Journal of Molecular Spectroscopy 263 (2010) 89–92

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

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

# High-resolution Fourier transform emission spectroscopy of the $A^1\Pi$–$X^1\Sigma^+$ system of $^{74}Ge^{80}Se$

B.J. Shetty [a], Adya P. Mishra [a,*], R.J. Kshirsagar [b], Richard D'Souza [a]

[a] Atomic & Molecular Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India
[b] High Pressure & Synchrotron Radiation Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

ARTICLE INFO

*Article history:*
Received 22 March 2010
In revised form 16 July 2010
Available online 23 July 2010

*Keywords:*
Fourier transform spectroscopy
Electronic transitions
Emission spectra
GeSe molecule

ABSTRACT

Natural germanium and selenium consist of, respectively, five and six stable isotopes. Several of these isotopes have considerable abundances and one should expect to observe the bands of at least six isotopic variants of germanium monoselenide (GeSe). In this paper, for the first time, the results of the high-resolution electronic spectrum of the main transition $A^1\Pi$–$X^1\Sigma^+$ of the specific isotopomer $^{74}Ge^{80}Se$, excited in a microwave discharge and recorded in the 33 500–26 000 $cm^{-1}$ region using a Fourier transform spectrometer, is discussed. From the rotational analysis of 25 bands involving $v''$ = 0–12 and $v'$ = 0–7, accurate vibrational and rotational constants of the $A^1\Pi$ state are determined. The present study has revealed perturbations in the $v'$ = 6 and 7 levels of the $A^1\Pi$ state.



## 1. Introduction

The germanium monoselenide (GeSe) molecule is a heavier member of the 10 valence electron series of inter-group (IVA and VIA) diatomics. Unlike the lighter molecules in this class (GeS, SiSe, etc.), investigation of the electronic spectrum of GeSe is limited to two early works [1,2]. Barrow and Jevons [1] first produced the spectrum in emission in the ultraviolet. Following this, Drummond and Barrow [2] observed the ultraviolet spectrum in absorption and attributed it to the $D^1\Pi$–$X^1\Sigma^+$ and $E^1\Sigma^+$–$X^1\Sigma^+$ transitions, in analogy with the other molecules like SiO, SiS, etc. However, the $D^1\Pi$ state is now redesignated as $A^1\Pi$ [3]. Subsequently, the molecule came under intense investigation in the microwave region [4–6]. Konno and Uehara studied extensively, the vibration–rotation spectrum of GeSe using a semiconductor diode laser (SDL) spectrometer [7]. As a result, the ground state, $X^1\Sigma^+$, of GeSe now remains well characterized. Recently, Manna and Das [8] studied several low-lying electronic states of GeSe by performing multi-reference and singles and doubles configuration interaction *ab initio* calculations. All these efforts not withstanding, to our knowledge, no high-resolution study of any of the electronic transitions of GeSe has been carried out so far. The major reason for this lacuna is the inherent isotopic complexity that arises in the spectrum of natural GeSe. This is because natural germanium and selenium consist of, respectively, five and six stable isotopes. Several of these isotopes have considerable abundances and one should expect to observe the bands of at least six isotopic variants of germanium monoselenide, ($^{70}Ge^{78}Se$, $^{70}Ge^{80}Se$, $^{72}Ge^{78}Se$, $^{72}Ge^{80}Se$, $^{74}Ge^{78}Se$ and $^{74}Ge^{80}Se$) in the spectrum of natural GeSe. This motivated us to commence a reinvestigation of the electronic spectrum of GeSe using single isotopes of germanium as well as of selenium. An initial low-resolution investigation of the main $A^1\Pi$–$X^1\Sigma^+$ transition in $^{74}Ge^{80}Se$ was reported by us, in which a total of 344 bands in the 35 000–25 000 $cm^{-1}$ region, most of them new, could be assigned [9]. In this paper, we report the results of analysis of the rotational structure in 25, relatively strong, bands of the $A^1\Pi$–$X^1\Sigma^+$ transition in $^{74}Ge^{80}Se$. Apart from providing accurate molecular parameters for the $A^1\Pi$ state, the present study reveals perturbations in the vibrational states $\acute{v}$ = 6 and 7 of the *A*-state.

## 2. Experimental details

The emission bands of $^{74}Ge^{80}Se$ were produced in a sealed quartz electrodeless discharge lamp (EDL) by microwaves (2450 MHz, ~100 W power). The method is similar to the earlier ones employed for the study of $Si^{78}Se$, $Si^{80}Se$, $^{70}GeS$ and $^{74}GeS$ [10–13], except that the single isotope $^{74}Ge$ (98%) in slight stoichiometric excess, was introduced into the quartz tube and the single isotope $^{80}Se$ (99%) was distilled into it subsequently. Prior to sealing the tube off the vacuum line, neon at a pressure of 5 torr was admitted to serve as a carrier gas. To maintain a steady vapor pressure of GeSe in the discharge column, the sealed tube was heated with an electrical furnace wound around a quartz envelope supporting the sealed tube.

The bands of GeSe belonging to the $A^1\Pi$–$X^1\Sigma^+$ transition in the 33 500–26 000 $cm^{-1}$ region were recorded on BOMEM DA8 Fourier transform spectrometer using a quartz beam splitter,

* Corresponding author. Fax: +91 22 2551 9613.
*E-mail address:* amishra@barc.gov.in (A.P. Mishra).

