Journal of Molecular Spectroscopy 325 (2016) 20–28

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

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

Vibrational–rotational spectra of GaF and global multi-isotopologue analysis

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ARTICLE INFO

Article history:
Received 21 March 2016
In revised form 19 May 2016
Accepted 19 May 2016
Available online 24 May 2016

Keywords:
GaF
Vibrational–rotational
Multi-isotopologue analysis
Dunham coefficients
Breakdown
Born–Oppenheimer approximation

ABSTRACT

In total, 521 vibrational–rotational spectral lines of the $\Delta v = 1$ transitions of ^{69}GaF and ^{71}GaF up to bands $v = 5$–4 and 4–3, respectively, were recorded in emission with a Fourier-transform spectrometer at unapodized resolution 0.010 cm^{-1} in range 625–660 cm^{-1}. The response of a HgCdTe detector enforced the lower limit, 625 cm^{-1}. To calibrate accurately the spectral lines, the absorption spectrum of CO_2 was simultaneously recorded, using dual sample cells, to serve as wavenumber standards. A set of 782 spectral lines comprising all present vibrational–rotational spectra of ^{69}GaF and ^{71}GaF, the reported laser-diode measurements of the $\Delta v = 1$ band sequence and the reported rotational spectra was subjected to a global multi-isotopologue analysis through fitting with 11 isotopically invariant, *irreducible* molecular parameters in a single set. Normalized standard deviation 1.093 indicates a satisfactory fit. For the effects of the breakdown of the Born–Oppenheimer approximation on GaF, the values of non-Born–Oppenheimer parameters $\Delta_B{}^{Ga}$, $\Delta_\omega{}^{Ga}$ and $r_{1q}{}^{Ga}(=r_{1q}{}^{F})$ are experimentally determined for the first time. To facilitate the calculations or predictions of spectral frequencies, the values of the Dunham coefficients of 24 Y_{ij} and 81 band parameters for both ^{69}GaF and ^{71}GaF were back-calculated with uncertainties using the 11 evaluated molecular parameters. To date, various types of *effective* B_e, r_e, ω_e, and k have been reported for GaF. Because, in the present work, Dunham coefficients Y_{ij} are algebraically expressed with the *genuine* B_e, ω_e, a_i $(i = 1, \ldots)$ and the non-Born–Oppenheimer correction parameters, the exact expressions for the physical significance of *effective* quantities are derivable. The various *effective* quantities of B_e, r_e, ω_e and k calculated with these expressions for the physical significance and the determined values of the fitted parameters of GaF agree satisfactorily with the reported values. The physical significance of the conventional treatments of adiabatic and nonadiabatic corrections for Δ_{01}^{Ga} and Δ_{10}^{Ga} is discussed.

1. Introduction

The first high-resolution spectra for the ground electronic state of GaF, a monohalide of an element in group 13, were the microwave measurements of ^{69}GaF and ^{71}GaF that Hoeft et al. [1] reported in 1970; they observed the hyperfine structure of rotational transitions J = 1–0 ($v = 0$, 1, 2, 3 for both ^{69}GaF and ^{71}GaF) and J = 2–1 ($v = 0$, 1, 2 for ^{69}GaF and $v = 0$ and 1 for ^{71}GaF) and measured the Stark effect, which revealed the electric dipole moment of ^{69}GaF at level $v = 0$. Honerjäger and Tischer [2] obtained the rotational g factor of ^{69}GaF on measuring the Zeeman effect for transition J = 1–0 ($v = 0$) of ^{69}GaF.

Tiemann et al. [3] reported correction parameter Δ_{01}^{Ga} for the Born–Oppenheimer approximation for GaF. Although they evaluated this value after measuring the pure rotational transitions, neither the measured line frequencies nor the details of the analysis were reported. Hoeft and Nair [4] reported rotational transitions J = 5–4 and 13–12 ($v = 0$, 1, 2 for ^{69}GaF and ^{71}GaF) and J = 12–11 ($v = 0$ for ^{71}GaF); they reported no observable breakdown of the Born–Oppenheimer approximation within the limits of their experimental errors. Wasylishen et al. [5] measured the hyperfine components of rotational transitions J = 1–0 ($v = 0$, 1, 2 for ^{69}GaF and $v = 0$, 1 for ^{71}GaF) with improved accuracy; they obtained improved nuclear quadrupolar coupling coefficients and rotational parameters with the fluorine spin–rotation parameter.

Using an FTIR spectrometer of a moderate resolution, Uehara et al. [6] measured the vibrational–rotational transitions of ^{69}GaF and ^{71}GaF in emission; they recorded vibrational–rotational bands $v = 1$–0 to 5–4 for ^{69}GaF and to 4–3 band for ^{71}GaF. Ogilvie et al. [7] reported measurements of the vibrational–rotational spectra of ^{69}GaF and ^{71}GaF in absorption with a laser-diode spectrometer; in total, 229 spectral lines for transitions $v = 1$–0 to 8–7 for both ^{69}GaF and ^{71}GaF were recorded.

