UCRL-ID-121512

Radiative Forcing Calculations for CH_3Br

Allen S. Grossman
Global Climate Research Division, L-262
Lawrence Livermore National Laboratory
P.O. Box 808
Livermore, CA 94550

William E. Blass
Dept. of Physics and Astronomy
University of Tennessee
Knoxville, TN 37996-1200

Donald J. Wuebbles
Dept. of Atmospheric Sciences
University of Illinois
Urbana, IL 61801

June 1995

Lawrence
Livermore
National
Laboratory

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information
P.O. Box 62, Oak Ridge, TN 37831
Prices available from (615) 576-8401, FTS 626-8401

Available to the public from the
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd.,
Springfield, VA 22161

Radiative Forcing Calculations for CH_3Br

Allen S. Grossman
Global Climate Research Division, L-262
Lawrence Livermore National Laboratory
P.O. 808
Livermore, CA 94551

William E. Blass
Dept. of Physics and Astronomy
University of Tennessee
Knoxville, TN 37996-1200

Donald J. Wuebbles
Dept. of Atmospheric Sciences
University of Illinois
Urbana, Il 61801

June 1995

Abstract

Methyl Bromide, CH_3Br, is the major organobromine species in the lower atmosphere and is a primary source of bromine in the stratosphere. It has a lifetime of 1.3 years. The IR methyl bromide spectra in the atmospheric window region, 7 - 13μ, was determined using a well tested Coriolis resonance and ℓ-doubling (and ℓ-resonance) computational system. A radiative forcing value of 0.00493 W/m^2/ppbv was obtained for CH_3Br and is approximately linear in the background abundance. This value is about 2 percent of the forcing of CFC-11 and about 278 times the forcing of CO_2, on a per molecule basis. The radiative forcing calculation is used to estimate the global warming potential (GWP) of CH_3Br. The results give GWPs for CH_3Br of the order of 13 for an integration period of 20 years and 4 for an integration period of 100 years (assuming CO_2 = 1, following IPCC [1994]). While CH_3Br has a GWP which is approximately 25 percent of the GWP of CH_4, the current emission rates are too low to cause serious atmospheric greenhouse heating effects at this time.

I. Introduction

Methyl Bromide, CH_3Br, is the major organobromine species in the lower atmosphere (Kaye et al., 1994, "K1"). The data of Singh et al. (1983) suggests that the most significant natural sources of CH_3Br are the oceans. A review by K1 of the measurements of Penkett et al. (1985) and Cicerone et al. (1988), shows an average northern hemisphere concentration of 12 - 15 pptv and an average southern hemisphere concentration of 1 - 11 pptv. K1 concludes that this gradient indicates a significant land based source which is most probably anthropogenic and due to fumigation. WMO (1994) reports a mean northern hemisphere concentration of between 11 - 15 pptv and a mean southern hemisphere concentration of 8 - 11 pptv. WMO (1994) gives a northern/southern hemisphere gradient in the CH_3Br mean mixing ratio in the range of 1.15 - 1.45, also indicating a significant land based source. The atmospheric lifetime for CH_3Br varies from 1.3 years, (IPCC, 1994) with a range of 1.2 - 2.0 years (WMO, 1994).

CH_3Br is also, on dissociation, an important source of bromine in the stratosphere, where its dissociation accounts for ~54 percent of the total (18 pt) bromine in the stratosphere and almost all of the reactive bromine (WMO, 1994). The resulting bromine is thought to be an

HH

important contributor to ozone destruction in the lower stratosphere (WMO, 1994). According to WMO (1994) the ozone depletion potential (ODP) of CH_3Br is 0.61. This index shows that CH_3Br is a reasonably effective ozone depleting agent, per unit mass emission, compared to CFC-11 (ODP = 1).

The main purpose of this paper is to calculate the tropospheric radiative forcing of CH_3Br using a correlated k-distribution radiative transfer model and a newly determined spectroscopic line data set for CH_3Br. The calculation will be done for a globally and annually averaged model atmosphere with a representative cloud distribution. Global warming potential (GWP) calculations for CH_3Br will be made and compared to GWP's for other trace gases as derived for IPCC (1994).

