asterisks (*) indicate that no spectral features were observed by the authors cited.

Both molecules exhibit their homonuclear nature in the solid in the same manner as they do in the gas and liquid, that is, by a dearth of strong transitions. Apparently the symmetric nature of the molecule prevents strong interaction with the lattice because only two transitions occur in the solid that do not also occur in the gas or liquid; and those transitions result from pure lattice modes. (This is more clearly shown in fig. 3 for O_2.) However, there are two frequency shifts (of 75 and 150 cm^{-1}, too small to appear in the figure) of some of the so-called "double" transitions in the visible which have been associated with a magnon resonance of the αO_2 lattice by Litvinenko *et al.* (1968) and by Wachtel and Wheeler (1971). Such shifts indicate that there is some interaction of lattice modes with the magnetic dipole of O_2. Lacking a magnetic dipole moment, N_2 does not have even this interaction.

The square brackets in figures 1 and 2 delineate the spectral region studied by the authors indicated directly below each bracket. Directly above each bracket is the range of solid thickness studied, with exception of the observations of Noble (1965), and Anderson and Leroi (1965), where the numbers give instead an estimate of the total thickness of material deposited. In all observations, the reported temperature was at least a few degrees below that of the α-β phase transition. Thus, all authors presumed their work to be done in the α phase. The word "annealed" in figure 1 means that a special annealing process was used to go from the gas to the α phase.

The 364 μm (27.5 cm^{-1}) magnon line in figure 1 was first observed by Blocker, Kinch, and West (1969). In footnote 3 of their paper they point out that the *thick crystals* and *unusual annealing process required to observe the line* probably account for it not having been seen before. The annealing process involved first condensing a large volume of pure gas onto a liquid helium cooled window, and then raising the sample temperature to 50 K (γ phase) and maintaining it there for some time before slowly cooling it through the $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ phase transitions. They also note that *unannealed gas samples* deposited at 4.2 K showed only an exponential attenuation that is *characteristic of scattering* by an amorphous powder of fine particles. By further slow variation of temperature, they showed that the 364-μm line gradually disappeared as the temperature increased to the $\alpha \rightarrow \beta$ transition at 23.8 K. They ascribed the source of the line to an antiferromagnetic resonance mode of the α phase lattice, that is to a $k = 0$ magnon. Wachtel and Wheeler (1970) constructed a phenomenological spin Hamiltonian (based on the known lattice structure and the assumption of isotropic antiferromagnetic electron exchange) which predicted not only the 364-μm line, but also a weaker line at 1560 μm (6.4 cm^{-1}). They repeated the earlier work and extended the observations to 2500 μm in order to measure the intensity ratio of the two lines. They also measured the magnetic field dependence of the lines to reinforce their identification as a magnon resonance. Wachtel and Wheeler (1971) thoroughly describe the structure of the solid molecule and how a magnon or phonon can interact with the ground configuration of the free molecule to produce shifts of some of the "double" transitions in the visible part of the spectrum.

Those shifts were studied by Eremenko *et al.* (1965), Eremenko and Litvinenko (1968), and by Litvinenko *et al.* (1968) in the α and β phases of a pure O_2 crystal, and also in a mixed crystal containing 15% N_2 and 85% O_2. They found that, like the 364 μm and 1560 μm lines, shifts of the "double" transitions gradually reduced to zero as the temperature increased toward the $\alpha \rightarrow \beta$ transition. They further observed that *the magnon shifts did not occur at all in the mixed crystal.* They concluded that the 15% N_2 impurity destroyed the large scale antiferromagnetic ordering of molecular spins thought necessary for the α phase lattice. Pavloshchuk and Shansky (1975) also observed shifts of the 1.06 μm and 1.26 μm IR transitions as progressively more and more N_2 was introduced into a mixed crystal. They describe mixed crystals where concentrations varied from (93% O_2 - 7% N_2) to (20% O_2 - 80% N_2). The calculated and observed oscillator strengths of the "double" transitions (Tsai and Robinson, 1969) are of the same magnitude as those of a magnetic dipole. English, Venables, and Salahub (1974) have also calculated the crystal structure and antiferromagnetism of the α phase.

The 143 μm (70 cm^{-1}) and 204 μm (49 cm^{-1}) phonon lines of αN_2 (fig. 2) were first observed by Anderson and Leroi (1966). They deposited the gas directly onto a liquid helium cooled window and observed a considerable amount of scattering. Attempts to remove the scattering by annealing were not successful. Schnepp (1967) calculated the intensities of these lines, which he considered to result from nonzero dipole derivatives of induced dipole moments associated with translational displacements of sublattices (phonon resonance). Ron and Schnepp (1967) measured their intensity ratio.

