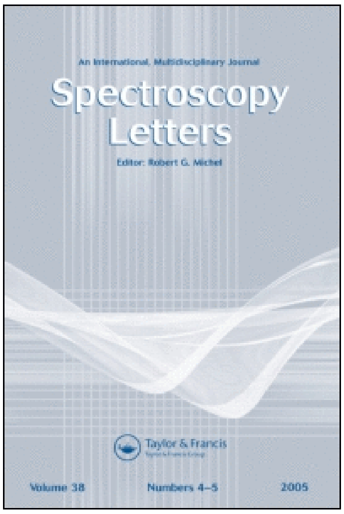

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Vibrational Structure of the B—X System of Isotopic Ago Molecules

V. Bojović[a]; A. Antić-Jovanović[a]; M. M. Stoiljkoviać[b]; M. Miletić[b]; D. S. Peĉić[b]
[a] Faculty of Physical Chemistry, University of Belgrade, Belgrade, F. R. Yugoslavia [b] Physical Chemistry Laboratory, Institute of Nuclear Sciences-Vinĉa, Belgrade, F. R. Yugoslavia

To cite this Article Bojović, V. , Antić-Jovanović, A. , Stoiljkoviać, M. M. , Miletić, M. and Peĉić, D. S.(1999) 'Vibrational Structure of the B—X System of Isotopic Ago Molecules', Spectroscopy Letters, 32: 5, 875 — 882

To link to this Article: DOI: 10.1080/00387019909350034

URL: http://dx.doi.org/10.1080/00387019909350034

SPECTROSCOPY LETTERS, 32(5), 875–882 (1999)

VIBRATIONAL STRUCTURE OF THE *B*—*X* SYSTEM OF ISOTOPIC AgO MOLECULES

Key words: Electronic spectra, silver oxide, isotopes

V. Bojović, A. Antić-Jovanović[♣] , M. M. Stoiljković*, M. Miletić*, D. S. Pešić*

Faculty of Physical Chemistry, University of Belgrade,
P. O. Box 137, 11001 Belgrade, F. R. Yugoslavia
*Physical Chemistry Laboratory, Institute of Nuclear Sciences-VINČA,
P. O. Box 522, 11001 Belgrade, F. R. Yugoslavia

ABSTRACT

Spectra of $^{107}Ag^{18}O$ and $^{107}Ag^{16}O$ molecules have been obtained in a low-pressure arc in oxygen atmosphere, and recorded with medium dispersion. Vibrational assignments for the bands of $B^2\Pi$—$X^2\Pi$ system were verified by the study of the oxygen isotope effect, and the vibrational constants were obtained for the states involved in transitions.

[♣] Corresponding author

www.dekker.com

INTRODUCTION

The gas-phase emission spectrum of AgO has been earlier reported by Loomis and Watson[1], Uhler[2] and Griffiths and Barrow[3]. Emission bands were observed in ultraviolet, blue and near-infrared regions. The $B^2\Pi$—$X^2\Pi$ (340-370 nm) and $A^2\Pi$—$X^2\Pi$ (410-480 nm) systems have been analysed[2, 3]. The nature of the ground $X^2\Pi$ state has been discussed in detail by Cheetham and Barrow[4] and Griffiths and Barrow[3, 5].

The matrix isolation technique enabled Griffiths and Barrow[5] to observe (0—0) bands of the (A—X) electronic transition of isotopic AgO molecules. In a recent paper Vujisić at al.[6] have studied the isotope shifts and vibrationally analyzed the (A—X) system of $^{107}Ag^{18}O$ molecule.

Recently O'Brien et al.[7] observed $A^2\Sigma^+$—$X^2\Pi_i$ transition of AgO that occurs in the near-infrared between 8 000 and 8 600 cm^{-1}.

The group of very weak complex bands obtained in emission in the spectral region of 550-650 nm[1-3], were tentatively attributed to the AgO molecule, but the emitter remained unidentified with certainty up to now.

