



PERGAMON

Journal of Quantitative Spectroscopy &
Radiative Transfer 82 (2003) 313–317

Journal of
Quantitative
Spectroscopy &
Radiative
Transfer

www.elsevier.com/locate/jqsrt

HBr and HI line parameters update for atmospheric spectroscopy databases

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Received 21 October 2002; received in revised form 20 February 2003; accepted 22 February 2003

Abstract

Recent work on new line parameters for the $X^1\Sigma^+(0-0),(0-1)$ H⁷⁹Br, H⁸¹Br bands and the $X^1\Sigma^+(0-0),(0-1)$ HI bands, which include hyperfine structure components, has been extended for an update of spectroscopic databases in use for atmospheric spectroscopy. The updated line parameters, now incorporated in HITRAN 2001, are discussed in comparison to HITRAN 1996.

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Keywords: HBr; HI; Infrared; Line parameters; Spectroscopic databases

1. HBr

The HBr line parameters in the 1996 HITRAN database [1] (“HITRAN” in what follows, unless specified otherwise) cover the bands with ($v'' = 0, v' = 0, 1, 2, 3, 4$) and ($v'' = 1, v' = 1$). These line parameters already include hyperfine structure (hfs) components for some of the pure rotation lines, taken from the SAO database [2] (using a slightly different value for the electric dipole moment than that used in the JPL catalog [3]). The vibration–rotation lines include only rotational structure (rs), and are based on the work of Tipping [4]. The HITRAN HBr (0–0) lines are comprised of

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hfs components for $J'' \leq 11$, and rs transitions from $J'' = 12$ to 23, also from [2]. The (0–1) lines extend to $J'' = 20$. The GEISA [5] line parameters for HBr were identical to those of HITRAN 1996.

Coffey et al. [6] describe the generation of a new set of line parameters for the $X^1\Sigma^+$ (0–1) $H^{79}\text{Br}$ and $H^{81}\text{Br}$ bands, which includes the hfs line components of the vibration–rotation transitions. Those (0–1) line positions were derived from energy levels calculated with rs and hfs spectroscopic constants. For the $v = 0$ and 1 rs constants we used those of Braun and Bernath [7], but with more significant digits (provided by Bernath, private communication, 1997). For the hfs constants, we used those of Di Lonardo et al. [8] for $v = 0$ and of De Natale et al. [9] for $v = 1$.

The resulting rs line positions for both isotopes are consistently lower by $0.001\text{--}0.003\text{ cm}^{-1}$ from the 1996 HITRAN lines for $J'' < 10$ lines. At higher J values the new line positions are higher than the HITRAN positions, with the difference increasing with J to $\approx 0.01\text{ cm}^{-1}$ at $J'' = 20$. This may be related to the improved calibration reference and high- J lines used by Braun and Bernath [7], who indicate accuracy better than 0.0001 cm^{-1} . Only the dominant hfs interaction due to the Br nuclei (nuclear spin $\frac{3}{2}$ for both ^{79}Br and ^{81}Br), was included. The sum of the theoretical relative line intensities of the hfs components, calculated by standard angular momentum techniques using the 6- j symbols (see Ref. [6] and Table 1 there), was normalized, for given J'', J' , to the intensity of the corresponding single rs line from the 1996 HITRAN listings. The HITRAN J''_{max} of 20 was also retained for the line list.

For the (0–0) lines we also used the rs constants of Braun and Bernath [7] (which provide an extension of the $v = 0$ rs constants of Di Lonardo et al. [8]) and the hfs constants of Di Lonardo et al. [8]. The electric dipole moment was taken from Dabbousi et al. [10]. Refs. [8,10] were the basis for the SAO [2] calculations. The hfs constants were derived from laboratory data [8] with $J'' \leq 9$, but we extended the calculated line parameters to $J'' \leq 16$. The HITRAN 1996 hfs line list is limited to $J'' \leq 11$; as mentioned above, it was adopted from the SAO database [2].