St. Louis and Schnepp (1969) remeasured the lines as a function of temperature and found that they also disappeared as the temperature increased to the $\alpha \rightarrow \beta$ phase transition at 35 K. They further observed that the lines had grossly different halfwidths and that their intensities were weaker, by a factor of about 5, than calculated. They concluded that the model used for the intensity calculations was not fully adequate. Wachtel (1972) has found some evidence of two very weak lines at 172 μm and 263 μm which she attributes to threefold degenerate $k = 0$ librational lattice modes. Those lines are not included in figure 2 because they were not reported by the three earlier observers who studied the same spectral region.

With regard to possible infrared contamination of a cooled telescope, it is important to note that the lines of both solid molecules result from resonance modes of *only* the α phase lattice, and that the magnon lines of αO_2 appear *only* after a careful annealing process has been followed to produce the α phase. Also, the magnon shifts did not occur in the mixed crystal. It is not clear from this review of the literature whether the failure to anneal prevents the magnon resonance from forming, or whether the scattering from the many small crystallites in the unannealed form overpowers the absorption.

What is quite significant to the contamination problem is the "collective" observation that *thin film* deposition of O_2 at liquid helium temperatures produces a strongly scattering polycrystalline solid which shows no absorption features between 3 μm and 2500 μm. Note that Anderson and Leroi (1965) did not anneal and they failed to observe the strongest magnon line at 364 μm, while both they and Blocker *et al.* (1969) specifically mention the strong scattering. The collision-induced fundamental band at 6.4 μm seen by Cairns and Pimentel (1965) appears only in quite thick samples, since Mantz *et al.* (1974) did not see it with thicknesses below 0.04 mm. Thus, it is clear from this review that scattering rather than absorption by the condensed natural atmosphere is the principal contamination problem for a cooled infrared space telescope.

COMPILATION OF GAS, LIQUID, AND SOLID SPECTRA

For the purpose of comparison, the spectral features of the gas and liquid were also compiled. They are listed together with those of the solid in tables 1 and 2; however, no claim is made to the completeness of their reference list as it is for the solid. In particular, the reviews by Krupenie (1972), and Lofthus and Krupenie (1977) contain much more complete lists for both gases and liquids than do these tables.

Figures 2 and 3 provide a graphic comparison of the spectral features of each molecule by physical state It should be noted here that the visible wavelength bands of oxygen's Schumann-Runge and Herzberg I and II systems have not been shown in the gas phase of figure 3 because they are only small parts of large ultraviolet systems and are seldom seen in absorption. For the same reason, three weak visible bands of the Rydberg system of nitrogen (Ledbetter, 1972) have not been shown in the gas phase of figure 2.

Collision-induced absorption was first observed by Crawford, Welsh, and Locke (1949) in the high pressure gas and liquid phases of O_2 and N_2. They showed that the fundamental vibrational transition arose from transient dipole moments induced by intermolecular forces during collisions in the high density phases. Collisions induce three bands in N_2 (fig. 2), but only the fundamental vibration has been observed in the solid (Smith *et al.*, 1950). Both the fundamental and its first overtone have been seen in high pressure gas (Shapiro and Gush, 1966). Spectral features attributed to the nitrogen dimer $[N_2]_2$, a transitory complex made of two molecules weakly bound by Van der Waals forces, have been observed superimposed on the fundamental band in a low temperature, long-path absorption cell by Long, Henderson, and Ewing (1973). Dianov-Klokov and Malkov (1973) see similar features in both a long-path cell and the Earth's atmosphere. A dimer of oxygen $[O_2]_2$ has been postulated by several authors, but according to Krupenie (1972) its presence has not been unequivocally established. Bosomworth and Gush (1965) describe unusually broad far IR bands in both N_2 and O_2 that are seen in both high pressure gas and liquid (Jones, 1970; Buontempo *et al.*, 1975). They are attributed to a coupled translation-rotation mode of the molecule interacting with a collision-induced dipole moment (Rastogi and Lowndes, 1977).

