International Journal of Infrared and Millimeter Waves, Vol. 12, No. 6, 1991

ON THE USE OF O_2 SPIN-ROTATION LINES FOR ELEVATION ANGLE CALIBRATION OF ATMOSPHERIC THERMAL EMISSION SPECTRA

K. V. Chance, W. A. Traub, K. W. Jucks, and D. G. Johnson

Harvard-Smithsonian Center for Astrophysics

Received February 7, 1991

Abstract

The magnetic dipole-allowed spin-rotation lines of O_2 potentially can be used for pointing calibration and confirmation of float altitude for far infrared spectra of the stratosphere obtained from balloon platforms. We demonstrate that current deficiencies in the spectroscopic database, particularly the air pressure-broadening coefficients, severely limit the capability of deriving useful pointing calibrations, and that precise pressure-broadening measurements for the transitions actually used in calibration are needed to improve this capability.

INTRODUCTION

Thermal emission spectroscopy from balloon and satellite platforms is capable of measuring a number of stratospheric gases that are important for understanding the photochemistry of the Earth's ozone layer (Chance et al., 1985, 1989; Traub et al., 1990, Carli et al., 1985, 1989; Carli and Park, 1988). The technique has the strength that it can make measurements throughout the diurnal cycle. A requirement for emission measurements is that, unlike solar absorption measurements, the instrument pointing must be absolutely determined without a built-in reference (i.e., the solar position). The need for absolute angular pointing information is particularly important in limb-viewing, the normal method for stratospheric measurements, where the measurement heights are steep functions of viewing angle. This determination must be made for a viewing platform, the balloon gondola, that is inherently subject to substantial tilts and pendulum motions. For measurements from satellite platforms which, due to their greater distance from the horizon, have measurement heights which are much stronger functions of viewing angle than for balloon platforms, absolute pointing calibration is even more demanding. The methods used to determine viewing angle include mechanical means (Coyle et al., 1986; Traub et al., 1986)

0195-9271/91/0600-0581$06.50/0

and the use of atmospheric lines from well-mixed constituents in the atmospheric spectra themselves. The use of atmospheric emission lines includes CO_2 in the mid infrared (Gille and Russell, 1984), and the magnetic dipole-allowed spin-rotational lines of O_2 in the far infrared (Abbas et al., 1987; Carli and Park, 1988). The latter study also used O_2 spin-rotational lines to determine the float height of the balloon gondola.

In this paper we discuss some radiative transfer considerations for determination of pointing information from line measurements and the current status of the line parameters available for the analysis of atmospheric spectra to obtain pointing information from O_2 far infrared lines.

CALCULATIONS AND DISCUSSION

At altitudes below 40 km the stratospheric lines of O_2 are well-approximated as Lorentzian lines with widths determined by pressure broadening from the ambient air (the Doppler/Lorentz crossover point for the highest frequency line considered here is at ~45 km). The lines have halfwidths of typically 2×10^{-4} - 2×10^{-3} cm^{-1} over the range of stratospheric pressure. The lines as observed by the current generation of instruments (e.g., Fourier transform spectrometers with resolutions of 0.003-0.004 cm^{-1}) are unresolved except in the lowest part of the stratosphere. This means that the information content is primarily in the line equivalent widths. As with most prominent lines in the far infrared stratospheric spectrum, the spin-rotational lines of O_2 are fully saturated, that is, the observed line equivalent widths are proportional to $\sqrt{Sb}$, where S is the line intensity, and b is the Lorentzian line width (Penner, 1959). Thus, the line intensities and the air pressure-broadening coefficients for O_2 at stratospheric temperatures are of equal importance for the determination of pointing or altitude information from measured spectra. The positions of the O_2 spin-rotational lines are precisely known from laboratory measurements (Mizushima et al., 1984; Boreiko et al., 1984; Pickett et al., 1981, Jennings et al., 1987) and can be readily identified in stratospheric spectra.

