

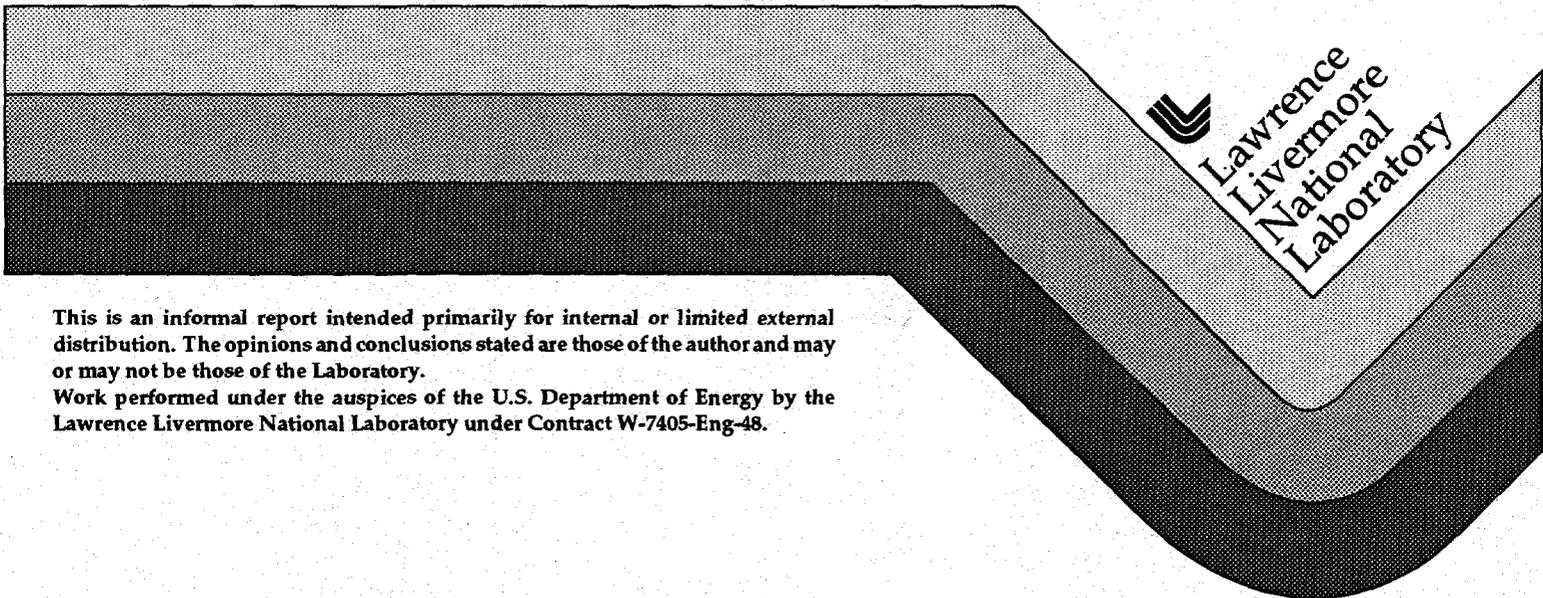
# Radiative Forcing Calculations for CH<sub>3</sub>Br

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



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

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## Abstract

Methyl Bromide, CH<sub>3</sub>Br, 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 - 13 $\mu$ , was determined using a well tested Coriolis resonance and  $\ell$ -doubling (and  $\ell$ -resonance) computational system. A radiative forcing value of 0.00493 W/m<sup>2</sup>/ppbv was obtained for CH<sub>3</sub>Br 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<sub>2</sub>, on a per molecule basis. The radiative forcing calculation is used to estimate the global warming potential (GWP) of CH<sub>3</sub>Br. The results give GWPs for CH<sub>3</sub>Br of the order of 13 for an integration period of 20 years and 4 for an integration period of 100 years (assuming CO<sub>2</sub> = 1, following IPCC [1994]). While CH<sub>3</sub>Br has a GWP which is approximately 25 percent of the GWP of CH<sub>4</sub>, the current emission rates are too low to cause serious atmospheric greenhouse heating effects at this time.

## I. Introduction

Methyl Bromide, CH<sub>3</sub>Br, 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<sub>3</sub>Br 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<sub>3</sub>Br mean mixing ratio in the range of 1.15 - 1.45, also indicating a significant land based source. The atmospheric lifetime for CH<sub>3</sub>Br varies from 1.3 years, (IPCC, 1994) with a range of 1.2 - 2.0 years (WMO, 1994).

CH<sub>3</sub>Br 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

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important contributor to ozone destruction in the lower stratosphere (WMO, 1994). According to WMO (1994) the ozone depletion potential (ODP) of CH<sub>3</sub>Br is 0.61. This index shows that CH<sub>3</sub>Br 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<sub>3</sub>Br using a correlated *k*-distribution radiative transfer model and a newly determined spectroscopic line data set for CH<sub>3</sub>Br. 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<sub>3</sub>Br will be made and compared to GWP's for other trace gases as derived for IPCC (1994).