Because the oxygen molecule has an electron spin and associated magnetic dipole moment that is absent in N_2, oxygen has several additional lines and bands. These can best be seen by comparing the gas spectra of figures 2 and 3. Since the lifetime of magnetic dipole transitions is long (~0.01-1 sec), they are most often apparent in gas where de-exciting collisions are not frequent. Long sight paths also help to make them apparent. However, it has been known for some time that the magnetic dipole electronic transitions in the visible and near IR are enhanced in the solid, liquid, and high pressure gas (Akimoto and Pitts, 1970). Blickensderfer and Ewing (1969a, 1969b) have shown that they are also enhanced in low temperature, low pressure gas. This enhanced absorption has a quadratic dependence on density and is attributed to collision-induced dipole moments (Robinson, 1967; Tabisz *et al.*, 1969). Figure 3 shows that the far IR magnetic dipole rotational lines of the gas are not present in the solid, while the collision-induced magnetic dipole electronic bands of the visible are. This occurs because rotational motions by a molecule are literally frozen out of the solid while electronic transitions within a molecule are not. Figure 3 clearly shows the gross change of the spectrum as one progresses through the stages of condensation from gas to solid, and how the magnon lines of the αO_2 lattice emerge.

SUMMARY AND CONCLUSION

This search and review of the literature has revealed the following points.

1. The spectrum of solid O_2 has been thoroughly studied from 0.33 μm to 2500 μm, with only a small gap from 1.25 μm to 3 μm omitted.

2. Only two transitions occur in solid O_2 that do not also occur in the gas and liquid. These result from purely lattice resonance modes.

3. Lattice resonance absorptions in O_2 and N_2 (and shifts in O_2) occur only in the α phase of the solid.

4. The magnon resonance absorption in αO_2 occurs only in *thick* (≥5 mm) samples which have been *specially annealed*.

5. A mixed crystal with 85% O_2 and 15% N_2 will condense, but it is quite doubtful that it has the large scale magnetic ordering necessary for a magnon resonant mode.

6. Thin film deposition (<0.05 mm) of O_2 gas on 4 K surfaces produces:

   a. No observed absorption features between 3 μm and 2500 μm

   b. A strongly scattering polycrystalline solid.

It is therefore concluded that scattering by a condensed phase of the naturally occurring atmosphere near 300 km is a more serious problem than absorption for the cold optics of SIRTF.

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TABLE 1.- OBSERVED O_2 ABSORPTION LINES AND BANDS

Wavelength (µm)	State[a]	Type of transition	Name	Reference
0.343-0.378 .397- .479 .494- .627	HPG, L, S	Collision-induced magnetic dipole electronic band transitions in two molecules simultaneously; with magnon or phonon shifts in the solid state	"Double" transitions	Landau *et al.* (1962) Eremenko *et al.* (1965) Wachtel and Wheeler (1971) Litvinenko *et al.* (1968) Tabisz *et al.* (1969)
0.69-0.76 .81-1.27	LGP, HPG, L, S	Magnetic dipole electronic bands in low pressure, long path gas. Collision induced transitions at higher density.	Atmospheric Infrared	Giver *et al.* (1974) Dianov-Klokov (1966) Pavloshchuk *et al.* (1975)
3.24	HPG	Collision-induced vibration band	1st overtone	Shapiro and Gush (1966)
6.43	HPG, L, S	Collision-induced vibration band	Fundamental	Cairns & Pimentel (1965) Smith *et al.* (1950)
41-220	HPG	Collision-induced rotation band	--	Bosomworth & Gush (1965)
60-450	Liquid	Collision-induced rotation band	--	Jones (1970)
86 105 120 165 204 267 387 706	LGP only	Magnetic dipole rotation lines	Magnetic dipole rotation	MacQueen *et al.* (1968) Gebbie *et al.* (1969)
364	Solid, α phase only	Magnon resonance line	--	Blocker *et al.* (1969)
1560		Magnon resonance line	--	Wachtel and Wheeler (1970)

[a] HPG = high pressure gas; L = liquid; S = solid; and LGP = long gas path at either one or only a few atmospheres.

TABLE 2.- OBSERVED N_2 ABSORPTION LINES AND BANDS

Wavelength (μm)	State[a]	Type of transition	Name	Reference
2.16	HPG	Collision-induced vibration band	1st overtone	Shapiro and Gush (1966)
4.33	HPG,L,S	Collision-induced vibration band	Fundamental	Shapiro and Gush (1966) Smith *et al.* (1950)
50–200	HPG	Collision-induced rotation band	--	Bosomworth and Gush (1965)
70–390	Liquid	Collision-induced rotation band	--	Jones (1970) Buontempo *et al.* (1975)
143	Solid, α phase only	Phonon resonance line	--	Anderson and Leroi (1966)
204		Phonon resonance line	--	Ron and Schnepp (1967) St. Louis and Schnepp (1969) Wachtel (1972)

[a] HPG = high pressure gas; L = liquid; and S = solid.

