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First observation of the rotational spectrum of the bromomethyl radical, CH₂Br

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The first high resolution rotational spectrum of the bromomethyl radical in the gas phase has been observed. The radical was produced in a fast flow system by hydrogen abstraction of CH₃Br by Cl or F atoms obtained from a 2450 MHz microwave discharge in Cl₂ or in CF₄, respectively. The rotational, quartic centrifugal distortion constants have been obtained as well as the electron spin–rotation interaction constants. The small positive inertial defect, $\Delta_0 = 0.032$ amu Å² deduced from the rotational constants of the CH₂⁷⁹Br species clearly indicates that the radical is planar in its ground vibronic state.

It has been well established that halogen atoms and radicals play an important role in catalytic reactions contributing in the stratospheric ozone destruction.¹⁻⁴ In particular, many studies have been devoted to the role of chlorine.^{5–9} Until recently, the chemistry of bromine-containing molecules and the adverse impact of bromine on the atmosphere have received little attention although there has been accumulating evidence for more than two decades that reactive bromine is also involved in the depletion of the ozone layer.¹⁰⁻¹² The concentration of bromine in the stratosphere is much lower than that of chlorine. However several studies have demonstrated that bromine is much more destructive to the stratospheric ozone than chlorine. Indeed, Garcia and Solomon have recently reported that bromine could be up to 100 times more efficient than chlorine, on an atom-per-atom basis.¹³ Methyl bromide is considered to be the major source of bromine in the atmosphere.¹⁴ CH₃Br is released into the atmosphere from both natural and anthropogenic sources.¹⁵ The main known removal process of this halomethane occurs via hydrogen abstraction by its reaction either with the hydroxyl radical or with chlorine, leading to the formation of the monobromomethyl radical, CH₂Br. This radical reacts further with other open shell species to release Br atoms for secondary reactions with ozone. The monobromomethyl radical is therefore a key transient for which it is essential to obtain accurate information from high-resolution spectroscopy. Such information is crucial to allow kinetic and photochemical laboratory studies in order to achieve a better understanding of the role played by bromomethane in the processes leading to the destruction of stratospheric ozone. In addition to its importance in atmospheric chemistry, the study of CH2Br is also of importance in order to compare its structure with those of its well-studied fluorine- and chlorine-analogues, CH2F16 and CH2Cl.17,18 These studies have revealed that CH2F is nearly planar whereas CH₂Cl is planar, the difference being attributed to the larger electronegativity of fluorine. CH2Br was first detected in

electron impact experiments with CH2Br2.19 An early matrix infrared study has suggested that this elusive species has a planar structure because of the large positive quartic term in the out-of-plane bending potential function.²⁰ This conclusion was later supported by EPR investigations.²¹ Davies et al. have recently reported the detection of this radical in the gas phase by far infrared laser magnetic resonance.²² They have also interpreted the spectra in terms of a planar structure. However, recent ab initio calculations²³ indicate that CH₂Br is most probably very slightly non-planar, if not planar. Depending on the structure, the ground electronic state is either ²A' (nonplanar) or ${}^{2}B_{1}$ (planar). This shows that the planarity still needs to be confirmed by high-resolution spectroscopic studies. Furthermore, high quality ground state constants will make the analysis of vibrational or electronic spectra of this radical significantly easier, and identification of CH2Br in such experiments more definitive if the ground state constants agree to within error with the millimeter wave values. In this letter, we report the detection and the identification of the first high resolution rotational spectrum of CH₂Br in the gas phase.

The millimeter wave (mmw) spectrometer used has been described in detail elsewhere.²⁴ It was adapted for the production of the CH₂Br radical. Briefly, it consists of a single-pass absorption system comprising a tunable mmw source, an absorption cell and a detector. The mmw radiation was obtained from two phase-locked backward wave oscillators, one emitting in the 160-260 GHz frequency region (Istok), the other one oscillating between 418-470 GHz (Thomson C.S.F.). The detection of the absorption signals was achieved with a helium-cooled InSb hot electrons bolometer (Q.M.C. Instruments). For improved sensitivity, source modulation at 70 kHz was used together with lock-in detection at twice this frequency, resulting in a second-derivative lineshape. Frequency scanning, data acquisition, signal processing and frequency measurement were controlled using a PC; the errors on the frequency measurement were estimated to be less than 50 kHz.