In the present work, the B—X system of $^{107}Ag^{18}O$ was vibrationally analyzed for the first time and obtained constants, using isotope shifts relations, compared with those of the $^{107}Ag^{16}O$ molecule. F-C factors of $^{107}Ag^{16}O$ were calculated using the present and Uhler's data[2].

EXPERIMENTAL DETAILS

The apparatus and technique used to produce the spectra of the AgO molecule have been described in a previous publication[6]. The emission spectra of AgO were excited in a low-pressure arc in an ordinary atmosphere in oxygen-18. The spectra were photographed with a 2mZeiss PGS-2 spectrograph using the first order, double passing of a 600 grooves/mm plane grating which gave 0.25 nm/mm dispersion. Ilford HP5 film was used to photograph the spectra. The exposure times with a 40 μm slit width of the spectrograph, varied from 15 to 30 min. Spectral lines from a d.c. iron arc were used as wavelength standards. The accuracy of the measurements for unblended bands was better than 0.5 cm^{-1}.

RESULTS AND DISCUSSION

The *B*—*X* System of the $^{107}Ag^{16}O$

The $B^2\Pi$—$X^2\Pi$ emission bands of $Ag^{16}O$ are situated between 340 and 370 nm, and include $\Delta v = 0 \pm 1$ sequences. Double-headed bands degraded to the violet, with P_1 and P_2 branches forming the heads in the $^2\Pi_{1/2}$—$^2\Pi_{1/2}$ and $^2\Pi_{3/2}$—$^2\Pi_{3/2}$ sub-systems, respectively. A total of 20 bands have been measured. Our measurements of the bands agree well with those given by Uhler[2] and partly with those by Loomis and Watson[1]. Table 1. gives a complete list of all detected $^{107}Ag^{16}O$ bands.

The bands are situated along a narrow Franck-Condon curve, with most intense (0,0) bands. The distribution of the relative intensity of the observed bands in the system, was verified by the computation of the Franck-Condon factors (F-C factors). The spectroscopic constants (ω_e, $\omega_e x_e$ and B_e) for the computation are taken from the present analysis (Table 3.) and Uhler's data[2]. The constants B'_e for the upper *B* state have been calculated by using an empirical relation $\omega_e x_e/\omega_e \sim \alpha_e/B_e$ [8]. Because of the approximate nature of B'_e the F-C factors are not expected to be very accurate, but reflect the general trend of the intensity distribution. The computations have been performed by using the

TABLE 1. Band heads and isotope shifts of the *B*—*X* system of AgO molecule (cm^{-1})

v′—v″	$^{107}Ag^{16}O$	$^{107}Ag^{18}O$	$^{107}Ag^{18}O - {}^{107}Ag^{16}O$	
			obs	calc
3—2	28716.8 (1)[b, d]	28689.4 (-8)[d]	-27.4	-27.2
	28664.3 (3)[b, c]	28637.0 (-1)[c]	-27.3	
5—4	28742.8 (0)[a, d]	28717.7 (4)[d]	-25.5	-25.2
	28684.5 (0)[a, c]	28659.8 (0)[c]	-25.5	
4—3	28733.1 (2)[b, d]	28708.0 (4)[d]	-25.0	-26.5
	28677.0 (1)[b, c]	28651.1 (1)[c]	-25.9	
2—1	28693.7 (1)[b, d]	28667.4 (7)[d]	-26.3	-27.3
	28643.9 (2)[b, c]	28617.2 (0)[c]	-26.7	
1—0	28664.3 (0)[b, d]	28636.6 (-6)[d]	-27.7	-26.7
	28617.0 (4)[b, c]	28591.3 (3)[c]	-25.7	
1—1	28179.4 (1)[b, d]	28176.5 (0)[d]	-2.9	-2.9
	28133.3 (2)[b, c]	28131.1 (0)[c]	-2.2	
0—0	28137.5 (0)[b, d]	28136.7 (5)[d]	-0.8	-1.1
	28094.3 (0)[b, c]	28093.1 (-3)[c]	-1.2	
2—3	28741.0 (2)[b, d]	27759.6 (0)[d]	-18.6	-18.7
	28694.9 (3)[b, c]	27713.5 (0)[c]	-18.6	
1—2	28700.0 (5)[b, d]	27721.2 (2)[d]	21.2	20.4
	28655.6 (2)[b, c]	27676.4 (-1)[c]	20.8	
0—1	28652.5 (0)[b, d]	27675.0 (6)[d]	22.5	22.7
	28610.6 (3)[b, c]	27634.0 (0)[c]	23.4	