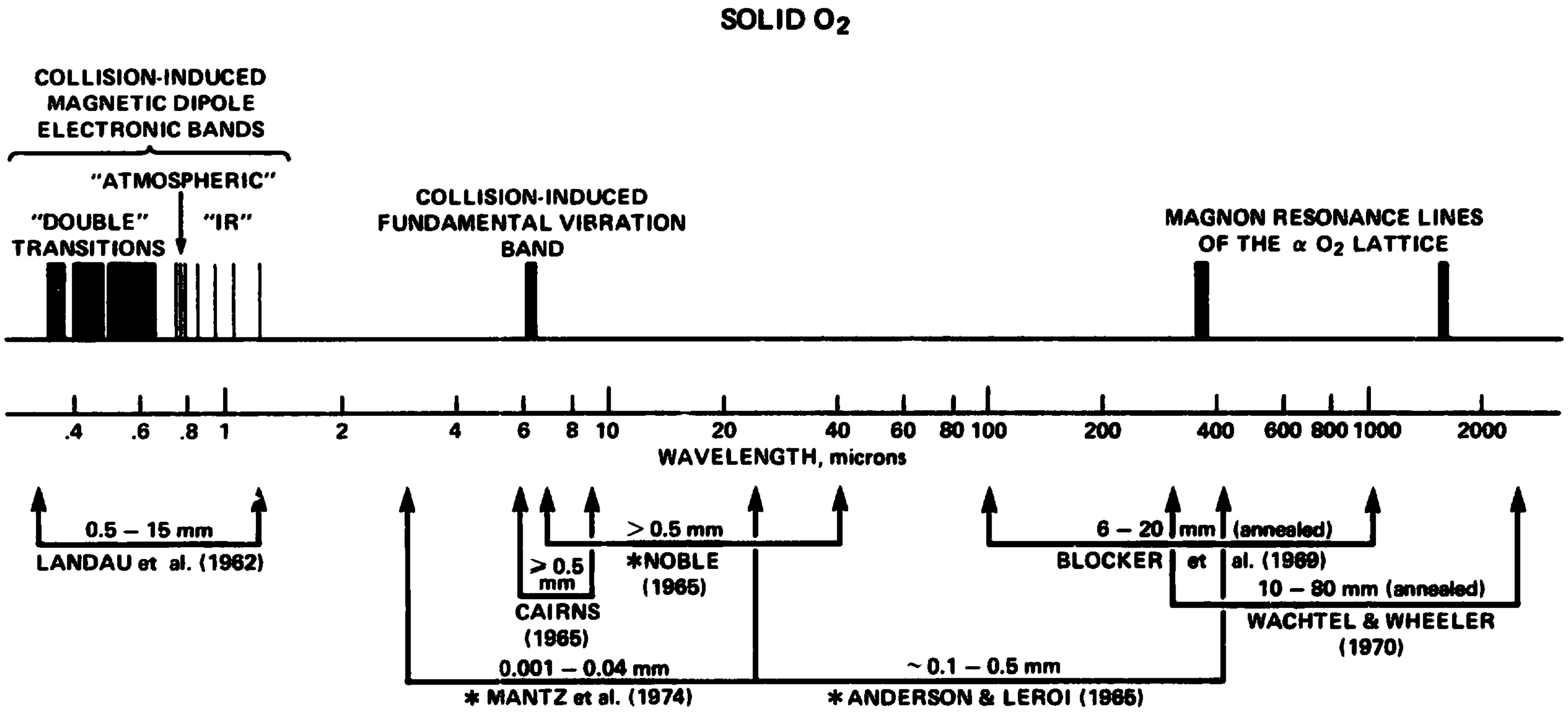

Figure 1.- The observed absorption spectrum of solid O_2 (from the literature). Square brackets delineate the spectral region studied by the authors indicated. An asterisk indicates that no features were seer. The observed lines and bands are indicated by rectangles whose widths approximate reported half-widths. Sample thicknesses are indicated within the brackets.