II. CH_3Br DATA

Methyl bromide has six fundamental vibration-rotation bands, ν_1 through ν_6 found at 2972, 1305, 611, 3056, 1445, and 952 cm^{-1} respectively (Graner, 1982). Graner (1982) summarizes and interprets all of the significant laboratory studies and analysis in a comprehensive review. Antilla et al. (1983) extended and improved upon the Graner (1982) and Graner and Blass (1975) analyses of ν_2 and ν_5 in a comprehensive laboratory study. The molecular parameters of Antilla et al. were used to model the ν_2 and ν_5 spectra in this work. For ν_3 and ν_6, the molecular parameters given by Graner (1982) as the best available parameters reduced from existing laboratory data were used in modeling the spectra. No attempt was made to model and use data from the ν_1 and ν_4 bands near 3000 cm^{-1}. The ν_4 band contributes only 7 percent of the fundamental intensity according to van Straten and Smit (1977) while the ν_1 and $2\nu_5$ bands are highly perturbed and not readily amenable to accurate modeling. These two bands contribute 28 percent of the fundamental intensity but were considered less consequential due to the position of the bands in the 3000 cm^{-1} region.

The methyl bromide vibration-rotation line spectra were modeled using a well tested Coriolis resonance and ℓ-doubling (and ℓ-resonance) computational system called PERTCOR (Blass, 1989). A discussion of PERTCOR modeling can be found in the literature (Daunt, et al., 1984). The model Hamiltonian is consistent with that of Antilla et al. (1983) and is discussed at length in Daunt et al., (1984) as well as by Blass (1987). The ν_2 and ν_5 bands were constructed using the molecular parameters of Antilla et al. (1983) including the effects of the Coriolis resonance, ℓ -doubling and ℓ -resonance. The computational system generates relative intensities taking the resonances into account. The dipole moment derivative ratio was retrieved from van Straten and Smit (1977). The calculated transitions were compared to the observed transitions of Antilla et al. (1983) Agreement was on the order of ± 1.0 mcm^{-1} (milli wavenumber) which was considered satisfactory for this work. That is to say, that the modeled line spectrum agreed with the published observations of Antilla et al. (1983) for all samples inspected. The modeled spectrum included all allowed transitions of consequent intensity whereas the laboratory data, while extensive, was not complete in this sense. The calculations were carried out for maximum J (total angular momentum quantum number) and K (angular momentum quantum number of projection on the principal symmetry axis) values of 50 insuring inclusion of transitions with intensities greater than 10^{-25} $cm^{-1}/(mol \cdot cm^2)$. Separate calculations were carried out for the two isotopic modifications of methyl bromide. Integrated absolute intensities were normalized to the isotopically apportioned absolute band intensities of van Straten and Smit (1977). Measured band strengths (van Starten and Smit, 1977) were apportioned 0.505 to ^{79}Br and 0.485 to ^{81}Br. A similar set of calculations produced the ν_3 and ν_6 transition frequencies and intensities. The molecular parameters used for ν_3 and ν_6 are those collected in the review paper by Graner (1982). In this case no resonance parameters were included since none are available. As in the case of ν_2 and ν_5 both isotopic variations of methyl bromide were treated separately and the intensity normalization was carried out in the same way).

For comparison purposes, the integrated fundamental band intensity for CH_3Br is approximately 1.19 x 10^{-17} $cm^{-1}/(mol \cdot cm^2)$. compared to approximately 1.35 x 10^{-17} $cm^{-1}/(mol \cdot cm^2)$. for CH_3Cl (Smith et al., 1985). Figure 1 displays the intensity distribution of the 31,155 methyl bromide rotation vibration transitions used in this study. The transition's absolute intensity was binned in 1 cm^{-1} bins and plotted. The intensity scale is in $cm^{-1}/(mol \cdot cm^2)$.