The O_2 electronic ground state is $^3\Sigma_g^-$: The molecule possesses an electronic spin angular momentum, S, of 1, with no net electronic orbital angular momentum. The total angular momentum, J, is determined from the coupling of the rotational angular momentum N with S. The spectrum of magnetic dipole-allowed transitions includes microwave lines (ΔN=0, ΔJ=1) and far infrared lines (ΔN=2, ΔJ=0,1); additional, much weaker, lines are allowed through the interaction of the molecular electric quadrupole moment with radiation. Only states with odd N are allowed for $^{16}O_2$. As the interaction with radiation for the magnetic dipole-allowed transitions is due to the magnetic dipole moment of very close to 2 Bohr magnetons, with small, well-determined corrections to the electron spin magnetic g factor from relativistic and diamagnetic effects, and inclusion of small terms from spin-orbit and spin-rotation interactions (Tinkham and Strandberg, 1955a,b; Bowers et al., 1959; Mizushima et al., 1984), the matrix elements from which line intensities are determined are quite accurate. Variation of the line intensities with temperature is due to the changing Boltzmann factors, which are readily calculated from the precisely-known energy levels. The overall intensities are calculable to at least 2% accuracy from the eigenvectors which diagonalize the Hamiltonian, and measured g-values (Tinkham and Strandberg, 1955a; Bowers et al., 1959; Boreiko et al., 1984; H. M. Pickett, private communication, 1990). The values in the current Air Force Geophysics Laboratory HITRAN listing (Rothman et al., 1987), however, are from earlier calculations and are in error by more than 5% for some lines.

Knowledge of air-broadening coefficients is currently much less precise than that of line intensities. A number of measurements of self-broadening, and a few of nitrogen-broadening or of air-broadening have been made on the microwave lines (Anderson et al., 1952; Hill and Gordy, 1954; Pickett et al., 1981; Stafford and Tolbert, 1963; Tinkham and Strandberg, 1955c; Zimmerer and Mizushima, 1961). Some of these studies have been made over temperature ranges which span the stratospheric temperature range (Hill and Gordy, 1954; Pickett et al., 1981; Tinkham and Strandberg, 1955c). Only a few measurements have been made of the far infrared, spin-rotational lines, including O_2 and N_2 broadening of the S_1Q_2 line at 14.17 cm^{-1} (Pickett et al., 1981) and two lines at higher frequency: the S_9Q_{10} line at 60.46 cm^{-1} and the $S_{13}Q_{14}$ line at 83.47 cm^{-1} (Jennings et al., 1987; Nolt et al., in preparation - K. Chance, private communication, 1990). The current HITRAN line parameter listing contains values for far infrared lines that are obtained from self-broadening (i.e., broadening only by O_2) studies of the $\Delta N=0$ microwave lines at 300 K (Battaglia and Cattani, 1968; Anderson, Smith, and Gordy, 1952; Hill and Gordy, 1954; Krupenie, 1972) by matching the lower state of the far infrared line with that of one of the microwave lines. They are extrapolated for spin-rotational transitions from states not included in the microwave measurements. These listings include a suggested temperature coefficient for all lines of n = -0.5, where $\gamma(T) = \gamma(296)(T/296)^n$. γ is the pressure-broadening coefficient and 296 K is the standard temperature for compilation. The value -0.5 is that for hard sphere broadening interactions. We note that measured temperature coefficients for air broadening vary considerably with transition, but tend to be somewhat larger than 0.5 (Hill and Gordy, 1954; Pickett et al., 1981; Tinkham and Strandberg, 1955c). The O_2 line parameters were added to the listing in present form in the 1982 update (Rothman et al., 1983). The HITRAN values are extensively used for the determination of pointing

TABLE 1. O_2 Air-Broadening Measurements (cm^{-1} atm^{-1})[a]

ν (cm^{-1})	γ(AFGL) 296 K	γ(other) 295-300 K	n(other)	γ(AFGL) 245 K	γ(other) 245 K
1.9496	0.0440	0.0525[b]	-0.85	0.0484	0.0623
1.9877	0.0420	0.0456[b]	-0.90	0.0462	0.0548
1.9735	0.0440	0.0510[b]	-0.84	0.0484	0.0604
1.9455	0.0430	0.0492[b]	-0.76	0.0473	0.0574
3.9611	0.0500	0.0546(24)[c]	-0.82	0.0550	0.0635(28)
14.1686	0.0450	0.0658(71)[c]	-0.15	0.0495	0.0677(73)
60.4554	0.0400	-	-	0.0440	0.0511(20)[d]
83.4685	0.0380	0.0441(43)[e]	-	0.0418	-

[a] Uncertainties are 1σ, in the final digits.
[b] Hill and Gordy, 1954. No uncertainties given.
[c] Pickett et al., 1981.
[d] Jennings et al., 1987. Measured at 245 K.
[e] Nolt et al., manuscript in preparation.

information from atmospheric measurements (Carli and Park, 1988).