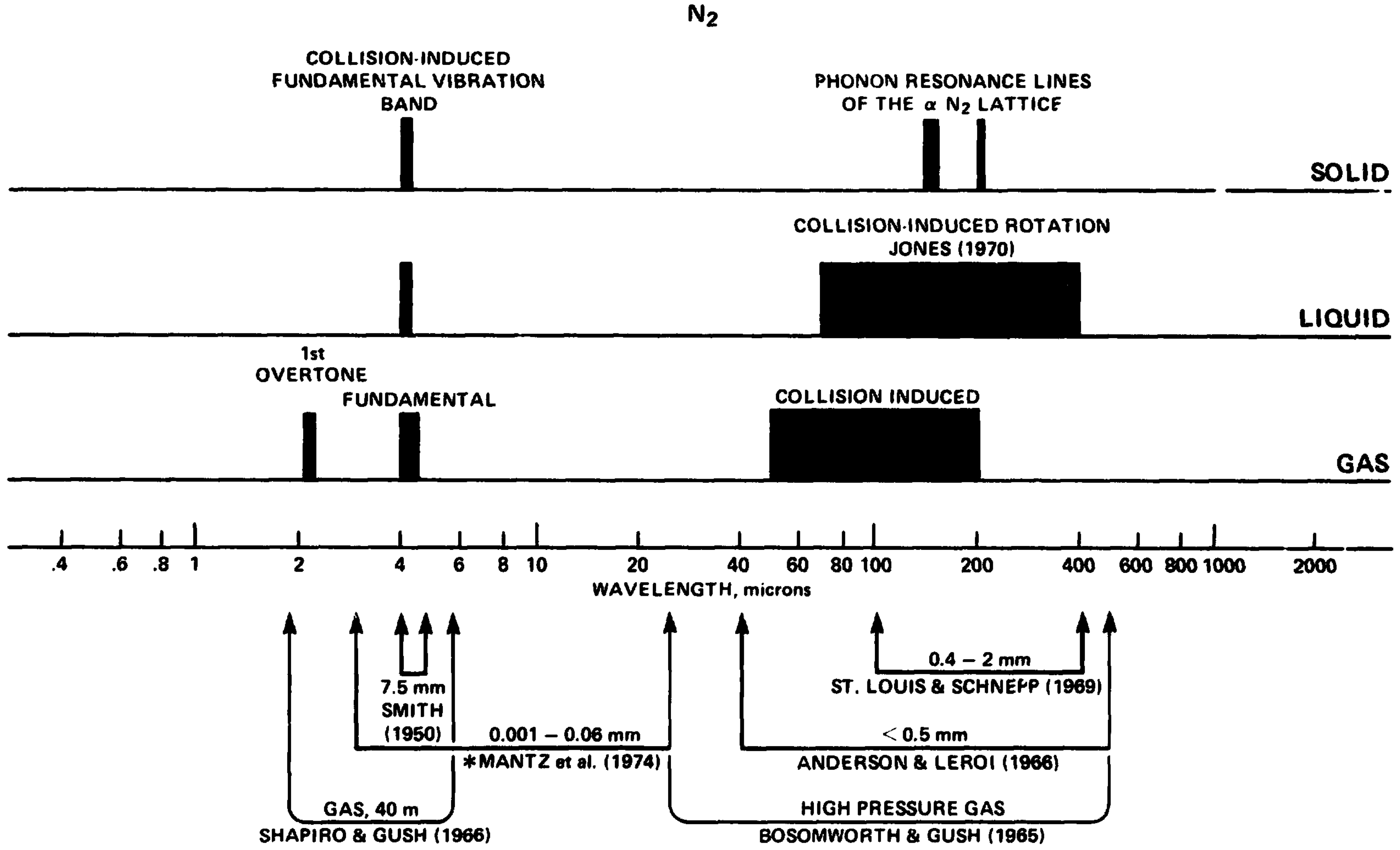

Figure 2.- The observed absorption spectra of N_2 differentiated by physical state (from the literature). Square brackets delineate the spectral region of the solid studied by the authors indicated; rounded brackets do the same for the gas. An asterisk indicates that no features were seen in the solid. The observed lines and bands are indicated by rectangles whose widths approximate reported half-widths. Sample thicknesses are indicated within the brackets.

