Isotopically invariant analysis of vibration–rotation transitions of HBr and its isotopologues

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Received 4 July 2006; in revised form 15 August 2006
Available online 24 August 2006

Abstract

The vibration–rotation transition frequencies of HBr and its isotopologues reported in the literature were simultaneously analyzed in a least-squares fit to determine isotopically invariant molecular parameters U_{kl} and Born–Oppenheimer breakdown parameters Δ_{kl}. A total of 692 lines was fitted to Watson's expression involving 25 adjustable parameters to a weighted unitless standard deviation of $\sigma \approx 0.91$. From new data in the far-infrared region and those of improved precision in the mid-infrared and the near-infrared region, the breakdown parameters for the bromine atom were determined; the parameter Δ_{10}^{Br} for the harmonic frequency improved the fit and Δ_{01}^{Br} for the rotational constant enabled us to obtain the information on the adiabatic correction to the Born–Oppenheimer approximation.
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1. Introduction

Spectroscopic studies on the hydrogen bromide molecule and its isotopologues have been made extensively, because their knowledge would be useful in various fields of science. Recently, the ozone layer depletion in the stratosphere is a serious problem in environmental science. Since HBr plays an important role in the depletion mechanism, the information on this molecule would be helpful for monitoring the ozone layer depletion. In metrology, transition frequencies of HBr/DBr can be used for the calibration of spectrometers and tunable laser devices as secondary frequency (or wavelength) standards in the infrared region. From the point of view of molecular quantum mechanics, these simple molecules are suitable for testing molecular theories and approximations such as the Born–Oppenheimer approximation.

Coxon and Hajigeorgiou examined in detail Born–Oppenheimer breakdown effects in hydrogen bromide [1]. The relative mass difference between ^{79}Br and ^{81}Br atoms was too small to determine the breakdown parameters for the bromine atom because of the poorer precision of the data available at that time. After their work, however, improved spectroscopic techniques in the infrared region provided new data as well as those of improved precision. In most of earlier measurements of vibration–rotation transitions of HBr, low-resolution spectra were observed with grating spectrometers in the near-infrared and the mid-infrared region [2–6]. In later measurements, high-resolution spectroscopy was performed: laser spectroscopy on overtone bands in the near-infrared region [7] and Fourier transform (FT) spectroscopy on the fundamental and hot bands in the mid-infrared region [8]. From the improved frequencies of vibration–rotation transitions of both H^{79}Br and H^{81}Br, the breakdown parameter Δ_{10}^{Br} may be determined for the harmonic frequency. Pure rotational transitions of HBr fall mostly in the far-infrared, or

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terahertz, region because of its large rotational constant. First, only the lowest $J = 1 \leftarrow 0$ transitions of both Br isotopologues of HBr were very precisely measured in the millimeter-wave region [9,10]. At that time, however, measurements of higher-J transitions were difficult due to lack of a tunable coherent far-infrared radiation source. Then several techniques for high-resolution spectroscopy were developed in the far-infrared region. Precise transition frequencies up to $R(8)$ of $H^{79}Br$ and $R(6)$ of $H^{81}Br$ were measured with a tunable far-infrared (TuFIR) spectrometer based on the difference frequency of two CO_2 lasers [11,12]. Further measurements of higher-J transitions were made with a far-infrared FT spectrometer [8]. In a later work, TuFIR measurements were extended to rotational transitions in the first excited vibrational state [13]. From these newly observed frequencies of pure rotational transitions of both $H^{79}Br$ and $H^{81}Br$, the breakdown parameter Δ_{01}^{Br} may be determined for the rotational constant.