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http://dx.doi.org/10.1016/j.jms.2016.05.005
0022-2852/

In this paper we report the first observation of the high-resolution FTIR spectra of ^{69}GaF and ^{71}GaF. Bands $v = 1$–0 to 5–4 of ^{69}GaF and $v = 1$–0 to 4–3 for ^{71}GaF were observed in emission. Due to the cutoff of the HgCdTe detector at 625 cm^{-1}, only the R-branch sides of the bands were measured. A set of spectral data comprising the present vibrational–rotational and reported vibrational–rotational and rotational transitions of ^{69}GaF and ^{71}GaF was subjected to a multi-isotopologue analysis using a non-Born–Oppenheimer Hamiltonian [8–11] with 11 fitting parameters of U_ω $(1 + m_\mathrm{e}\Delta_\omega{}^\mathrm{F}/M_\mathrm{F})$, U_B $(1 + m_\mathrm{e}\mathit{\Delta}_B{}^\mathrm{F}/M_\mathrm{F})$, a_i ($i = 1, 2, \ldots, 6$), $\mathit{\Delta}_\omega{}^\mathrm{Ga}$, $\mathit{\Delta}_B{}^\mathrm{Ga}$, and $r_{1q}{}^\mathrm{Ga}(=r_{1q}{}^\mathrm{F})$ that are based on the traditional concept of molecular parameters; note that these molecular parameters for GaF are irreducible because ^{19}F is a single stable nuclide. Non-Born–Oppenheimer parameters $\mathit{\Delta}_\omega{}^\mathrm{Ga}$, $\mathit{\Delta}_B{}^\mathrm{Ga}$ and $r_{1q}{}^\mathrm{Ga}(=r_{1q}{}^\mathrm{F})$, for the effects of the breakdown of the Born–Oppenheimer approximation, are first determined experimentally in this work. The multi-isotopologue analysis employed herein is comprehensively reviewed in Ref. [8] and has been applied to LiH [9], HCl [12,13], HF [11,14], and CS [15]. In the latter work on CS [15], only 22 molecular parameters in a single set to fit 3974 spectral lines for seven isotopologues generated 42 Y_{ij} and 351 band parameters for each of the 12 isotopologues of CS. The generated values of Y_{ij} and band parameters agree satisfactorily with the reported values. For GaF, *effective* B_e, r_e, ω_e and k of various kinds have been reported [3–7]. As Dunham's coefficients Y_{ij} in the present work are algebraically expressed using the *genuine* B_e, ω_e, a_i ($i = 1, \ldots$), and the non-Born–Oppenheimer correction parameters, the exact expressions for the physical significance of these *effective* quantities are derivable. The values of the various *effective* quantities of B_e, r_e, ω_e and k evaluated using these expressions and the determined values of the fitted parameters of GaF agree satisfactorily with the reported *effective* values.

The present method of analysis therefore simultaneously reproduces the micro-structures (i.e., various kinds of *effective* equilibrium quantities) and macro-structures (i.e., values of Y_{ij} and band parameters of many isotopologues) of diatomic molecules.

2. Experiments

The spectra were measured for GaF in a high-temperature cell made of an alumina tube (inner diameter 42 mm, length 600 mm). The center portion of the tube (length 200 mm), was heated with a SiC spiral heater; both ends of the tube were cooled with water jackets. To generate GaF, a mixture of Ga (10 g) and AlF_3 (10 g) was charged inside the cell and heated to 1870 K. Argon buffer gas (pressure 8 kPa) was admitted to minimize the migration of the sample vapour from the hot zone of the cell. At one end of the tube, a KRS-5 (thallium bromoiodide) window was mounted to transmit the infrared radiation of GaF from the heated gas. The radiation was focused on the emission port of a Fourier-transform spectrometer (Bruker IFS-125HR).

Using a KCl beam splitter and a HgCdTe detector (77 K), we recorded the vibrational–rotational transitions of the $\mathit{\Delta}v = 1$ bands of GaF at unapodized resolution 0.010 cm^{-1} in range 625–660 cm^{-1}; the response of the HgCdTe detector defined the lower limit, 625 cm^{-1}. To calibrate the wavenumbers of the GaF spectrum, we recorded simultaneously the spectra of GaF and CO_2 as a calibration standard. A gas sample cell (length 15 cm) containing CO_2 (160 Pa) was located in the sample compartment of the spectrometer to absorb the incident emitted radiation, generating the CO_2 spectrum of band 01^10–00^00. Fig. 1 shows a portion of the simultaneously recorded spectra of GaF and CO_2. Bands $v = 1$–0 to 5–4 for ^{69}GaF and $v = 1$–0 to 4–3 for ^{71}GaF were observed. During integration of the measurements 297 scans were added.

