Journal of Molecular Spectroscopy 262 (2010) 30–36

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms

High resolution spectroscopy of DOBr and molecular properties of hypobromous acid

E.A. Cohen [a,*], H.S.P. Müller [a,b], T.L. Tan [c], G.A. McRae [a,d]

[a] Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109-8099, USA
[b] I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, 50937 Köln, Germany
[c] Natural Sciences and Science Education, National Institute of Education, Nanyang Technological University, NIE BLK7, 1 Nanyang Walk, Singapore 637616, Singapore
[d] Department of Mechanical and Aerospace Engineering, Carleton University, Ottawa, ON, Canada K1S 5B6

ARTICLE INFO

Article history:
Received 3 March 2010
In revised form 20 April 2010
Available online 27 April 2010

Keywords:
Hypobromous acid
Rotational spectra
Infrared spectra
Quintic anharmonic resonance
Harmonic force field

ABSTRACT

The ν_1 and ν_2 bands of DOBr centered near 2668.8 and 852.0 cm^{-1} respectively have been observed at 0.006 cm^{-1} resolution. The ν_1 band is perturbed by a quintic anharmonic resonance ($\Delta K_a = 0$) with $3\nu_3 + \nu_2$. In addition, the millimeter wave spectra arising from the $\nu_2 = 1$ and $\nu_3 = 1$ states have been observed. All rotational and vibrational spectra from both bromine isotopologs have been fitted with a single calculation. The perturbation in the ν_1 band has been well described. Equilibrium rotational and centrifugal distortion constants and changes in quadrupole coupling with the BrO stretch and DOBr bend have been determined. The equilibrium structure has been derived from the DOBr and HOBr rotational constants. The harmonic force field has been calculated and compared with those of related molecules as well as with those derived from ab initio calculations.

1. Introduction

Since the first observation of HOBr and DOBr rotational and infrared spectra by Koga et al. [1] several high resolution studies have appeared [2–7]. These, as well as numerous reports of the optical spectrum, reaction kinetics, and ab initio studies have been undertaken as a part of a larger program to characterize reactive halogen containing molecules which may participate in the catalytic destruction of atmospheric ozone. Most of the cited references refer to this application of their studies.

This study extends the range of observed high resolution spectra for DOBr and utilizes these results along with available HOBr studies to improve the equilibrium structure and harmonic force field. The analysis of the ν_1 band of DOBr now includes energy levels to $K_a = 8$ and explicitly treats the $\Delta K = 0$ quintic anharmonic resonance of ν_1 with $3\nu_3 + \nu_2$. The DOBr ν_2 band has been analyzed and millimeter rotational spectra of the $\nu_2 = 1$ state have been included in the fit. Additional measurements of the rotational spectra of the ground and $\nu_3 = 1$ states have been made. All available high resolution DOBr spectra have been fit with a single global calculation in which many parameters are common to both isotopomers.

2. Experimental

The conditions for the earlier infrared and microwave experiments have been described in the previously cited works [2,5]. DOBr ν_2 spectra were taken under the same experimental conditions described in Ref. [5] and were calibrated using D_2O positions calculated from Toth's energy levels [8]. Because of the poor signal to noise ratio and the fact that all of the available calibration features were between 880 and 930 cm^{-1}, an additional uncertainty of approximately 0.0006 cm^{-1} should be added to the tabulated ν_2 band origin uncertainties. The ν_2 isotope shift as well as other parameters are unaffected. Additional DOBr millimeter spectra below 800 GHz were taken with the Jet Propulsion Laboratory (JPL) spectrometer [9] with the synthesis previously used at JPL [2]. Rotational spectra above 800 GHz were obtained with a spectrometer utilizing a microwave synthesizer and amplifier–multiplier chains [10–12].

3. DOBr spectra

All spectra to be discussed were fitted to a Watson *S*-reduced Hamiltonian in a I^r representation with additional terms to describe the quintic anharmonic resonance between ν_1 and $3\nu_3 + \nu_2$. These terms are given by an effective Hamiltonian

* Corresponding author.
E-mail address: Edward.A.Cohen@jpl.nasa.gov (E.A. Cohen).

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doi:10.1016/j.jms.2010.04.009