 CH_2Br was generated in a fast flow system by hydrogen abstraction of monobromomethane by chlorine or fluorine. The 1 m long absorption cell in Pyrex was equipped with a coil for creating a magnetic field to confirm that the detected lines were paramagnetic by on/off measurement. At one end a vertical Pyrex crosspiece was used to connect to a partially choked diffusion pump below the cell and to a pressure gauge mounted above the cell. At the other end, a horizontal Pyrex crosspiece was used to introduce CH_3Br vapour and Cl_2 or CF_4 separately. This method allowed *in situ* production of the reactive species. The outer end of each crosspiece was sealed by a Teflon window mounted at Brewster angle in order to improve transmission and to reduce standing waves. Cl₂ diluted with He (2:100) or CF₄ mixed with Ar (CF₄:Ar = 1:10) were used as a source for atomic chlorine or fluorine, respectively. Cl or F atoms were produced by a microwave discharge in a small quartz tube placed at the entrance of the second crosspiece and surrounded by a cavity fed by radiation from a magnetron at 2450 MHz. The power of the microwave discharge was kept as low as possible (≈ 20 W). The optimised partial pressure for CH₃Br was 7 × 10⁻³ mbar, and the total pressure was 1.5 × 10⁻² mbar.

Before initiating our search for the spectra, we decided to extend the measurement of the spectra of $CH_2^{35}Cl$ and $CH_2^{37}Cl$ (natural abundances: ³⁵Cl: 75.77%, ³⁷Cl: 24.23%) in the 418–470 GHz frequency region. We have used the molecular constants published by Endo *et al.*¹⁷ to predict the spectra falling within this range. The analysis of the spectra is now in progress for publication. The observation of the spectral lines of the monochloromethyl radical has allowed us to optimize the experimental conditions in order to maximize our chance to detect transitions of the bromomethyl radical. In particular, we found that the use of CI_2 led to a much clearer spectrum than the use of CF_4 .

We have afterwards guided our search for CH2Br according to the rotational constants deduced from the ab initio structure²³ of this radical in the ground state together with the centrifugal distortion constants obtained for CH2Cl.17 The calculated A, B and C rotational constants are listed in Table 1. The *ab initio* B + C value of $CH_2^{79}Br$, 22 304 MHz,²³ agrees with the value reported by Davies *et al.*, 22 305 MHz.²² More importantly, this group has also assigned the main rotational quantum number $N = 20 \leftarrow 19$ to the unresolved lines lying at 14.88 cm⁻¹ (446 091 MHz). This frequency falls in a range where our spectrometer has its highest sensitivity. Bromine has two stable isotopes of nearly equal abundances (79 Br: 50.69%, ⁸¹Br: 49.31%). The spectra of the two isotopomers should then be detected with the same intensity. Assuming a planar structure, the dipole moment of CH₂Br lies along the C₂ symmetry axis, which is the axis of the least moment of inertia. The rotational spectrum should hence display the characteristic *a*-type pattern of a slightly asymmetric prolate rotor ($\kappa =$ -0.996). In addition, owing to the electron spin-rotation interaction, each rotational level is split into two, leading to a fine structure in the spectrum. As a first estimate of the fine splittings, we have used for the prediction the ε_{ii} constants of CH_2Cl^{17} (see Table 1). The two components of the $N = 20 \leftarrow 19, K_a = 0$ lines of CH₂⁷⁹Br were predicted at 444597 and 444680 MHz. The four $K_a = 1$ components were calculated to lie at 440736, 440772, 450320 and 450767 MHz. The corresponding calculated set of transition frequencies for

the $C{H_2}^{81}Br$ species was shifted to the lower frequencies by about 1600 \pm 40 MHz.