## II. CH<sub>3</sub>Br DATA

Methyl bromide has six fundamental vibration-rotation bands,  $\nu_1$  through  $\nu_6$  found at 2972, 1305, 611, 3056, 1445, and 952 cm<sup>-1</sup> 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  $\nu_2$  and  $\nu_5$  in a comprehensive laboratory study. The molecular parameters of Antilla et al. were used to model the  $\nu_2$  and  $\nu_5$  spectra in this work. For  $\nu_3$  and  $\nu_6$ , 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  $\nu_1$  and  $\nu_4$  bands near 3000 cm<sup>-1</sup>. The  $\nu_4$  band contributes only 7 percent of the fundamental intensity according to van Straten and Smit (1977) while the  $\nu_1$  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<sup>-1</sup> region.

The methyl bromide vibration-rotation line spectra were modeled using a well tested Coriolis resonance and  $\ell$ -doubling (and  $\ell$ -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  $\nu_2$  and  $\nu_5$  bands were constructed using the molecular parameters of Antilla et al. (1983) including the effects of the Coriolis resonance,  $\ell$ -doubling and  $\ell$ -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  $\pm 1.0$  mcm<sup>-1</sup> (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<sup>-25</sup> cm<sup>-1</sup>/(mol · cm<sup>2</sup>). 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 Straten and Smit, 1977) were apportioned 0.505 to <sup>79</sup>Br and 0.485 to <sup>81</sup>Br. A similar set of calculations produced the  $\nu_3$  and  $\nu_6$  transition frequencies and intensities. The molecular parameters used for  $\nu_3$  and  $\nu_6$  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  $\nu_2$  and  $\nu_5$  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<sub>3</sub>Br is approximately  $1.19 \times 10^{-17} \text{ cm}^{-1}/(\text{mol} \cdot \text{cm}^2)$ , compared to approximately  $1.35 \times 10^{-17} \text{ cm}^{-1}/(\text{mol} \cdot \text{cm}^2)$ , for CH<sub>3</sub>Cl (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  $1 \text{ cm}^{-1}$  bins and plotted. The intensity scale is in  $\text{cm}^{-1}/(\text{mol} \cdot \text{cm}^2)$ .

### III. Parameters of the Calculations

In a recent publication (Grossman et al., 1995, "G1") the radiative forcing of CH<sub>3</sub>Cl was calculated using a detailed correlated k-distribution model for the absorption by the major atmospheric molecular absorption species (H<sub>2</sub>O, CO<sub>2</sub>, O<sub>3</sub>, CH<sub>3</sub>Cl, CH<sub>4</sub>, and N<sub>2</sub>O) to calculate the fluxes in the 0 - 3000  $\text{cm}^{-1}$  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<sub>3</sub>Br 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 ( $\Delta\nu(1/2)/4$ ), 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  $\text{cm}^{-1}$ , in 25  $\text{cm}^{-1}$  subintervals. In addition to CH<sub>3</sub>Br absorption, absorption due to H<sub>2</sub>O, CO<sub>2</sub>, O<sub>3</sub>, CH<sub>4</sub>, and N<sub>2</sub>O was included in the calculations. Although ambient concentrations of CH<sub>3</sub>Br 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<sub>3</sub>Br. 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<sub>3</sub>Br 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<sub>3</sub>Br 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<sub>3</sub>Br are shown in Table 1.

**TABLE 1.** Tropospheric radiative forcing calculations for CH<sub>3</sub>Br.

INCLUDED BANDS	RADIATIVE FORCING(W/m <sup>2</sup> /ppbv)
v <sub>2</sub> , v <sub>3</sub> , v <sub>5</sub> , v <sub>6</sub> (100 ppbv forcing)	4.9310 <sup>-3</sup>
v <sub>2</sub> , v <sub>3</sub> , v <sub>5</sub> , v <sub>6</sub> (1 ppbv forcing)	5.3310 <sup>-3</sup>

The results of Table 1 show that the tropospheric radiative forcing of CH<sub>3</sub>Br due to the v<sub>2</sub>, v<sub>3</sub>, v<sub>5</sub>, and v<sub>6</sub> bands. In the atmospheric window region from 7 - 13μ the above bands represent close to 100 percent of the absorption of CH<sub>3</sub>Br. In the range 2.5 - 20μ the above bands represent approximately 65 percent of the total absorption of CH<sub>3</sub>Br. The results of G1 for a similar compound, CH<sub>3</sub>Cl, 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<sub>3</sub>Br abundance. It appears that the radiative forcing is linear to within approximately 10 percent in the abundance of CH<sub>3</sub>Br between forcings of 1 and 100 ppbv. Using the radiative forcing formulae given in IPCC (1990), the radiative forcing of CH<sub>3</sub>Br is about 2 percent of that of CFC-11 and about 278 times that of CO<sub>2</sub>, on a per molecule basis.

