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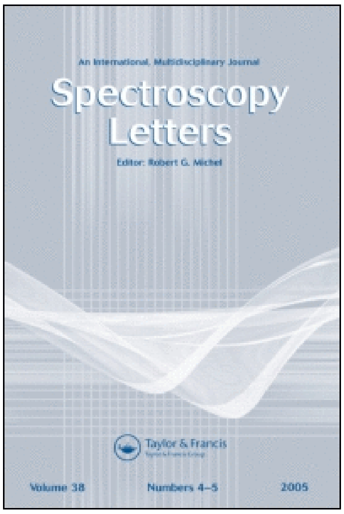

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BLUE (A-X) SYSTEM OF $^{107}Ag^{18}O$ MOLECULE

Key words: Electronic spectra, silver oxide, isotopes

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ABSTRACT

The blue $A^2\Pi$-$X^2\Pi$ emission system of the $^{107}Ag^{18}O$ molecule excited in a low-pressure arc, was recorded in the region 400-475 nm with medium dispersion. The vibrational analysis, supported by isotope shifts study, of the red-degraded bands has been made. The final set of the improved $^{107}Ag^{16}O$ and the new $^{107}Ag^{18}O$ vibrational constants of the two sub-systems involved in transition are determined.

INTRODUCTION

Our knowledge regarding the spectra of diatomic transition metal oxides in the gas phase are not yet conclusive. Bands of the spectra assigned to AgO molecule have been correlated to the transitions between excited electronic energy levels and the ground state. The bands are situated in the two regions: ultraviolet degrading bands between 340-370 and those degraded to longer wavelengths between 410 and 460 nm.

The first systematic study of AgO spectra was done by Loomis and Watson(1). They observed ultraviolet and the blue emission bands in a d.c. arc,

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between silver electrodes operating in a stream of oxygen. Authors analysed the vibrational structure and concluded that the bands are due to $^2\Sigma$-$^2\Sigma$ and $^2\Pi$-$^2\Sigma$ systems with a common lower state. Uhler(2) has carried out the new vibrational and the first rotational analysis of few bands of both systems obtained in high current low-pressure arc between silver electrodes. Author has ascribed the ultraviolet bands to $B^2\Pi$-$X^2\Pi$ and those in blue region to $A^2\Pi$-$X^2\Pi$ transitions respectively. The results of a new analysis of the A-X system obtained in emission from a hollow-cathode discharge, have been reported by Griffiths and Barrow(3). The results largely confirmed Uhler's analysis, and suggested a possible resolution of the anomaly of the character of the $X^2\Pi$ state. The same authors(4) have investigated the electronic spectra of CuO, AgO and AuO isolated in rare gas matrices at low temperatures. In AgO spectrum (0-0) band of the A-X electronic system has been detected. Observed small isotope effect with oxygen-18, and correlation with A-X gas phase system, confirm that the traped species is certainly AgO molecule.

For a long time, a group of weak bands in near-red region has been observed in spectroscopic investigation of AgO molecule(1,2,3). However, the emitter of these bands has not been known up to present.

The aim of the present study has been to obtain the improved $Ag^{16}O$, and the new vibrational constants of isotopic $Ag^{18}O$ molecules. The results obtained are presented in this paper.

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EXPERIMENTAL

The $Ag^{18}O$ bands have been obtained in emission using a low-pressure arc burning in an atmosphere of oxygen-18 (95 atom %, supplied by Isotec, Inc.) between the water-cooled silver electrodes. The design of the discharge chamber was described elsewhere(5,6). A d.c. power supply, opperated at 1 kV and 0.9 A, was used to mantain the discharge. A total pressure of 10-16 kP gave a stable discharge during the exposure times. The spectra were photographed on a Hilger E478 glass spectrograph, which gave a dispersion of about 0.7 nm/mm in the blue region. The A-X system was also recorded in the first order of a 600 grooves/mm grating (disper. 0.5 nm/mm) on a 3-m Eagle spectrograph. Exposure times between 2 and 6 hours were required to obtain the spectra with reasonably good intensity on a Ilford HP5 film. Iron arc lines were used as a comparision spectrum. The band head positions were measured with an uncertainty of about 0.5 cm^{-1} for unblended bands.

RESULTS

The A-X system is the most prominent AgO system. In emission spectrum between 400-475 nm, 15 red-degraded bands occur in pairs, similar in appearance to ordinary AgO bands, but displaced by isotope separation. The bands of each pair are separated by a constant interval of 172 cm^{-1}. The bands belong to $A^2\Pi_{3/2}$ - $X^2\Pi_{3/2}$ and $A^2\Pi_{1/2}$ - $X^2\Pi_{1/2}$ sub-systems of the $A^2\Pi$ - $X^2\Pi$ transition, where the R_2 and R_1 branches form the heads respectively. In the present study the observation of the $Ag^{18}O$ data has enable four more weak bands of this system, namely (1-5), (1-6), (1-7) and (1-8), to be identified. Wavenumbers of the known $Ag^{16}O$ bands measured here have been well consistent with previous results(2,3). In Table 1., the wavenumbers and the vibrational assignments of the observed bands for both isotopomers are given. The bands of each pair are of approximately equal intensity. The strongest bands are (0-0) bands. The rapid change of intensity in the v''=0 progression follow the change of Franck-Condon factors calculated with the large effective value of anharmonicity constant ($\omega_e x_e$=33.5)(3) of the upper state. The band (2-0) has not been observed.