These line parameters were used for the balloon emission measurements of HBr in the stratosphere reported by Traub et al. [11] and by Nolt et al. [12]. University of Denver calculations with the Di Lonardo et al. [8] constants for the rs and hfs constants duplicated the SAO hfs calculations for both line positions and intensities. These calculations revealed a few cases in the HITRAN 1996 line list in which some isotopic identifications and hyperfine branch symbols were switched. Specifically, the isotopic identification and hyperfine branch symbols of the transitions $P1.5 R0$ and $Q1.5 R0$ were interchanged. For the $P1.5 R1$, $Q2.5 R1$ and $R0.5 R1$, isotopic identifications, ground state energies and hf branch symbols were placed incorrectly. Note also that the HITRAN 1996 hf quantum numbers were truncated to integers. With the Braun and Bernath [7] rs constants we get slightly lower ν values; the difference increases slowly with J to $\approx 0.0004\text{ cm}^{-1}$ at $J'' = 16$. Our new rs lines, with the new ν , S , and E'' values can replace the HITRAN lines for $J'' = 17\text{--}24$. The differences in the ν and S values are $\lesssim 0.001\text{ cm}^{-1}$ and $\lesssim 4\%$, respectively.

For both the (0–0) and (0–1) bands the air- and self-broadening half-widths and the coefficient for the temperature dependence of the air-broadening half-widths were retained from the 1996 HITRAN compilation for each of the individual hfs components. For reasons related to the HITRAN partition functions, as described by Goldman et al. [13], the values for the weighted transition moments squared, \mathfrak{R}_{lu} , were not retained. The new HBr line parameters have been adopted for the HBr reference cells used for instrument calibration at the NDSC (Network for the Detection of Stratospheric Change) sites [14].

2. HI

The HI line parameters were the same in both the 1992 and 1996 versions of the HITRAN database. These were also adopted in the 1992 SAO database, originate from the work of Tipping [4] and did not include hfs for either pure rotation or vibration–rotation. The (v'', v') band coverage is the same as for HBr. The HITRAN (0–0) and (0–1) lines extended to $J'' = 25$ and 22, respectively. The GEISA [5] line parameters for HI were identical to those of HITRAN. The JPL catalog [3] does not include HI lines.

Goldman et al. [15] describe the generation of a new set of line parameters for the $X^1\Sigma^+$ (0–0) and (0–1) H^{127}I bands, which includes the hyperfine structure line components. The previous HI pure-rotation work of Chance et al. [16] forms the basis for the new (0–0) line parameters. New high-resolution laboratory spectra of the (0–1) region were analyzed for improved spectroscopic constants and line parameters. As expected, the hfs splitting in HI is significantly larger than that of HBr, but the HI line intensities are weaker.

Calculating the (0–0) HI lines with only the rs constants from Chance et al. [16] yields line positions which are consistently lower than those on HITRAN 1996 by up to 0.002 cm^{-1} for high J values. The newly calculated (0–0) hfs line positions [16] are consistent with the experimental values to $\pm 0.00002\text{ cm}^{-1}$. The new (0–0) hfs line intensities, within a J -multiplet, sum up to values close to HITRAN, confirming the use of the same dipole moment in both calculations. Our new (0–0) hfs lines were limited to $J'' \leq 16$. For higher J'' up to 25 we calculated new rs lines, with ν values lower than HITRAN by $\lesssim 0.002\text{ cm}^{-1}$ and almost identical intensities.

The laboratory spectra in the HI (0–1) region were recorded with a Bruker 120M interferometer at NCAR, Boulder and analyzed for new spectroscopic constants [15]. It has been established that the measured HI line positions are accurate to $\pm 0.0002\text{ cm}^{-1}$. The line positions calculated from the newly derived rs constants are lower than HITRAN, by ≈ 0.008 and $\approx 0.002\text{ cm}^{-1}$ at the high- J P -branch and R -branch, respectively. The sum of the calculated relative line intensities of the hfs components for a given J -multiplet was normalized to the intensity of the corresponding single rs line from the 1996 HITRAN listing. We have limited the new hfs (0–1) lines to $J'' \leq 14$. The new (0–1) rs lines extend from $J'' = 15$ to 18, less than the $J''_{\text{max}} = 22$ used in HITRAN. This choice is related to the anomalies in the HITRAN S values for P -lines of $J'' > 13$, and that $P(14)$ is missing. We kept these HITRAN S values, but they should be revised. The HITRAN high- J R -lines do not show these anomalies.