We use the approximation for the calculation of the GWP, given in G1, to calculate the GWP of CH<sub>3</sub>Br,

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

(1)

where the *a*'s are the radiative forcing values at the tropopause in W/m<sup>2</sup> 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<sub>3</sub>Br, is 1.45. The Table 2 shows the results of a calculation of the GWP for CH<sub>3</sub>Br for integration periods of 20, 100, and 500 years.

**TABLE 2. Global Warming Potential for CH<sub>3</sub>Br.**

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<sub>3</sub>Br given in Table 2 are approximately 5 to 9 percent of GWP's of CH<sub>4</sub>, on a per kilogram basis (IPCC, 1994). K1 gives an annual CH<sub>3</sub>Br 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<sub>3</sub>Br 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<sub>3</sub>Br are about 0.002 - 0.003 percent of the anthropogenic methane contribution. Thus, at present, serious greenhouse effects due to CH<sub>3</sub>Br 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.

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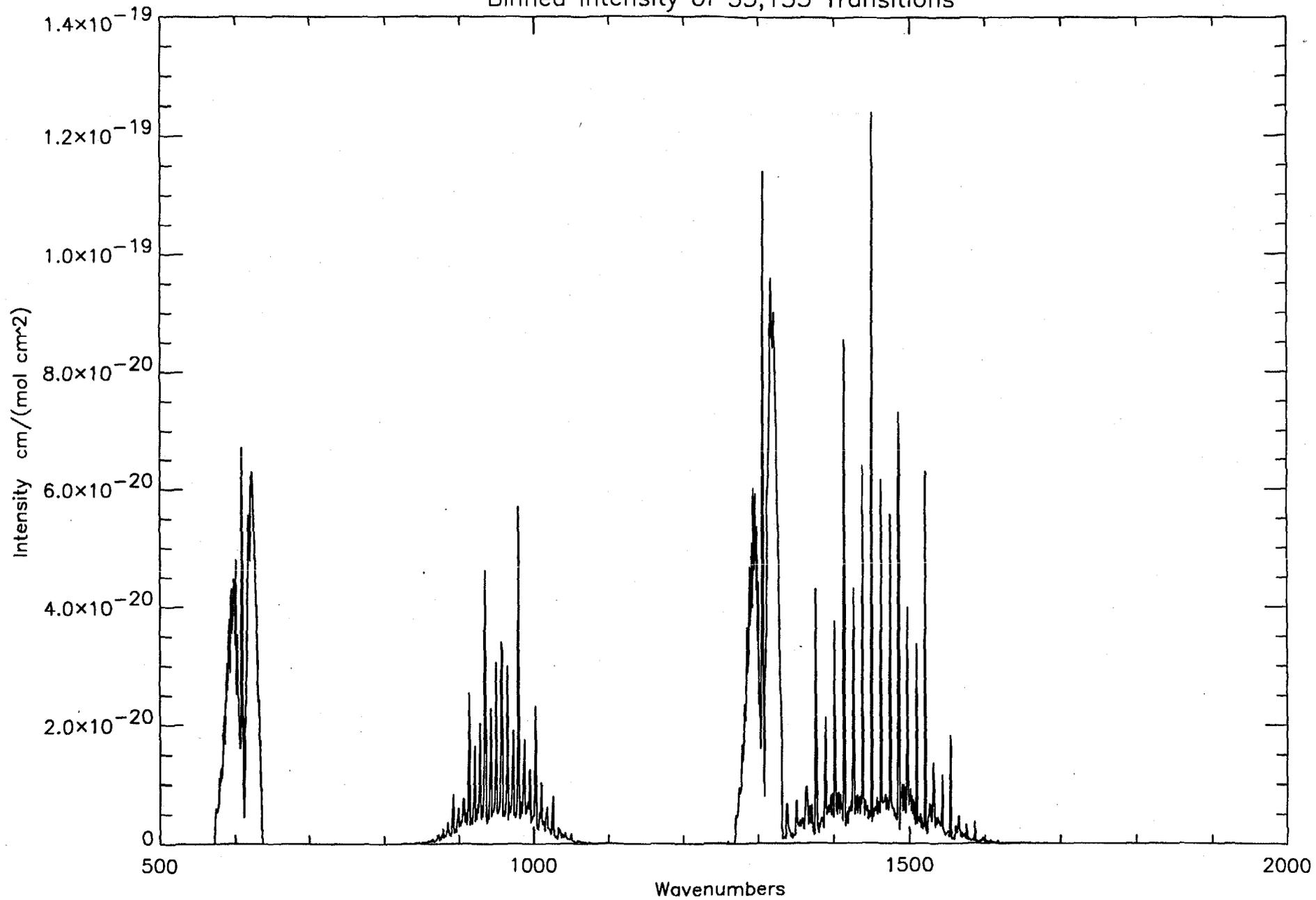
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### Figure Captions

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,  $\text{CH}_3^{79}\text{Br}$  and  $\text{CH}_3^{81}\text{Br}$ , used in this study.

Binned Intensity of 35,155 Transitions



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