III. Parameters of the Calculations

In a recent publication (Grossman et al., 1995, "G1") the radiative forcing of CH_3Cl was calculated using a detailed correlated k-distribution model for the absorption by the major atmospheric molecular absorption species (H_2O, CO_2, O_3, CH_3Cl, CH_4, and N_2O) to calculate the fluxes in the 0 - 3000 cm^{-1} wavenumber range. The direct calculation of the molecular k-distributions contains the following steps. First the HITRAN91 database (Rothman et. al., 1991) is utilized to determine the line transitions and physical properties of the selected lines. At this point the new CH_3Br spectral line data is combined with that of the HITRAN91 line data. Second, a modified version of the FASCODE2 code (Clough et. al., 1986) is used to calculate a finely gridded $(\Delta\upsilon(1/2) / 4)$, set of monochromatic absorption coefficients, with full allowance for the overlap of neighboring lines, for each layer in the atmosphere. Third, a sorting code, ABSORT, is used to calculate the k-distributions functions for each homogeneous atmospheric layer. The method produces fluxes that are accurate to well within 10 percent when compared to detailed line by line calculations.

Flux and radiative forcing calculations were made using the correlated k-distribution radiative transfer model for a globally and seasonally averaged model atmosphere (Wuebbles et al., 1994 and G1). The tropopause in the globally-averaged atmosphere is specified as the altitude at which the temperature gradient in the troposphere decreases to 2K/km. This occurs at a pressure of 166 mb (~13.2km). Altitude resolution in the model atmosphere was 1km at altitudes between 0 and 20km, and 2km at altitudes between 20 and 60km. The ground temperature was 291K. A cloud distribution model based on Harshvardhan et al. (1987) was used in the radiative transfer calculations. The cloud distribution in the globally averaged atmosphere consists of three layers, each 1km thick, with bases at 2km (low), 4km (middle), and 10km (high). Fractional cloud cover amounts are 0.31 (low), 0.09 (middle), and 0.17 (high).

The radiative transfer calculations to determine the tropospheric radiative forcing were carried out over the wavenumber range of 500 - 3000 cm^{-1}, in 25 cm^{-1} subintervals. In addition to CH_3Br absorption, absorption due to H_2O, CO_2 O_3, CH_4, and N_2O was included in the calculations. Although ambient concentrations of CH_3Br are on the order of 1 - 15 pptv we will assume a background atmosphere mixing ratio of 0.0 since a forcing of 1 ppbv constitutes a 100 fold increase over the background and that the forcing will be linear over the small amount of background CH_3Br. Radiative forcing calculations were made for mixing ratios of 0.0("ambient"), 1 ppbv (forced), and 100 ppbv (forced), scaled with altitude in order to produce a radiative forcing which is numerically significant. WMO (1994) indicates that while the mixing ratio of CH_3Br is essentially constant in the troposphere, it rapidly declines with altitude in the stratosphere. This will cause a decrease in the radiative forcing at the tropopause over that calculated using a constant forcing perturbation at all altitudes. A weighting function based on the ratio of the mixing ratio of CH_3Br at each stratospheric altitude to that at the troposphere was constructed. The radiative forcing perturbation applied at each stratospheric altitude was taken as the product of the abundance weighting function and the standard perturbation (1 or 100 ppbv).

IV. Results and Discussion

The tropospheric radiative forcing calculations for CH_3Br are shown in Table 1.

TABLE 1. Tropospheric radiative forcing calculations for CH_3Br.

INCLUDED BANDS	RADIATIVE FORCING($W/m^2/ppbv$)
$\nu_2, \nu_3, \nu_5, \nu_6$ (100 ppbv forcing)	4.9310^{-3}
$\nu_2, \nu_3, \nu_5, \nu_6$ (1 ppbv forcing)	5.3310^{-3}

The results of Table 1 show that the tropospheric radiative forcing of CH_3Br due to the ν_2, ν_3, ν_5, and ν_6 bands. In the atmospheric window region from 7 - 13μ the above bands represent close to 100 percent of the absorption of CH_3Br. In the range 2.5 - 20μ the above bands represent approximately 65 percent of the total absorption of CH_3Br. The results of G1 for a similar compound, CH_3Cl, indicate that the contribution to the radiative forcing from the spectral regions outside of the atmospheric window region are negligible. Calculations were performed using both 1 ppbv and 100 ppbv concentrations to insure that the 1 ppbv forcing result was numerically significant and to determine the linearity effects in the forcing as a result of increased CH_3Br abundance. It appears that the radiative forcing is linear to within approximately 10 percent in the abundance of CH_3Br between forcings of 1 and 100 ppbv. Using the radiative forcing formulae given in IPCC (1990), the radiative forcing of CH_3Br is about 2 percent of that of CFC-11 and about 278 times that of CO_2, on a per molecule basis.