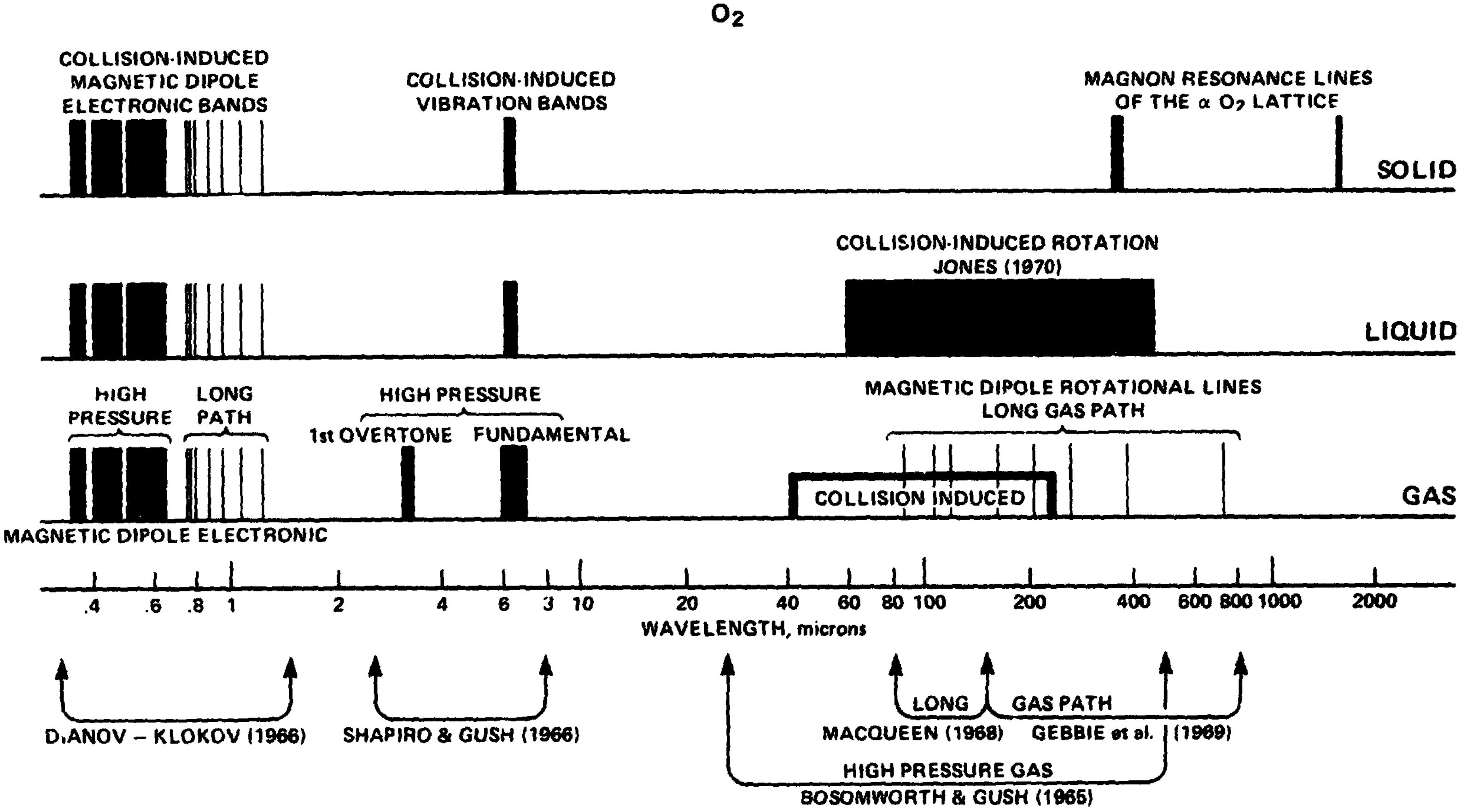

Figure 3.- The observed absorption spectrum of O_2 differentiated by physical state (from the literature). Rounded brackets indicate literature sources for the gas spectra. The solid spectrum is from figure 1. Rectangle widths approximate reported half-widths.

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16 Abstract

With the inclusion of one unpublished spectrum, the literature reveals that the absorption spectrum of the solid oxygen molecule has been thoroughly studied from visible to millimeter wavelengths. Only two lines appear in the solid that do not also appear in the gas or liquid. A similar result is implied for the solid nitrogen molecule because it also is homonuclear. The observed infrared absorption lines result from lattice modes of the α phase of the solid, and disappear at the warmer temperatures of the β, γ, and liquid phases. They are not observed from polycrystalline forms of O_2, while strong scattering is. It is concluded that scattering rather than absorption is the principal natural contamination problem for cooled infrared telescopes in low Earth orbit.

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