[a] Data taken from our measurements.

[b] Data taken from Ref. 2.

[c] P_1-Bandheads of $^2\Pi_{1/2}$—$^2\Pi_{1/2}$ sub-system.

[d] P_2-Bandheads of $^2\Pi_{3/2}$—$^2\Pi_{3/2}$ sub-system.

The numbers in brackets denote ($\nu_{obs} - \nu_{calc}$) in units of 0.1 cm^{-1}.

modified program developed by Felenbok[9]. The method is based on the assumption that the upper $B^2\Pi$ and lower $X^2\Pi$ state follow the Morse potential curve. Table 2. contains the F-C factors ($q_{v'v''}$) and relative intensities of the detected bands. It is apparent from the comparison that the relative intensities follow the calculated F-C factors. Taking into consideration the spectral response of the photographic emulsion, the predicted relative intensities based on the F-C factors, are in reasonable agreement with the experimentally observed intensities.

TABLE 2. Franck-Condon factors for *B*—*X* system of ^{107}Ag^{16}O

v′ \ v″	0	1	2	3	4	5	6
0	.727+0 10	.274+0 4	.250-1	.443-3	*	*	*
1	.220+0 4	.362+0 3	.362+0 3	.547-1	*	*	*
2	.452-1	.276+0 4	.182+0	.414+0 4	.813-1	*	*
3	.723-2	.905-1 2	.226+0 4	.949-1	.439+0 4	.100+0	*
4	*	.197-1	.123+0	.235+0	.539-1	.456+0 4	.110+0
5	*	.316-2	.339-1	.141+0	.199+0	.359-1	.473+0
6	*	*	.653-2	.469-1	.149+0	.168+0	.301-1

Upper entry: $q_{v'v''}$, the sign and final digit indicate the power of 10 to which the entry should be raised.

* F-C factors < .001

Lower entry: Intensities in the Table are estimated on a scale of ten.

The *B*—*X* System of the ^{107}Ag^{18}O

The outstanding bandheads of the ^{107}Ag^{18}O isotopic species are given in the second column of Table 1. In all,10 bands of this molecule have been measured in the region 340-370 nm. The observed intensities of the band heads are in accordance with those expected for the $^2\Pi$—$^2\Pi$ transition ; double-headed bands with the separation of about 47 cm^{-1}, degraded to the violet. These bands are appreciably shifted from the corresponding bands of ^{107}Ag^{16}O molecule.

Columns 3 and 4 (Table 2) give the values for the vibrational isotope shifts observed experimentally and calculated by using the first order isotope shift equation :

$$v^i - v = (\rho-1)\,[\omega'_e\,(v'+1/2) - \omega''_e\,(v''+1/2)],$$

The vibrational constants ω_e of the $B^2\Pi$ and $X^2\Pi$ state of ^{107}Ag^{16}O molecule from the present analysis and reduced mass constant $\rho = [\mu(^{107}\mathrm{Ag}^{16}\mathrm{O})/\mu(^{107}\mathrm{Ag}^{18}\mathrm{O})]^{1/2} = 0.95034$

were used. Only the vibrational numbering scheme given by Uhler, gives good overall agreement between experiment and calculation, thus establishing the vibrational assignment of the bands.