We then carried out the search for the $N = 20 \leftarrow 19$ lines of CH₂Br by scanning the 439-452 GHz frequency range. The observed spectrum appeared so congested that we proceeded in two steps: at first we scanned using the experimental conditions described above. Subsequently we repeated the measurement by applying a magnetic field along the cell in order to both distinguish only the transitions sensitive to a magnetic field and to eliminate the numerous and often strong absorption lines of CH₃Br. This procedure led to the detection of more than 40 unidentified paramagnetic lines, most of them lying in the 443-447 GHz frequency region. These lines could also be observed using CF₄ for the production of fluorine instead of chlorine, but they disappeared when CH₃Br was replaced with CH₃Cl. At this stage, the chemical tests and the comparison with the ab initio calculations support strongly the detection of the two isotopomers of CH₂Br. Moreover, the majority of the transitions appeared as partly resolved doublets or triplets, sometimes as singlets. This hyperfine structure could be due to the nuclear spins of bromine $(I(^{79}Br) = I(^{81}Br) = 3/2)$ and of hydrogen $(I(H) = \frac{1}{2})$. By comparison with the predictions, we were quickly able to recognize two sets of lines of nearly equal intensity, each set displaying an identical pattern. The average difference between the transitions of these two sets is 1609 MHz, a value very close to the calculated one. A stick spectrum of the detected lines is shown on Fig. 1.

However, the electron spin-rotation interaction led obviously to a strong mixing of the various K_a components. It was therefore not possible to readily recognize a typical *a*-type R branch pattern of a prolate asymmetric top, preventing us from assigning the spectrum. We have consequently extended the measurement in the lower frequency region in order to observe the various K_a components of the $N = 19 \leftarrow 18$ series,



Fig. 1 Stick diagram of the $N = 20 \leftarrow 19$ transitions for the CH₂¹⁹Br and CH₂⁸¹Br species.

Table 1Molecular constants of CH2⁷⁹Br, CH2⁸¹Br and CH2³⁵Cl in the ground vibronic state

Parameter ^a	CH ₂ ⁷⁹ Br		CH ₂ ⁸¹ Br		
	Ab initio ^b	Experimental ^c	Ab initio ^b	Experimental ^c	CH ₂ ³⁵ Cl ^{cd}
A	278041.8	273774.8(87)	278041.8	274052.2(113)	274380(31)
В	11375.7	11395.1281(92)	11333.8	11353.1712(75)	15948.0282(50)
С	10928.6	10932.2056(90)	10889.9	10893.5319(73)	15057.0443(49)
\varDelta_N		0.0121011(25)		0.0120101(20)	0.022550(22)
Δ_{NK}		0.324795(39)		0.319403(171)	0.50968(10)
Δ_K		23.52^{e}		23.52^{e}	22.85 ^f
$10^3 \delta_N$		0.4684(30)		0.5149(28)	1.274(40)
δ_K		0.1880(38)		0.1584(31)	0.3325
E _{aa}		-12535.06(88)		-12531.45(89)	-3149.45(14)
E _{bb}		-697.684(69)		-695.986(67)	-237.623(46)
E _{cc}		69.221(56)		69.626(63)	11.814(40)
Δ_{NK}^S		0.3270(127)		0.3270 ^g	0.1120(65)
Δ_K^S		0.719(42)		0.719^{g}	0.2635(77)

^{*a*} In megahertz. ^{*b*} From ref. 23. ^{*c*} One standard deviation in parentheses. ^{*d*} Values in parentheses have been converted from ref. 17 to one standard deviation. ^{*e*} Fixed to the value of H_2C^{30} Se, from ref. 27. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 27. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 27. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 27. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 27. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 27. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 27. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 27. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 27. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 27. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 27. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 27. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 27. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 27. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 27. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 27. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 27. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 27. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 27. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 28. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 29. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 29. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 29. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 29. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 29. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 29. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 29. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 29. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 29. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 29. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 29. ^{*f*} Fixed to the value of H_2C^{30} Se, from ref. 29. ^{*f*} Fixed to the value of H_2C^{30} Se, from



