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Reference spectroscopic data for hydrogen halides, Part II: The line lists

Gang Li [a,*], Iouli E. Gordon [a], Photos G. Hajigeorgiou [b], John A. Coxon [c], Laurence S. Rothman [a]

[a] Harvard–Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge, MA 02138, USA
[b] University of Nicosia, Department of Life and Health Sciences, Nicosia 1700, Cyprus
[c] Dalhousie University, Department of Chemistry, Halifax, Nova Scotia B3H 4J3, Canada

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ABSTRACT

Accurate spectroscopic parameters for the hydrogen halides, namely HF, HCl, HBr, and HI, together with their deuterated isotopologues, are crucial for the quantitative study of terrestrial and planetary atmospheres, astrophysical objects, and chemical lasers. A thorough evaluation of all the hydrogen halide line parameters in previous HITRAN editions has been carried out. A new set of line lists was generated for the HITRAN2012 edition using methods described here. In total, 131,798 entries were generated for numerous pure-rotational and ro-vibrational transitions (fundamental, overtone, and hot bands) for hydrogen halides and their deuterated species in a standard HITRAN 160-character format. Data for the deuterated isotopologues have been entered into HITRAN for the first time. The calculations employ the recently developed semi-empirical dipole moment functions [Li G, et al. J Quant Spectrosc Radiat Transfer 2013;121:78–90] and very accurate analytical potential energy functions and associated functions characterizing Born–Oppenheimer breakdown effects. Line-shape parameters have also been updated using the most recent available experimental and theoretical studies. Comparison with the previous HITRAN compilation has shown significant improvements.

1. Introduction

The importance of hydrogen halides (namely: HF, HCl, HBr, and HI) has long been recognized for atmospheric, astrophysical and industrial applications. In the terrestrial atmosphere, HF and HCl have been monitored intensively by many satellite missions after being listed among the anthropogenic chlorofluorocarbons (CFCs) pollutant trace gases in the Montreal Protocol three decades ago [1]. In particular, HF and HCl have been proven to be the main fluorine and chlorine reservoir gases, with maximum abundances in the middle terrestrial atmosphere around 1.5 ppbv and 3 ppbv, respectively. Cl and ClO are generated from HCl by photochemical processes. These species act as the main catalysts in the ozone depletion process. Therefore, long-term monitoring of the abundance of stratospheric HF and HCl, including the vertical profiles, facilitates the understanding of their generation, distribution and transport; eventually this knowledge will help our characterization of ozone distribution. The first global profile of HCl became available in 1996 using the Microwave Limb Sounder (MLS) instruments on board the UARS satellite [2]. Various other space-based instruments were also used for monitoring HCl and ClO, including the Sub-Millimeter Receiver (SMR) onboard Odin [3], the

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[*] Correspondence to: Harvard–Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, MS-50, 60 Garden Street, Cambridge, MA 02138, USA. Tel.: +1 617 496 2593.
E-mail address: gangli@cfa.harvard.edu (G. Li).

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Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) on board Envisat [4], the Atmospheric Chemistry Experiment (ACE) on board SCISAT-1 [5], the updated MLS on board EOS-Aura [6], the Superconducting Submillimeter-Wave Limb-Sounder (SMILES) on board the International Space Station [7], and the Terahertz and submillimeter Limb Sounder (TELIS) on board the MIPAS-B2 gondola [8]. HCl and HF are also very abundant gases after SO_2 in volcanic plumes [9]. Specifically, measurement of the SO_2/HCl and HF/HCl ratios can provide information about the chemical composition of the volcanic gas mixture as well as the equilibrium temperatures of the stored gases.