We use the approximation for the calculation of the GWP, given in G1, to calculate the GWP of CH_3Br,

$$GWP(C_i) = \frac{m_{CFC-11}}{m_i} \cdot \frac{a_i}{a_{CFC-11}} \cdot \frac{\tau_i}{\tau_{CFC-11}} \cdot \frac{\left(1 - \exp(-t/\tau_i)\right)}{\left(1 - \exp(-t/\tau_{CFC\text{-}11})\right)} GWP(CFC - 11) \ , \quad (1)$$

where the a's are the radiative forcing values at the tropopause in W/m^2 per ppbv, the m's are the molecular mass, and the τ's are the atmospheric lifetimes. The molecular mass ratio, CFC-11 to CH_3Br, is 1.45. The Table 2 shows the results of a calculation of the GWP for CH_3Br for integration periods of 20, 100, and 500 years.

TABLE 2. Global Warming Potential for CH_3Br.

20 YEARS	100 YEARS	500 YEARS
12.8	3.9	1.2

For CFC-11, the lifetime of 50 years, and GWP's at 20, 100, and 500 years, 5000, 4000, and 1400, are taken from IPCC (1994). The GWP's of CH_3Br given in Table 2 are approximately 5 to 9 percent of GWP's of CH_4, on a per kilogram basis (IPCC, 1994). K1 gives an annual CH_3Br emission of approximately 100 - 150 thousand tons per year. WMO (1994) gives an annual emission rate of 121 thousand tons per year with an uncertainty range of 36 - 178 thousand tons per year. Of this approximately 33 percent (K1) to 63 percent (WMO, 1994) of the global emissions are assumed to be anthropogenic. Given a methane emission rate of approximately 500 Tg/year (WMO, 1991) with an assumed anthropogenic component of approximately 50 percent, the global warming effects of CH_3Br are about 0.003 - 0.004 percent of the anthropogenic methane contribution (IPCC, 1994). If the larger methane GWP values calculated by Wuebbles et al. (1994) are used, the global warming effects of CH_3Br are about 0.002 - 0.003 percent of the anthropogenic methane contribution. Thus, at present, serious greenhouse effects due to CH_3Br are not a problem and will not become a problem unless very large releases of this gas occur.

Acknowledgments

A part of this work was performed and supported by the Department of Energy's Domestic and International Energy Policy Office of Environmental Analysis, Office of Health and Environmental Research, Environmental Science Division, and by the Environmental Protection Agency. The authors would like to acknowledge Ted Bakowsky who assisted with the numerical calculations.

References

Antilla, R., C. Betrencourt-Stirnemann, and J. Dupre, 1983: The infrared bands nu2 and nu5 of CH_3Br with Coriolis interaction. *J. Molec. Spectrosc.*, Vol. 100, pp. 54–74.

Blass, W. E., 1989: Unpublished program PERTCOR for modeling Coriolis resonance, ℓ-doubling, and resonance in axially symmetric molecules.

Blass, W. E., 1987: Systematic approach to the analysis of aerturbed spectra, Part I. *Applied Spectroscopy Reviews,* **23**, pp. 1–58 .

Cicerone, R., L. Heidt, and W. Pollock, 1988: Measurements of atmospheric methyl bromide and bromoform. *J. Geophys. Res.*, Vol. 93, 3745–3749.

Clough, S.A., F.X. Kneizys, E.P. Shettle, and G.P. Anderson, 1986: Atmospheric radiance and transmittance: FASCODE2. *Proceedings of the Sixth Conference on Atmospheric Radiation*, 141–144, Williamsburg, VA.