Fig. 2. Observed spectrum of the $10_{1,10}$ - $9_{1,9}$, J = 9.5-8.5 transition of $CH_2^{81}Br$, using (a) CF_4 or (b) Cl_2 for the reaction with CH_3Br . The dashed lines have been obtained with a magnetic field to confirm that the CH2Br lines are paramagnetic. The spectrum was recorded by

integrating 20 scans with 1 Hz repetition rate and 10 ms time constant

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focusing our search on the 79Br species. This led to the detection of 22 new paramagnetic lines in the 422-425 GHz frequency span. In addition, some $K_a = 1$ lines for both N series and for the two isotopic species turned out to be difficult to detect because they fall in frequency regions where strong transitions of CH3Br were observed. These lines were finally observed after a more careful search. An example of a $K_a = 1$ transition obtained by using either chlorine or fluorine is given in Fig. 2. The observation of the $K_a = 1$ transitions proved to be decisive in the identification of the spectrum of $CH_2^{79}Br$. Indeed, after several attempts, a least squares fit of the $K_a = 0$, 1 and 2 components of the $N = 20 \leftarrow 19$ and $N = 19 \leftarrow 18$ series of $CH_2^{79}Br$ allowed us to assign the $K_a = 3-6$ components successfully. The $K_a = 0$ lines of $CH_2^{79}Br$ have been observed at 445248 and 445465 MHz. The four $K_a = 1$ components lie at 441317, 441377, 450320 and 450767 MHz. The identification of the spectrum of CH₂⁸¹Br was then straightforward. Repeating this procedure eventually led to the measurement of 59 rotational lines for the $CH_2^{79}Br$ isotopic species corresponding to N = 9, 10 and $19 \le N \le 21$, K_a \leq 6 in the 160–470 GHz frequency range. For the $CH_2^{81}Br$ isotopomer, only 42 transitions corresponding to N = 9, 10 and $19 \leq N \leq 21, K_a \leq 6$ have been measured. The average frequencies of the hyperfine components have been used for the fit. These frequencies were fitted to a Watson A-reduced Hamiltonian in the I^r representation.²⁵ Predictions and fittings were made using Pickett's programs SPFIT and SPCAT.²⁶ The adjusted rotational, centrifugal distortion and fine structure constants for the two isotopic species are listed in Table 1 together with the CH2³⁵Cl parameters for comparison. The ab initio rotational constants are in good agreement with those obtained from the fit. Moreover, the experimentally determined B + C value of CH₂⁷⁹Br, 22327.3 MHz, is very close to the one reported by Davies et al. (22305 MHz). In addition, this group has noticed when studying the radical by LMR spectroscopy that all K_a components except $K_a = 1$ are very closely spaced²² (within 0.16 cm⁻¹, *i.e.* 4800 MHz approximately, for the $N = 30 \leftarrow 29$ transition). Fig. 1 shows that our identification confirms their observation. The centrifugal distortion constants of CH₂Br given in Table 1 are of the same order of magnitude than the ones of CH₂Cl. Their signs are also identical. Finally, the ε_{aa} spin-rotation interaction constant is about four times larger in CH2Br than in CH2Cl. Such a difference was already observed between the CH₂Cl and CH₂F radicals.¹⁷

The fact that reaction of CH₃Br with Cl or F atoms led to the observed transitions together with the relatively good agreement between the experimental and ab initio A, B and C constants for both isotopic species enables us to ascertain that we have observed the rotational spectrum of the monobromomethyl radical. This is the first high-resolution spectroscopic identification of this species. Work directed toward the analysis of the hyperfine structure is in progress. The small positive value of the inertial defect, $\Delta_0 = 0.032$ amu Å² proves the planarity of CH₂Br in the ground vibronic state.

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