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Coherent Raman spectra of the ν_1 mode of $^{10}BF_3$ and $^{11}BF_3$

Robynne Kirkpatrick [a], Tony Masiello [b], Alfons Weber [c], Joseph W. Nibler [a,*]

[a] *Department of Chemistry, Oregon State University, Corvallis, OR 97331-4003, USA*
[b] *Pacific Northwest National Laboratory, P.O. Box 999, Mail Stop K8-88, Richland, WA 99352, USA*
[c] *National Institute of Standards and Technology, Gaithersburg, MD 20899, USA*

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Abstract

High resolution (0.001 cm^{-1}) coherent anti-Stokes Raman spectroscopy (CARS) was used to directly examine the ν_1 symmetric stretching mode of the planar symmetric D_{3h} molecules $^{10}BF_3$ and $^{11}BF_3$. Simulations of the spectra were done using ν_1 rovibrational parameters deduced from published infrared hot-band and difference-band studies and the close similarity to the observed CARS spectra confirms the validity of the infrared constants. No significant perturbations by Fermi resonance or Coriolis interactions with nearby states are observed, in marked contrast to the case of sulfur trioxide, a similar D_{3h} molecule recently studied. In the harmonic approximation, the $^{10}BF_3$ and $^{11}BF_3$ ν_1 Q-branches would be identical since the isotopic substitution is at the center of mass but, interestingly, the ν_1 stretching frequency for $^{11}BF_3$ is found to be 0.198 cm^{-1} *higher* than for the lighter $^{10}BF_3$ isotopomer. This counterintuitive result is reproduced almost exactly (0.200 cm^{-1}) by ab initio calculations (B3LYP/cc-pVTZ) that included evaluation of cubic and quartic force constants and x_{ij} anharmonicity constants. The ab initio computations also predict to within 1% the ΔB, ΔC changes in the rotational constants in going from the ground state to the $\nu_1 = 1$ vibrational level. The results illustrate nicely the complementary interplay of modern infrared, Raman, and ab initio methods in obtaining and analyzing rovibrational spectra.

Keywords: Coherent Raman spectroscopy; CARS spectroscopy; Rovibrational spectrum; High resolution; Ab initio; Boron trifluoride; Boron-10, Boron-11

1. Introduction

In a recent series of papers [1–11], we have used high resolution infrared and coherent Raman methods to examine the spectroscopic properties of sulfur trioxide and boron trifluoride. Both molecules are classic examples of a planar symmetric top of D_{3h} symmetry. Each is a colorless reactive gas that fumes in the presence of moist air, hydrolyzing to form either sulfuric acid or hydrogen fluoride and boron hydroxides. SO_3 is of considerable industrial significance and it plays an important role in sulfur chemistry in the atmosphere [12]. BF_3 is widely used in the semiconductor industry for boron doping by ion implantation. It finds use as a catalyst in many chemical operations because of its ability to act as a strong Lewis acid due to an empty 2*p* valence orbital that readily accepts a donated electron pair. The D_{3h} molecular structure of BF_3 can be understood in terms of three boron sp^2 hybrid orbitals, each containing one electron from boron and one from fluorine. A similar hybridization picture can be applied to SO_3, with both electrons in each bond contributed by S. However, for SO_3, resonance forms involving a double bond can also be drawn and these too favor the observed trigonal planar structure.

Because of their high symmetry and relative simplicity, SO_3 and BF_3 are appealing prototypes for theoretical and experimental studies. High level ab initio electronic structure calculations have been performed on both molecules, including the computation of higher order cubic and quartic terms in the potential describing the atomic motion [13,14]. Four fundamental vibrational modes

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[*] Corresponding author. Fax: +1 541 737 2062.
E-mail address: Niblerj@chem.orst.edu (J.W. Nibler).

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occur for both molecules, of symmetry species $\Gamma = A_1'(R) + A_2''(IR) + 2E'(IR,R)$. All four fundamental transition frequencies have been deduced for $^{32}S^{16}O_3$, $^{34}S^{16}O_3$, $^{32}S^{18}O_3$, and $^{34}S^{18}O_3$ isotopomers [1–9], along with many transitions to combination or overtone states. Special interest has focused on the ν_1 symmetric stretching mode which can only be seen directly by Raman methods but whose transition frequency has been deduced from infrared active hot-bands and difference-bands. Fig. 1 shows the Q-branch coherent Raman (CARS) spectra for this mode for the various SO_3 isotopomers. The spectra show remarkable changes in both the pattern and positions of the transitions when isotopic substitutions are made. For example, substitution at the central S atom would not be expected to produce any change in the rotational constants or in the vibrational frequency since this position is at the center of mass of the molecule. However, the band shifts down about 0.5 cm^{-1} for $^{34}S^{16}O_3$ relative to $^{32}S^{16}O_3$ while an opposite upward shift of 1 cm^{-1} is observed for $^{34}S^{18}O_3$ relative to $^{32}S^{18}O_3$. Dramatic variations in the Q-branch patterns are also observed. With much effort, it was found that multiple Fermi resonant and Coriolis interactions with nearby states had to be considered to analyze the experimental spectra. Key features in this were the prediction of some of the interaction constants from the ab initio calculations and an exquisite sensitivity of the CARS Q-branch patterns to the rovibrational parameters deduced from the more resolved infrared hot bands.