Daunt, S. J., A. K. Atakan, W. E. Blass, G.W. Halsey, D. E. Jennings, D. C. Reuter, J. Susskind, and J. W. Brault, 1984: The 12 μm band of ethane: High resolution laboratory analysis, *Astrophysical Journal*, **280**, pp. 921–935.

Graner, G. and W.E. Blass, 1975: The ν_2 and ν_5 vibration – rotation bands of methyl bromide, *Journal de Physique*, **36**, 769 – 772.

Graner, G., 1982: The methyl bromide molecule: a critical consolidation of perturbations in spectra, *J. Molec. Spectrosc.,* Vol. **90**, pp. 394–438.

Grossman, A.S., K.E. Grant, and D. J. Wuebbles, 1995: Radiative forcing calculations for CH_3Cl. LLNL Report UCRL-ID-118065 (G1).

Harshvardhan, R. Davies, D.A. Randall, and T.G. Corsetti, 1987: A fast radiation parameterization for atmospheric circulation models, *J. Geophys. Res.*, Vol. **92**, D1, pp. 1009–1016.

Intergovernmental Panel on Climate Change (IPCC): Climate Change; The IPCC Scientific Assessment, Cambridge University Press, Cambridge, UK, 1990.

Intergovernmental Panel on Climate Change (IPCC): Climate Change 1992; The Supplementary Report to the IPCC Scientific Assessment, Cambridge University Press, Cambridge, UK, 1992.

Intergovernmental Panel on Climate Change (IPCC): Climate Change 1994; Radiative Forcing of Climate Change, Cambridge University Press, Cambridge, UK, 1994.

Kaye, J. A., S. A. Penkett, and F. M. Ormond, 1994: Report on concentrations, lifetimes, and trends of CFC's, halons, and related species. NASA Reference Publication 1339, NASA *Office of Mission to Planet Earth, Science Division, Washington, DC.*

Penkett, S., B. Jones, B. Rycroft, and D. Simmons, 1985: An interhemispheric comparison of bromine compounds in the atmosphere. *Nature*, **318**, 550–553.

Rothman, L.S., R.R. Gamache, R.H. Tipping, C.P. Rinsland, M.A.H. Smith, D.C. Benner, V. Malathy Devi, J.M. Flaud, C. Camy-Peyret, A. Perrin, A. Goldman, S.T. Massie, L.R. Brown, and R.A. Toth, 1992: The HITRAN molecular database: Editions of 1991 and 1992. *J. Quant. Spectrosc. Radiat. Transfer.*, **48**, N5, pp 469–507.

Singh, H. B., L. J. Salas, and R. E. Stiles, 1983: Selected man made halogenated chemicals in the air and ocean environment. *J. Geophys. Res.*, **88**, 3684–3690.

Smith, M. A., C.P. Rinsland, Bernard Fridovich, and K. Narahari Rao, 1985, in *Molecular Spectroscopy: Modern Research,* (K. Narahari Rao, Ed.), Vol. III, Chap. 3, p.111, Academic Press, Orlando, FL.

van Straten, A. J., and W. M. A. Smit, 1977: Absolute infrared intensities of methyl bromide and all deuterium derivatives. *J. Chem. Phys.*, **67**, 970.