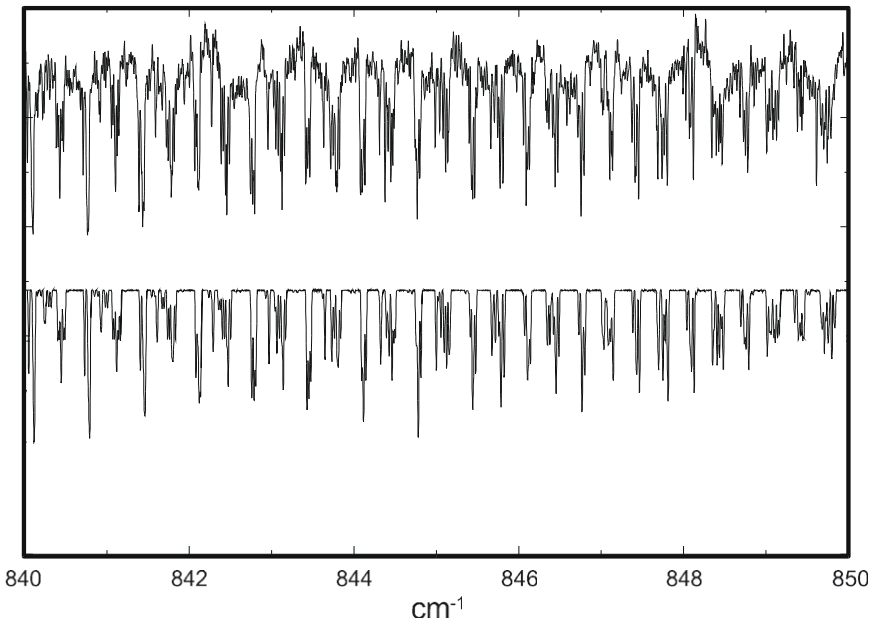

Fig. 1. A portion of the P branch of the v_2 band of DOBr. The observed spectrum is at the top and the simulation is below.

$$\mathscr{H}_5 = \left(K_{1,2333} + K^z_{1,2333}P^2_z\right)q_1q_2q^3_3, \tag{1}$$

with

$$\langle v_1, v_2, v_3, J, K|\mathscr{H}_5|v_1 - 1, v_2 + 1, v_3 + 3, J, K\rangle = [2v_1(v_2 + 1)(v_3 + 1)(v_3 + 2)(v_3 + 3)]^{1/2}(K_{1,2333} + K^z_{1,2333}K^2)/8. \tag{2}$$

The constants to be reported for the observed resonances are

$$\widetilde{K}_{1,2333} = \sqrt{3}K_{1,2333}/4$$
$$\widetilde{K}^z_{1,2333} = \sqrt{3}K^z_{1,2333}/4. \tag{3}$$

The fitted data include rotational spectra of the ground, $v_2 = 1$ and $v_3 = 1$ states and infrared spectra of the v_1 and v_2 bands.

The DOBr v_2 band is much weaker than the v_1 band. It contains only μ_a type transitions and is quite dense. This is illustrated in Figs. 1 and 2. Although the observed spectrum was quite noisy, it was adequate for the purpose of this study. Six hundred forty five features were used in the fit. Because of blending, these include only 259 single lines and 239 unresolved asymmetry doublets. The remainder are blends of two or more lines whose positions are calculated as the intensity weighted sums of their components. A plot of J versus K_a for the assigned transitions is shown in Fig. 3. Note that many of the high K_a transitions are assigned as parts of blends. Only five of the $K_a = 6$ assignments are isolated asymmetry doublets and no unblended $K_a = 7$ features were observed. Nine DO^{79}Br and 10 DO^{81}Br $v_2 = 1$ rotational transitions improve the accuracy of the rotational constants. The rotational data contain two $K_a = 2 \leftarrow 1$ for each species with the remainder $K_a = 0 \leftrightarrow 1$.

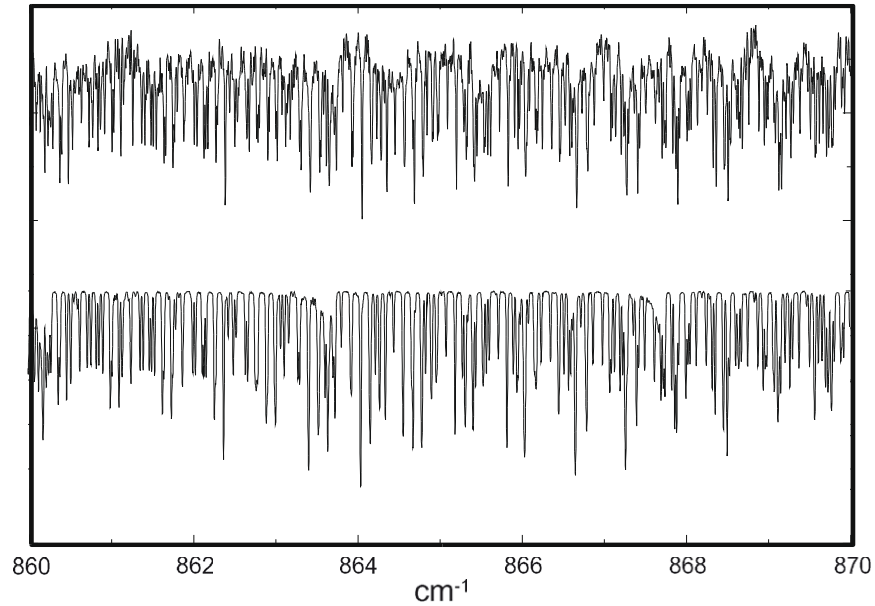

Fig. 2. A portion of the R branch of the v_2 band of DOBr. The observed spectrum is at the top and the simulation is below.