The work on SO_3 shows the beneficial interplay of modern infrared, Raman, and ab initio methods in obtaining and analyzing rovibrational spectra. For BF_3, high resolution infrared spectra have recently been reported [10,11] as has one ab initio calculation that included anharmonic constants [14]. The ν_1 parameters were characterized deductively from the infrared spectra using combinations of transitions originating from the ground state and from a thermally populated ν_1 state. Description of the symmetric stretching mode of $^{10}BF_3$ resulted from analyzing the $110^00^0 \leftarrow 000^00^0$ and $110^00^0 \leftarrow 100^00^0$ A_2'' transitions, as well as from the combination of $001^10^0 \leftarrow 100^00^0$ and $001^10^0 \leftarrow 000^00^0$ E' excitations [10]. Similarly, parameters for $^{11}BF_3$ were inferred using the aforementioned state changes as well as the $100^01^1 \leftarrow 100^00^0$ and $100^01^1 \leftarrow 000^00^0$ E bands [11]. In analyzing these data to deduce the parameters for the forbidden ν_1 mode, coupling of the ν_1 levels to other states was not found to be necessary. However, an unusual 0.2 cm^{-1} *upward* shift in the band origin was seen for $^{11}BF_3$ relative to $^{10}BF_3$. The purpose of the CARS measurements presented here then was to obtain a direct view of this transition to confirm this shift and to see if the Q-branch structure of the CARS spectrum could be reproduced in simulations using the ν_1 parameters deduced in the infrared studies. A situation somewhat similar to that described here for the Q-branches of the totally symmetric vibrations of BF_3 and SO_3 was also encountered in the case of the Q-branch of the totally symmetric $B\ldots B$ stretching mode (ν_4) of diborane, $^{11}B_2H_6$ (D_{2h}) [15]. In that work, it was necessary to resort to a “band contour” analysis, matching Q-branch spectra computed with the aid of the ground-state parameters determined by infrared spectroscopy to the observed one [16]. A more accurate and satisfactory determination of the parameters for the ν_4 state of $^{11}B_2H_6$, and also of $^{10}B_2H_6$, was facilitated by the subsequent observation and analysis of their $\nu_{17} - \nu_4$ difference bands [17].

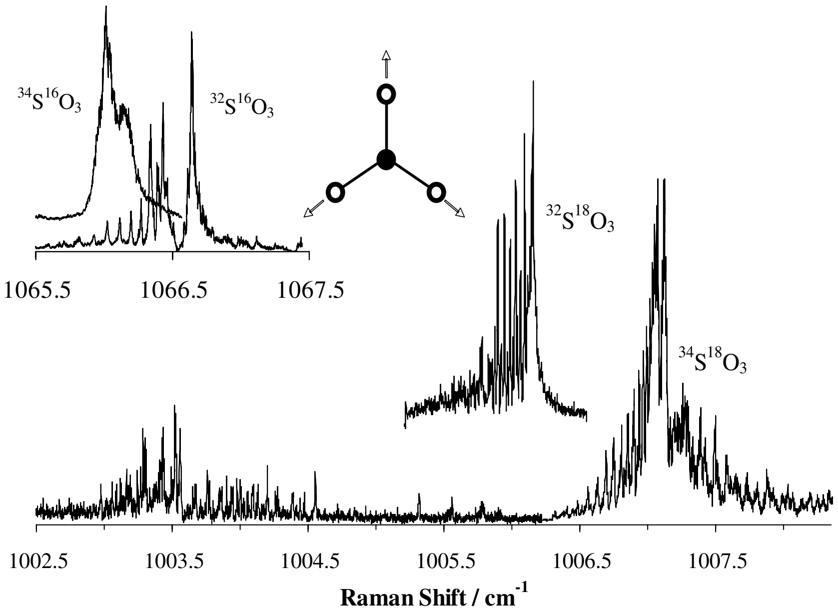

Fig. 1. The ν_1 mode and experimental CARS Q-branch spectra for D_{3h} isotopomers of SO_3.