We compare the parameters in the HITRAN listing with other, mostly more current, measurements at stratospheric temperature, to see the implications for analysis of stratospheric spectra. The comparison is made at 245 K, corresponding to a typical balloon float altitude of 38 km and to the temperature of the published air pressure-broadening measurement for the S_9Q_{10} line at 60.46 cm^{-1} (Jennings et al., 1987). Values chosen for comparison include those where air-broadening and its temperature dependence have been measured, plus the additional far infrared measurements. Table 1 shows the values in the HITRAN listing at the standard 296 K temperature; the other measurements at temperatures of 295-300 K (plus that of the 60.46 cm^{-1} lines at its 245 K measurement temperature) and their temperature coefficients when available; the HITRAN values calculated at 245 K; and the other values at 245 K. Measured values in the table include 1σ uncertainties, when available.

The measured air-broadening values at 245 K (column 6) for which experimental uncertainties are available have an average 1σ uncertainty of 6%. Note that the uncertainties for the lines at 3.96 and 14.17 cm^{-1} are calculated without including uncertainties in temperature dependences and, thus, may be slightly low. The uncertainties for air-broadening of rotational lines taken from O_2-broadening of rotationless lines in HITRAN (column 5) are unknown. Battaglia and Cattani (1968) estimate the error for their microwave self-broadening studies at 5-7%, and Anderson, Smith, and Gordy estimate the error for theirs at 20% (two lines from this latter study are used in HITRAN); these values cannot, of course be applied to the far infrared lines since they do not take the different quantum levels and different broadening partners into account. The column 6 values are systematically 23±8% larger than the values derived from the HITRAN database using the recommended temperature coefficient of 0.5. Thus, pointing or gondola altitude results obtained using the HITRAN coefficients will be uncertain by at least 24% in airmass, even before consideration of other experimental error sources. This amount corresponds to an error of ~2 km in balloon altitude or measurement tangent height. The 23% systematic bias that our calculations suggest corresponds to measurement altitudes that are low by a corresponding amount and, thus, retrieved relative concentrations (i.e., mixing ratios) for other species that are correspondingly low. Note that our calculated bias is highly uncertain, and that we do not recommend applying it as a correction for calibrations (we note that it includes measurements for which there are no published uncertainties). Rather, we consider it to be a determination that shows the scale of possible errors and a preliminary indication that it may be possible to extend measured pressure-broadening coefficients with appropriate theoretical calculations once sufficient laboratory measurements of sufficient accuracy are obtained. For the present, only lines with measured air-broadening coefficients, and their temperature dependences, are reliable for calibration of field spectra. Measurement uncertainties from the laboratory translate directly into proportional uncertainties in pointing or altitude and must be included in the subsequent error analyses for atmospheric constituent determinations.

REFERENCES

Abbas, M. M., J. Guo, B. Carli, F. Mencaraglia, A. Bonetti, M. Carlotti, and I. G. Nolt, Stratospheric O_3, H_2O, and HDO distributions from balloon-based far-infrared observations, *J. Geophys. Res. 92,* 8354-8364 (1987).

Anderson, R. S., W. V. Smith, and W. Gordy, Line-breadths of the microwave spectrum of oxygen, *Phys. Rev 87,* 561-568 (1952).

Battaglia, A., and M. Cattani, Broadening of oxygen in the microwave region at low pressures, *Nuovo Cimento Ser. 10 54B,* 293-303 (1968).

Boreiko, R. T., T. L. Smithson, T. A. Clark, and H. Wieser, Line strengths and positions of the submillimeter magnetic dipole transitions of O_2, *J. Quant. Spectrosc. Radiat. Transfer 32,* 109-117 (1984).

Bowers, K. D., R. A. Kamper, and C. D. Lusig, Paramagnetic resonance absorption in molecular oxygen, *Proc. R. Soc. Lond. A 251,* 565-574 (1959).

Carli, B., F. Mencaraglia, A. Bonetti, M. Carlotti, and I. Nolt, Detection of atomic oxygen and further line assignments in the far-IR stratospheric spectrum, *Int. J. of IR and MM Waves 6,* 149-176 (1985).

Carli, B., and J. H. Park, Simultaneous measurement of minor stratospheric constituents with emission far-infrared spectroscopy, *J. Geophys. Res. 93,* 3851-3865 (1988).

Carli, B., B. M. Dinelli, F. Mencaraglia, and J. H. Park, The mixing ratio of the stratospheric hydroxyl radical from far-infrared emission measurements, *J. Geophys. Res. 94,* 11,049-11,058 (1989).