Besides their importance in the terrestrial atmosphere, hydrogen halides (specifically, HF and HCl) have also been identified in various astrophysical objects including planetary atmospheres, carbon stars, and the interstellar medium. In 2010, Sonnentrucker et al. [10] measured for the first time the column density of HF along the sight line of the continuum sources W49N and W51. One of their major discoveries is that the abundance of HF with respect to H_2 is consistent with the theoretical prediction [11,12] that HF is the main fluorine reservoir for these clouds. For this reason, they proposed HF as an excellent molecular hydrogen tracer that provides a sensitive probe of clouds retaining a small H_2 column density. Another study of the carbon-rich star IRC+10216 with the Herschel SPIRE and PACS spectrometers by Cernicharo et al. [13] has quantified the abundance of HCl using the rotational lines from $J=1\leftarrow0$ up to $J=7\leftarrow6$ of HCl. They found that HCl is produced in the innermost layers of the circumstellar envelope and it has an abundance of eight orders of magnitude larger than molecular hydrogen, H_2. In our solar system, HF and HCl have been found to be the two most important minor gaseous constituents on Venus. In a recent study, Bertaux et al. [14] measured for the first time the vertical profile of HF and HCl on Venus using the SPICAV/SOIR spectrometers on board the Venus Express spacecraft. Their results suggest that HCl is less abundant than measured 40 years ago. Moreover, the search for gaseous hydrogen halides on giant planets, such as Saturn and Jupiter, is also of great interest [15].

Another motivation of the present study is from industry. Hydrogen halides have attracted industrial interest for their excellent properties as chemical lasers. Powerful megawatt chemical lasers using HF, DF, HCl or HBr as resonance gases have already been developed [16,17]. Currently, the lack of knowledge of the Einstein *A*-coefficients in the high-lying vibrational levels limits the further enhancement of the output and efficiency. It is thus critically important to derive a reliable set of spectroscopic parameters extending to high vibrational levels for ready reference.

With a few exceptions, most of the spectroscopic parameters of hydrogen halides in the HITRAN database [18] had not been updated since the last major work in 1990 by Tipping [19]. In the mean time, many new experimental measurements have become available [20–28], warranting a major revision of the hydrogen halide parameters in the database. Recently, we reinvestigated the dipole moment functions (DMFs) of the hydrogen halides using the most up-to-date experimental line-intensity measurements and an advanced direct fit approach [29]. It has been shown that line intensities calculated using these DMFs are much superior to those in the previous HITRAN compilation. In addition, the reliability of the line-intensity predictions for lines involving high vibrational levels has increased. These advantages have been achieved, through (1) using the most recent reliable experimental intensity data with appropriate weights; (2) employing measured intensities of all ro-vibrational transitions rather than deducing the rotationless matrix elements from them as was commonly done until now; (3) using theoretical data to constrain their behaviors at internuclear distances in the long-range region. In this paper, we will focus on development of the other spectroscopic parameters, including line positions, line-shape parameters and line shifts. The line position calculations were carried out using program LEVEL [30] by adopting the accurate potential energy and Born–Oppenheimer breakdown (BOB) functions for the $X^1\Sigma^+$ ground states that have been determined recently by Coxon and Hajigeorgiou [31]. Ultimately, a total number of 34,376, 83,691, 8980, 4751 entries were generated for HF/DF, HCl/DCl, HBr/DBr, and HI/DI, respectively. The evaluation of the new calculated line positions was carried out by comparing them with the most up-to-date experimental values as well as to the previous HITRAN compilations. The new calculated line positions have been found to be in excellent agreement with the best available experimental values and have been shown to be a significant improvement over the previous HITRAN compilations. We will generally refer to Ref. [18] as HITRAN2008, but most of the conclusions apply to all post-1996 editions of HITRAN. In Section 2, we briefly explain our direct-potential-fit (DPF) procedures for determining the potential energy functions (PEF) and present the results of the PEF fits.

2. Methodology

In the present work, we have employed the potential energy and Born–Oppenheimer breakdown (BOB) functions for the $X^1\Sigma^+$ ground states of HF, HCl, HBr, and HI that have been determined recently in full analytical form by Coxon and Hajigeorgiou [31]. All available pure rotational and vibration–rotation spectroscopic data available for the *X* states of all isotopologues of the four hydrogen halides, as well as the $B^1\Sigma^+\leftarrow X^1\Sigma^+$ emission band system data for HF/DF and HCl/DCl, were employed in the direct potential fit (DPF) determinations of the various radial functions. Significant improvements have been made over the results of earlier work on HF [32], HCl [33], HBr and HI [34], especially in terms of the mathematical models for the potential energy and BOB functions. In particular, there is an emphasis in Ref. [31] on taking proper account of the behavior of each