As the vibrational constants of the upper and the lower states are rather close to each other, the expected isotopic separation v^i-v for the ^{107}AgO — ^{109}AgO molecules for the Δv = 0 sequence lie within the experimental error of the measurements of band heads. Since the intensity distribution in the system follow a narrow Condon parabola, the higher sequences with Δv = ±2, which are favorable for the study of the isotope effects, are too weak to be observed.

Molecular Constants

The analysis was performed for more abundant isotopic species $^{107}Ag^{16}O$ and $^{107}Ag^{18}O$. All detected bands fit into a simple Deslandres scheme. Following Uhler's analysis, the vibrational levels of the upper and lower states can be represented by the quadratic vibrational equation[7]:

$$G(v) = \omega_e (v+1/2) - \omega_e x_e (v+1/2)^2$$

The values of ω_e and $\omega_e x_e$ for the electronic states involved in transition, as well as the system origine ν_e were calculated using the data of all band heads in a nonlinear least-squares procedure. The vibrational constants with estimated errors for observed electronic transitions of the AgO molecule have been collected in Table 3.. The ν_{calc} for the bands obtained with these constants, are included in Table 1. Constants for the $^{107}Ag^{16}O$ molecule are compared with the previous results. Good agreement with the results of Uhler is an evidence for accuracy of the measurements and the correctness of the analysis.

TABLE 3. Vibrational constants for *B* and *X* states of AgO molecules (cm^{-1})

	Const.	*B*		*X*		Ref.
		$^2\Pi_{3/2}$	$^2\Pi_{1/2}$	$^2\Pi_{3/2}$	$^2\Pi_{1/2}$	
	T_e	X_2+28113.9	X_1+28072.1	X_2	X_1	2
		X_2+28114.2 (1)	X_1+28072.9 (3)	X_2	X_1	*
$^{107}Ag^{16}O$	ω_e	539.1	535.7	490.7	489.9	2
		539.1 (2)	533.7 (3)	490.8 (3)	489.8 (3)	*
	$\omega_e x_e$	6.15	6.34	2.87	3.05	2
		6.15 (1)	5.31 (2)	2.93 (2)	3.05 (4)	*
	T_e	X_2+28114.1 (2)	X_1+28072.1 (5)	X_2	X_1	*
$^{107}Ag^{18}O$	ω_e	512.2 (6)	508.9 (1)	466.7 (8)	467.5 (6)	*
	$\omega_e x_e$	5.61 (3)	5.53 (6)	2.26 (7)	3.02 (9)	*

* This work

Figures in parenthesis are one standard deviations in units of the last significant figures.

The vibrational constants for $^{107}Ag^{18}O$ derived directly from the spectrum are in good agreement with those calculated on the basis of the isotopic relation using the constants of the $^{107}Ag^{16}O$ obtained in the present work and Uhler's data[2].

REFERENCES

1. Loomis FW and Watson TF. Phys. Rev. 1935; 48: 280.
2. Uhler U. Ark. Fys. 1954; 7: 125.
3. Griffiths MJ, Barrow RF. J. Phys. B: Atom. Molec. Phys. 1977;10: 925.
4. Cheetham CJ and Barrow RF. Adv. High Temp. Chem. 1967; 1: 7.
5. Griffiths MJ and . Barrow RF. J. C. S. Faraday II 1977; 73: 943.
6. Vujisić BR, Savović JJ, Bojović V and Pešić DS. Spectrosc. Lett. 1993; 26: 1529.
7. O'Brien LC, Wall SJ and Sieber MK. J. Mol. Spectrosc. 1997; 183: 57.
8. Herzberg G. *Spectra of Diatomic Molecules*, 2nd ed. New York: Van Nostrand Reinhold Co., 1950: 149.
9. Felenbok P. C. R. Acad.Sc. 1963; 256: 2334.

Date Received: August 10, 1998
Date Accepted: April 15, 1999