Chance, K. V., W. A. Traub, B. Carli, I. G. Nolt, and J. V. Radostitz, Far-infrared spectroscopy of the earth's stratosphere, *Proc. AIAA/NASA Earth Observing System Conference,* AIAA-85-3006 (1985).

Chance, K. V., D. G. Johnson, and W. A. Traub, Measurement of stratospheric HOCl: concentration profiles, including diurnal variation, *J. of Geophys. Res. 94,* 11,059-11,069 (1989).

Coyle, L. M., G. Aurilio, G.U. Nystrom, J. Bortz, B.G. Nagy, K.V. Chance, and W.A. Traub, Design of a single-axis platform for balloon-borne remote sensing, *Review of Scientific Instruments 57,* 2512 (1986).

Hill, R. M., and W. Gordy, Zeeman effect and line breadth studies of the microwave lines of oxygen, *Phys. Rev. 98,* 1019-1022 (1954).

Gille, J. C., and J. M. Russell III, The Limb Infrared Monitor of the Stratosphere: experiment description, performance, and results, *J. Geophys. Res. 89,* 5125-5140 (1984).

Jennings, D. A., K.M. Evenson, M.D. Vanek, I.G. Nolt, J. V. Radostitz, and K.V. Chance, Air- and oxygen-broadening coefficients for the O_2 rotational line at 60.46 cm^{-1}, *Geophys. Res. Lett. 14,* 722-725 (1987); erratum *Geophys. Res. Lett. 14,* 981 (1987).

Krupenie, P. H., The spectrum of molecular oxygen, *J. Phys. Chem. Ref. Data 1,* 423-534 (1972).

Mizushima, M., L. R. Zink, and K. M. Evenson, Rotational structure of $^{16}O_2$, $^{16}O^{17}O$, and $^{16}O^{18}O$ ($X^3\Sigma_g^-$) from Laser Magnetic Resonance spectra, *J. Mol. Spectrosc. 107,* 395-404 (1984).

Penner, S. S., *Quantitative Spectroscopy and Radiative Transfer,* Addison-Wesley, Reading, MA, London U. K., 1959.

Pickett, H. M., E. A. Cohen, and D. E. Brinza, Pressure broadening of oxygen and its implications for cosmic background measurements, *Astrophysical Journal 248,* L49-L51 (1981).

Rothman, L. S., R. R. Gamache, A. Barbe, A. Goldman, J. R. Gillis, L. R. Brown, R. A. Toth, J.-M. Flaud, and C. Camy-Peyret, AFGL atmospheric absorption line parameters listing: 1982 edition, *Applied Optics 22,* 2247-2256 (1983).

Rothman, L. S., R. R. Gamache, A. Goldman, L. R. Brown, R. A. Toth, H. M. Pickett, R. L. Poynter, J.-M. Flaud, C. Camy-Peyret, A. Barbe, N. Husson, C. P. Rinsland, and M. A. H. Smith, The HITRAN database:

1986 edition, *Appl. Opt. 26,* 4058-4097, 1987.

Stafford, L. F., and C. W. Tolbert, Shapes of oxygen absorption lines in the microwave frequency region, *J. Geophys. Res. 68,* 3431-3435 (1963).

Tinkham, M., and M. W. P. Strandberg, Theory of the fine structure of the molecular oxygen ground state, *Phys. Rev. 97,* 937-951 (1955a).

Tinkham, M., and M. W. P. Strandberg, Interaction of molecular oxygen with a magnetic field, *Phys. Rev. 97,* 951-966 (1955b).

Tinkham, M., and M. W. P. Strandberg, Line breadths in the microwave magnetic resonance spectrum of oxygen, *Phys. Rev. 99,* 537-539 (1955c).

Traub, W. A., K.V. Chance, and L.M. Coyle, Performance of a single-axis platform for balloon-borne remote sensing, *Review of Scientific Instruments 57,* 2519 (1986).

Traub, W. A., D. G. Johnson, and K. V. Chance, Stratospheric hydroperoxyl measurements, *Science 247,* 446-449 (1990).

Zimmerer, R. W., Precision Zeeman modulation microwave spectrometer, *Review of Scientific Instruments 31,* 106-111 (1960).

Zimmerer, R. W., and M. Mizushima, Precise measurement of the microwave absorption frequencies of the oxygen molecule and the velocity of light, *Phys. Rev. 121,* 152-155 (1961).