3. Spectral calibration

All spectral line centers were determined through fitting the measured line profiles to pseudo-Voigt functions with software (OPUS, Bruker software supplied with the spectrometer); a pseudo-Voigt function is a weighted sum of Gaussian and Lorentzian contributions. The spectral positions of bands $v = 1$–0 to 5–4 for ^{69}GaF and $v = 1$–0 to 4–3 for ^{71}GaF were calibrated with the simultaneously recorded CO_2 spectrum of which the wavenumbers were adopted from Guelachvili and Rao [16]. The calibrated spectral lines of ^{69}GaF and ^{71}GaF, in total 521, are listed in Table S1(a) in Supplementary material. The uncertainties are estimated to be ±0.001 cm^{-1}, but ±0.002 cm^{-1} for weaker lines for which $*$ is added to the wavenumbers listed in Table S1(a). The influence of the hyperfine structure on line width due to the nuclear spins of Ga and F is 0.001 cm^{-1} for the $R(5)$ and $P(6)$ lines, which include the smallest J number of the present observations. Since the present measurements were made with an unapodized resolution of 0.010 cm^{-1}, we ignored the influence of the hyperfine structure on line positions throughout. The diode-laser measurements of vibrational–rotational transitions reported by Ogilvie et al. [7] are listed in Table S1(b) in Supplementary material; the microwave measurements of the rotational transitions reported by Hoeft et al. [1], by Hoeft and Nair [4] and by Wasylishen et al. [5] are listed in Table S1(c) in Supplementary material. The reported uncertainty in the diode-laser measurements is ±0.0005 cm^{-1}. The uncertainties of the microwave measurements are indicated in Table S1(c).

4. Analysis

The multi-isotopologue analysis employed herein is based on a non-Born–Oppenheimer effective Hamiltonian expressed with determinable molecular parameters [8–11,14] as follows,

$$H = -B_\mathrm{e}(1+\delta\Delta_B)\frac{d^2}{d\xi'^2} + \frac{B_\mathrm{e}(1+\delta\Delta_B)}{(1+\xi')^2}\left(1+\sum_{i=1}\delta r_{iq}(\xi')^i\right)J(J+1) + \frac{[\omega_\mathrm{e}(1+\delta\Delta_\omega)]^2}{4B_\mathrm{e}(1+\delta\Delta_B)}\xi'^2\left(1+\sum_{i=1}a_i(1+\delta\Delta_{aiq})(\xi')^i\right), \tag{1}$$

in which

$$\xi' = (1+\delta\Delta_B/2)\xi + \delta\Delta_B/2 = (1+\delta\Delta_B/2)\frac{r-r_\mathrm{e}}{r_\mathrm{e}} + \delta\Delta_B/2, \tag{2}$$

with $B_\mathrm{e} = h/(8\pi^2 c\mu r_\mathrm{e}^2)$ and $\omega_\mathrm{e} = (1/2\pi c)\,(k/\mu)^{1/2}$ (both in unit cm^{-1}). Quantity μ denotes the reduced mass of a molecule, $(1/\mu) = (1/M_a) + (1/M_b)$, with masses M_a and M_b of *atoms* A and B, respectively. All molecular parameters B_e, ω_e, a_1, $\ldots$ are those of the traditional concept in the Born–Oppenheimer scheme whereas non-Born–Oppenheimer effects are all included in the correction parameters; r_e is the equilibrium internuclear distance and k is the force coefficient at r_e of the Born–Oppenheimer potential. Notations B_e, r_e and k in this work imply the physical significance of the commonly used parameters B_e^BO, r_e^BO and k^BO, respectively. The correction parameters $\delta\mathit{\Delta}_B$, $\delta\mathit{\Delta}_\omega$, $\delta\mathit{\Delta}_{aiq}$ ($i = 1, 2, \ldots$), and δr_{iq} ($i = 1, 2, \ldots$) are for the corrections of the breakdown of the Born–Oppenheimer approximation for the reduced equilibrium rotational constant U_B, where $U_B = \mu B_\mathrm{e}$, for the reduced harmonic vibrational wavenumber U_ω, where $U_\omega = \mu^{1/2}\omega_\mathrm{e}$, for the Dunham potential constants, a_1, a_2, $\ldots$, and for the radial part of the rotational energy, respectively.

For a pair of quantities x_i^a and x_i^b, the symbol δx_i denotes $\delta x_i = (m_\mathrm{e}/M_a)\ x_i{}^\mathrm{a} + (m_\mathrm{e}/M_b)\ x_i^b$, in which x_i stands for a non-Born–Oppenheimer correction parameter such as $\mathit{\Delta}_B$, $\mathit{\Delta}_\omega$, r_{iq} or $\mathit{\Delta}_{aiq}$, (*e.g.*, $\delta\mathit{\Delta}_B = (m_\mathrm{e}/M_a)\ \mathit{\Delta}_B{}^\mathrm{a} + (m_\mathrm{e}/M_b)\ \mathit{\Delta}_B^b$, in which m_e is the mass of the electron). The non-Born–Oppenheimer correction parameters are combinations of $q_i{}^\mathrm{a,b}$, $r_i{}^\mathrm{a,b}$ and $s_i{}^\mathrm{a,b}$, which are the expansion