0022-2852/$ - see front matter © 2010 Elsevier Inc. All rights reserved.
doi:10.1016/j.jms.2010.07.007

photo-multiplier detector and appropriate filters. The spectra were recorded in three parts (26 000–29 000, 28 000–31 000, and 30 500–33 500 $cm^{-1}$) at an apodized resolution of 0.05 $cm^{-1}$ by co-adding 300 scans. A few atomic lines (mainly of Ge and Hg present as impurity) observed in the spectrum were used for internal calibration. The spectra were smoothened using five point FFT. A multi-peak Gaussian fit was used to determine the positions of the partially resolved or overlapping lines. The smoothening of spectra and multi-peak Gaussian fit was achieved using standard packages in Origin Lab, version 6.1.

## 3. Results and discussion

A portion of the high-resolution spectrum (28 000–3 1000 $cm^{-1}$) of the *A*–*X* transition of $^{74}Ge^{80}Se$ was reported in Fig. 2 of Ref. [9]. An overview of the spectrum in the region 30 650–32 650 $cm^{-1}$ is given in Fig. 1. The spectrum is dominated by sequences consisting of red degraded bands, separated by ~145–130 $cm^{-1}$. In Ref. [9] we reported a comprehensive vibrational analysis of the bands. In the present work, we report rotational analysis of 25 bands, listed in Table 1, involving $v''$ = 0–12 and $v'$ = 0–7. The bands taken up for analysis were so chosen that they are strong and involve common vibrational levels in the upper and/or in the lower electronic states. Each band shows a strong *Q*-branch, a head forming *R*-branch and a *P*-branch, characteristic of a $^1\Pi$–$^1\Sigma$ transition. The signal to noise ratio was not always very good and as mentioned in Section 2, the spectrum was smoothened using five point FFT method. Also for most of the bands, many lines of pairs of branches (either *P* and *Q* or *R* and *Q* and for some bands *P* and *R*) are overlapped or remained unresolved. Such structures were resolved by a multi-peak Gaussian fit. In all bands the structure extends beyond *J* = 100. A portion of the rotational structure of 1–3 band around

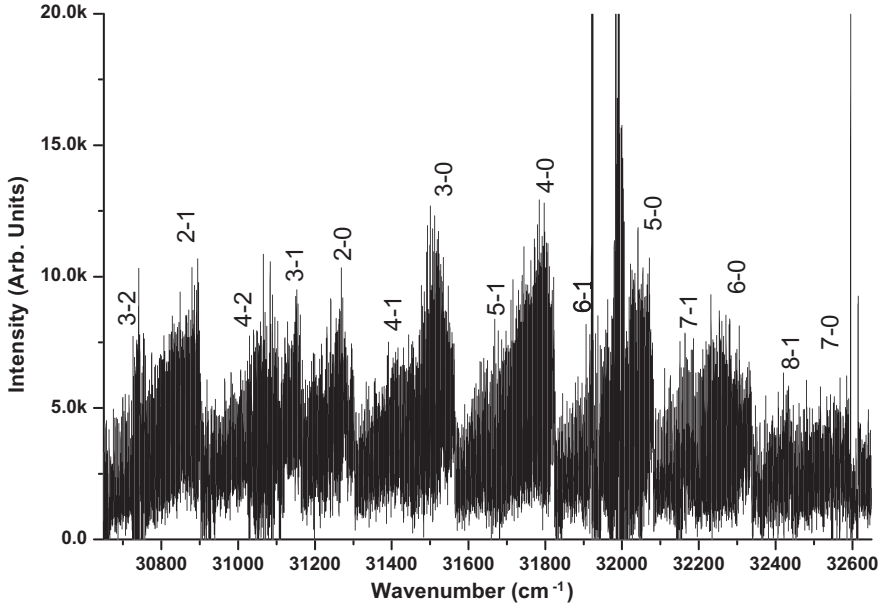


**Fig. 1.** An overview spectrum showing the $A^1\Pi$–$X^1\Sigma^+$ bands of $^{74}Ge^{80}Se$. The strong lines correspond to atomic transitions.

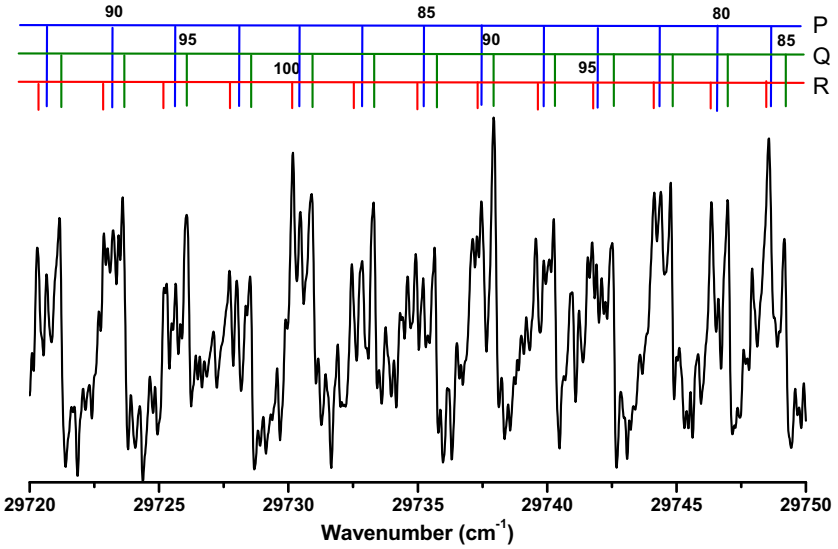


**Fig. 2.** A portion of the rotational structure of the 1–3 band with assignments (resolution = 0.05 $cm^{-1}$).