In this paper, the transition frequencies of HBr and its isotopologues reported in the literature, including the new and improved frequencies mentioned above, have been simultaneously analyzed to determine isotopically invariant molecular parameters U_{kl} and Born–Oppenheimer breakdown parameters Δ_{kl} according to Watson's expression [14]. The determined parameters could be used to predict transition frequencies and to calculate various molecular properties of HBr/DBr such as the electric dipole moment function [15]. Recently, an alternative method, which was used by Coxon and Hajigeorgiou to analyze transition frequencies of hydrogen bromide, has become increasingly common. This method is sometimes called the "direct potential fits" method, in which the Schrödinger equation is solved for a Hamiltonian model including a parameterized potential energy function and Born–Oppenheimer breakdown functions. The differences between its eigenvalues are compared with observed frequencies to optimize the parameters in the model. It is possible to calculate vibrational energies E_v, rotational constants B_v, and the set of centrifugal distortion constants from those parameters, if necessary. Le Roy [16] reviewed this method in detail. Although the procedure is more complicated, the "direct potential fits" method requires smaller numbers of parameters and has a better ability to predict transition frequencies outside the range analyzed. Despite these advantages, the data have been analyzed in the present work by using the conventional, but more common and simpler, Watson's expression, because our attention is focused on the breakdown of the Born–Oppenheimer approximation in the rotational constant. It has been shown that the breakdown effects are successfully revealed by the conventional analysis of precise rotational transition frequencies in the submillimeter-wave and the far-infrared region [17,18]. Besides, it would be worthwhile to provide a set of isotopically invariant parameters by the conventional method for comparison with those obtained by the "direct potential fits" method. Only for HCl and HBr of hydrogen halides, the breakdown parameters for halogenic

atoms are determinable, because F and I atoms in the HF and HI molecules have no isotope. For HCl, the accurate breakdown parameters have already been determined from a global analysis of vibration–rotation transitions [19] and from a detailed analysis of rotational transitions observed by high-resolution spectroscopy in the submillimeter-wave and the far-infrared region [18]. Thus, for HBr, the determination of the breakdown parameters for the bromine atom is a principal objective of the present study. On the basis of Watson's theory [20], a physical interpretation of the obtained breakdown parameters for the rotational constant has been given in comparison with those for HCl.

2. Data set of observed frequencies

In this section, the data set analyzed here is described in detail. The following transition frequencies of $H^{79}Br$ and $H^{81}Br$ were used. As for the vibration–rotation spectra, the 1–0 and 2–1 bands were observed with a FT spectrometer [8]. Laser spectroscopy of the 3–0, 5–0, and 6–0 overtone bands was performed in the near-infrared region with GaAs semiconductor and titanium sapphire lasers [7]. The precision of the observed frequencies is $\approx 0.001 \, cm^{-1}$ and is improved by one order of magnitude in comparison with the precision of earlier measurements with grating spectrometers. The transition frequencies of the 7–0 band were measured with a grating spectrometer and added to the data set [5]. The two-tone frequency-modulation spectroscopy was performed on the 8–0 band with a dye laser [21]. However, the precision of measured wavenumbers was limited to the order of $\approx 0.1 \, cm^{-1}$ and excluded from the data set in the final fit. As for pure rotational spectra in the ground vibrational state, the hyperfine spectra of the $R(0)$ transitions of both Br isotopologues in the millimeter-wave region [10] and then those of higher-J transitions up to $R(8)$ of $H^{79}Br$ and $R(6)$ of $H^{81}Br$ in the far-infrared region were observed with a TuFIR spectrometer [11]. From the determined molecular constants, hypothetical hyperfine-free frequencies were calculated with an uncertainty of a few hundred kilohertz dependent on lines and were included into the data set. Emission spectra of higher-J transitions were also observed with a FT spectrometer; frequencies of the $R(25)$–$R(31)$ transitions were measured with an uncertainty less than $0.001 \, cm^{-1}$ [8]. In the first excited vibrational state, the hyperfine spectra of the $R(2)$–$R(9)$ transitions of $H^{79}Br$ and the $R(2)$–$R(8)$ transitions of $H^{81}Br$ were observed with a TuFIR spectrometer, and hypothetical hyperfine-free frequencies were calculated with an uncertainty of several hundred kilohertz [13].

The following transition frequencies of $D^{79}Br$ and $D^{81}Br$ were used. The vibration–rotation transitions of the 1–0, 2–0, 3–0, 4–0, and 5–0 bands were systematically measured with an uncertainty of 10^{-3}–$10^{-2} \, cm^{-1}$ [22,23]. Then improved measurements of the 1–0 band were made; the $R(0)$–$R(6)$ and $P(1)$–$P(9)$ transitions were observed with a FT spectrometer [24]. For several selected lines, heterodyne frequency measurements were made with CO and