For both (0–0) and (0–1), the air- and self-broadening half-widths and the coefficient for the temperature dependence of the air-broadening half-widths were retained from the 1996 HITRAN compilation for each of the individual hfs components. However, half-width measurements for HI have been quite sparse. As in the case of HBr, the weighted transition-moments squared were not retained [13].

A summary of the updated line parameters, now in HITRAN 2001 (Rothman et al. [17]), is presented in Table 1. The accuracy indices in the table follow the definitions given in recent editions of the HITRAN database and are retained in the 2001 edition [17]. Note that the total band intensities are very similar to those reported in the HITRAN band sums. However, the new hfs line components yield new values for S_{min} and S_{max} .

New studies by Bulanin et al. [18] provide new values of the intensities and self-broadening for the $P(1) - P(10)$ and $R(0) - R(15)$ lines in the fundamental band. The new intensity values are

Table 1
Summary of updated HBr, HI line parameters

Molecule (# lines)	Band (v'', v') $\nu_0(\text{cm}^{-1})$	Update	ΣS	S_{\min}	S_{\max}	Accuracy indices for ν, S, γ
H⁷⁹Br (154)	(0,0)	hfs ^a , rs ^b	2.3971E–18	7.949E–28	1.211E–19	6,8,3
	—					
(364)	(0,1)	hfs ^c , rs ^d	7.2325E–19	9.450E–33	2.293E–20	4,5,2
	2558.913					
H⁸¹Br (154)	(0,0)	hfs ^a , rs ^b	2.3317E–18	7.754E–28	1.178E–19	6,8,3
	—					
(355)	(0,1)	hfs ^c , rs ^d	7.0333E–19	1.528E–32	2.229E–20	4,5,2
	2558.529					
H¹²⁷I (245)	(0,0)	hfs ^e , rs ^f	1.0680E–18	6.128E–27	3.423E–20	6,8,2
	—					
(390)	(0,1)	hfs ^g , rs ^h	1.9344E–20	1.644E–30	5.442E–22	4,5,1
	2229.581					

S values are in units of $\text{cm}^{-1}/(\text{molecules}^{-1} \text{cm}^{-2})$ at 296 K.

ΣS values are very close to HITRAN values. S_{\min} , S_{\max} based on individual lines, now with hfs components.

^a $J''_{\max} = 16$. New ν, E'', S .

^b $J'' = 17$ to 24. New ν, E'', S . $S(\text{hfs})$ summed to $S(\text{rs})$.

^c $J''_{\max} = 20$. New ν, E'' , relative S normalized to HITRAN rs.

^dNo rs lines.

^e $J''_{\max} = 16$. New ν, E'', S .

^f $J'' = 17$ to 25. New ν, E'', S . $S(\text{hfs})$ summed to $S(\text{rs})$.

^g $J''_{\max} = 14$. New ν, E'' , relative S normalized to HITRAN rs.

^h $J'' = 15$ to 18. New ν, E'' . HITRAN S values.

systematically higher than the HITRAN 1996 values, at increasing deviation from $\sim 2\%$ near the band center to 13–40% for the highest- J lines. Such results were expected on the basis of previous measurements by Riris et al. [19], which were not implemented in the HITRAN 1996 compilation.

Acknowledgements

The work at the University of Denver was supported in part by the NSF and in part by the NASA Upper Atmosphere Research Program. Acknowledgment is made to the National Center for Atmospheric Research, which is sponsored by the National Science Foundation, for computer time used in this project.

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