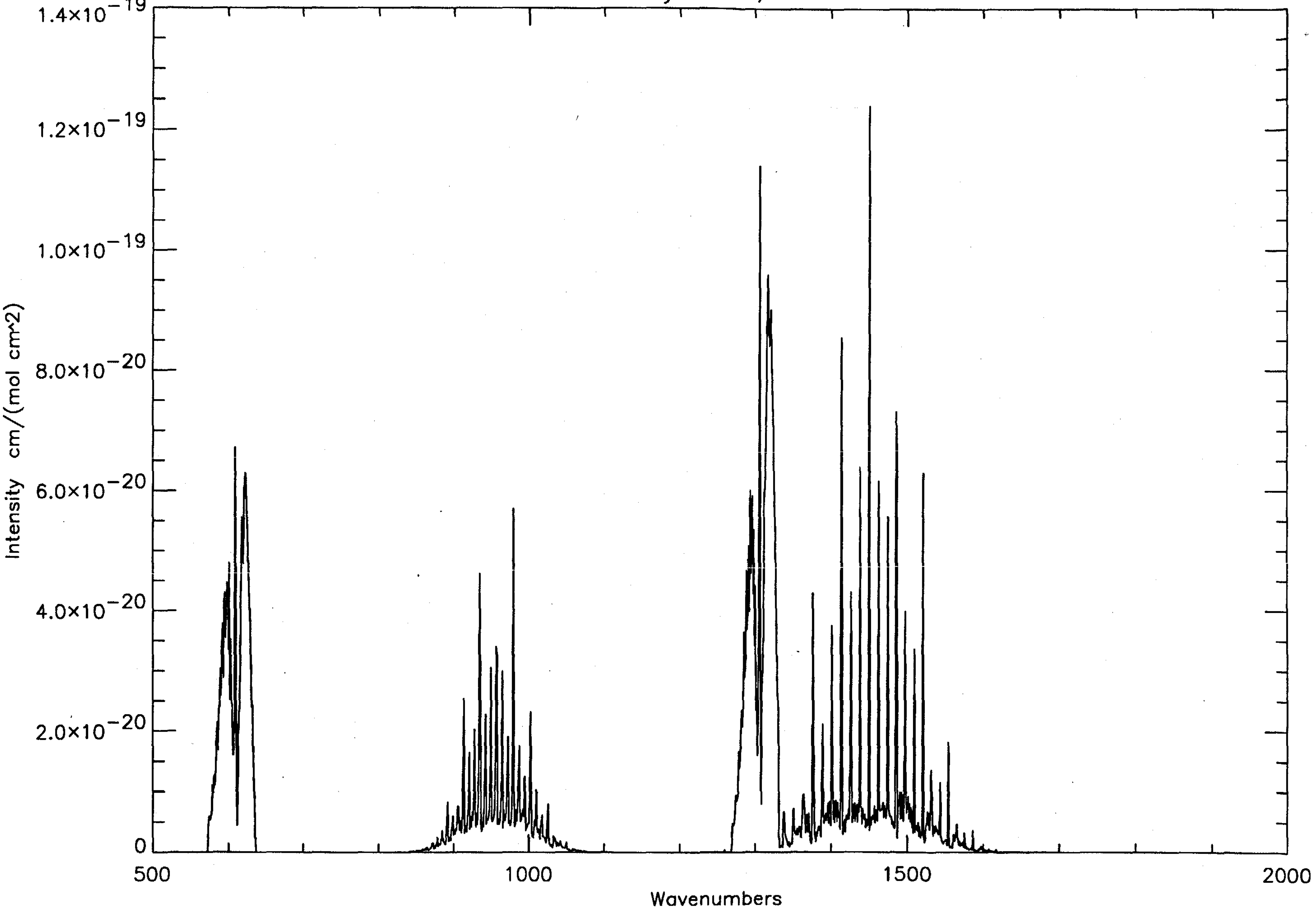
WMO, World Meteorological Organization, 1991: Scientific Assessment of Ozone Depletion: 1991, Global Ozone Research and Monitoring Project Report 25, Geneva.

WMO, World Meteorological Organization, 1994: Scientific Assessment of Ozone Depletion: 1994, Global Ozone Research and Monitoring Project Report 25, Geneva.

Wuebbles, D.J., A.S. Grossman, J. S. Tamaresis, K. O. Patten, A. Jain, and K. E. Grant, 1994: Indirect global warming effects of tropospheric ozone induced by surface methane emission. *Proceedings of the 17th Annual Review Conference on Atmospheric Transmission Models*, Bedford, MA, in press. LLNL Report UCRL-ID-118061.

Figure Captions

Figure 1. Absolute intensity distribution of 31,155 methyl bromide rotation-vibration transitions in the four fundamental vibration rotation bands for each of the isotopmers, $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$, used in this study.


Binned Intensity of 35,155 Transitions

This document (UCRL-ID-121512) replaces the document recently received.