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The Isotope Effect

The isotope shifts of the bands of the A-X system of $^{107}Ag^{18}O$ relative to $^{107}Ag^{16}O$ are obtained as the difference of the bandheads. The observed isotope shifts thus obtained for all observed bands are listed in Table 1. respectively. The vibrational isotope shifts were calculated from the standard expression(7) using the vibrational constants of the A and X states of the $^{107}Ag^{16}O$ taken from the Uhler(2) and $\rho=[\mu(^{107}Ag^{16}O)/\ \mu(^{107}Ag^{18}O)]^{1/2}=0.95034$, and are listed in the same Table. The satisfactory agreement support the assignment of the observed bands, as well as the vibrational numbering in the $A^2\Pi$ and $X^2\Pi$ states given by Uhler. The isotope shift as well as Uhler's vibrational scheme show that Loomis and Watson's values for v' quantum numbers are to be revised by one unit.

TABLE 1.

Band Heads and Isotope Shifts of the A-X System of AgO Molecules (cm^{-1})

v'-v"	$^{107}Ag^{16}O$	$^{107}Ag^{18}O$	$^{107}Ag^{18}O$ - $^{107}Ag^{16}O$	
			$\Delta\nu_{obs}$	$\Delta\nu_{calc}$
1-0	Ag*	Ag*		-5.6
	24481.8 (4) [a,d]	24476.0 (-8)	-5.8	
0-0	24416.0 (0) [a,e]	24422.5 (0)	6.5**	6.2
	24244.5 (0) [a]	24250.6 (-2)	6.1	
0-1	23931.1 (-2) [a]	23962.6 (-3)	31.5	30.0
	23760.3 (-2) [a]	23790.1 (-2)	29.8	
1-2	23693.5 (2) [a]	Ag*		41.4
	23518.9 (-4) [a]	23562.1 (9)	43.2	
0-2	23452.4 (2) [a]	23503.7 (10)	51.3	53.1
	23281.7 (-7) [a]	23334.2 (-4)	52.5	
1-3	23220.0 (0) [a]	23284.5 (4)	64.5	64.0
	23046.7 (-4) [a]	23111.7 (8)	65.0	
0-3	22973.3 [a,f]	23057.4 (5)	84.1	75.7
	22811.0 (8) [a]	22885.1 (7)	74.1	
1-4	22751 [b]	22842.7 (9)	92	86.0
	22578 [b]	22664.9 (8)	87	
1-5	22290.2 (-3)	22399.0 (2)	108.8	107.4
	22120.6 (3)	22225.2 (-6)	104.6	
1-6	21834.6 (2)	21962.2 (-4)	127.6	128.1
	21666.3 (5)	21790.4 (-6)	124.1	
1-7	21384.9 (9)	21531.7 (5)	146.8	148.4
	21216.6 (-5)	21362.8 (9)	146.2	
1-8	20939.2	21101.3 (-4)	162.1	168.1
2-6	22015 [b]	22139.2	124	120.6 [c]
	21834.5 [b]	21950.1	115.6	120.0 [c]
2-7	21564 [b]	21702.3	138	139.7 [c]
	21384 [b]	21524.8	141	142.0 [c]
2-8	21115 [b]	21283.7	169	162.0 [c]
	20943 [b]	21101.8	159	164.0 [c]

* Not observed due to overlaping atomic line. ** The shift between the lowest energy bands of $Ag^{18}O$ and $Ag^{16}O$ in xenon matrices is 5 cm^{-1} (4).

[a] Data taken from Ref. (2). [b] Data taken from Ref. (3). [c] Calculated from the Eq. : $\Delta G'_{v+1/2}(Ag^{18}O)=\rho\,[\Delta G'_{v+1/2}(Ag^{16}O)]$. [d] R_1 - Bandheads of $^2\Pi_{1/2}$ - $^2\Pi_{1/2}$.

[e] R_2 - Bandheads of $^2\Pi_{3/2}$ - $^2\Pi_{3/2}$. [f] Uncertain.

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

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The position of (2-6), (2-7) and (2-8) bands in Deslandres table, given by Griffiths and Barrow(3), which are not included in Uhler's vibrational sheme, were verified by isotopic displacement. The upper state $\Delta G'_{v+1/2}$ ($Ag^{18}O$) values have been compared to the $\Delta G'_{v+1/2}$ ($Ag^{16}O$) by converting with the isotopic relationship: $\Delta G'_{v+1/2}$ ($^{107}Ag^{18}O$)=ρ [$\Delta G'_{v+1/2}$ ($^{107}Ag^{16}O$)]. The corresponding values are listed in Table 1. A reasonably good agreement between calculated and isotope shift measurements confirm the assignments of these bands as a part of the A-X transition. The measured isotope splitting are also used to demonstrate that AgO is the emitter of the spectrum.

The natural silver is the mixture of two isotopes ^{107}Ag and ^{109}Ag, with relative abundances of 51.4 and 48.6 % respectively. The vibrational isotope separation of ^{107}AgO - ^{109}AgO for the most intense bands near system origine is the order of magnitude of 0.2-0.9 cm^{-1}, and was not observed.

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Molecular Constants

A few new bands and the well agreement between our measurements of $Ag^{16}O$ bands and those given previously by Uhler(2) and partly by Griffiths and Barrow(3), provide an opportunity to reevaluate the vibrational constants given previously by these authors. The band-heads R_2 and R_1 of the sub-bands listed in Table 1., were fitted to the standard quadratic vibrational equation(7):

$$\nu\ (v',v'')_{3/2,1/2} = T_{e\ 3/2,1/2} + G'(v) - G''(v)$$

where ν (v',v"), T_e and G(v) have a usual meaning(7).

Band-heads positions and corresponding vibrational assignments, have been used as input in the least-squares fitting procedure. From this fit, the origins of the sub-systems of the A-X system, the vibrational constants ω_e and $\omega_e x_e$ of state X, and ω_e of state A were obtained. The constants are given in Table 2. along with their standard deviations. Due to comparison, Table 2. contains also the vibrational constants for $^{107}Ag^{16}O$ isotopic species obtained previously. Up to now, the most reliable molecular parameters of the $A^2\Pi$ and $X^2\Pi$ states of $^{107}Ag^{16}O$ have been given by Uhler(2). Uhler's data, with new Griffiths and Barrow's(3) and our measured bands of the higher vibrational levels of the $A^2\Pi$ state, allowed us to obtain better precision. The results are given in the third row of the Table 2.

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TABLE 2.
Vibrational Constants for A and X States of AgO Molecules (cm^{-1})

		A		X		
	Const.	$^2\Pi_{3/2}$	$^2\Pi_{1/2}$	$^2\Pi_{3/2}$	$^2\Pi_{1/2}$	Ref.
	T_e	X_2+24539.9	X_1+24370.5	X_2	X_1	(2)
		24412.30 [a]				(3)
		X_2+24540.0(2)	X_1+24370.2(3)	X_2	X_1	*
$^{107}Ag^{16}O$	ω_e	241.0 [b]	237.2	490.3	490.5	(2)
				490.2	490.9_1	(3)
		241.1(2) [b]	236.9(2)	490.5(1)	489.9(2)	*
	$\omega_e x_e$			2.8_5	3.0_4	(2)
				2.8_4	3.1	(3)
				2.86(1)	2.94(2)	*
	T_e	X_2+24540.0(2)	X_1+24369.4(9)	X_2	X_1	*
$^{107}Ag^{18}O$	ω_e	228.5(9) [b]	226.4(5)	464.7(4)	465.6(5)	*
	$\omega_e x_e$			2.37(4)	2.56(6)	*

[a] ν_{00} ($^2\Pi_{3/2}$ - $^2\Pi_{3/2}$); [b] $\Delta G_{1/2} = \omega_e - 2\,\omega_e x_e$; * This work
Figures in parenthesis are one standard deviations in units of the last significant figures.

It can be seen that the constants derived from the all identified bands are in good agreement with those calculated by Uhler. The discrepancies are within the probable errors of the calculations.

The vibrational constants of the $^{107}Ag^{18}O$ molecule given in last columns are compared to the corresponding ones obtained from those of the natural isotope. The agreement between constants is satisfactory. Conclusion which can be drawn from the Table 2. is, the consistency of isotopic analysis results with the vibrational assignments that we have made for the bands observed.

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REFERENCES

1. F. W. Loomis and T. F. Watson, Phys. Rev. 1935; **48**: 280.
2. U. Uhler, Ark. Fys. 1954; **7**: 125.
3. M. J. Griffiths and R. F. Barrow, J. Phys. B: Atom. Molec. Phys. 1977; **10**: 925.
4. M. J. Griffiths and R. F. Barrow, J. C. S. Faraday II 1977; **73**: 943.
5. V. Bojović, Ph. D. Thesis, University of Belgrade 1992.
6. B. R. Vujisić and D. S. Pešić, Fizika 1972; **4**: 69.
7. G. Herzberg, *Spectra of Diatomic Molecules*, 2nd ed. New York: Van Nostrand Reinhold Co., 1950: 149.

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