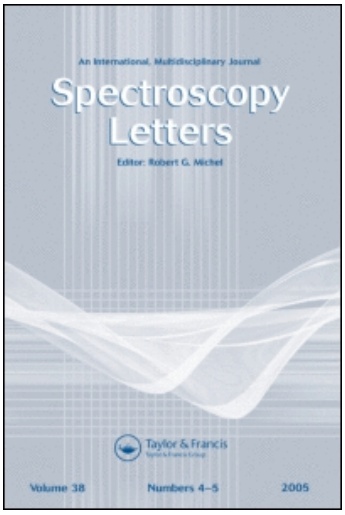

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Intracavity Electronic Absorption Spectra of MoO and WO Molecules in the Visible Region

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INTRACAVITY ELECTRONIC ABSORPTION SPECTRA OF MoO AND WO MOLECULES IN THE VISIBLE REGION

Key words: intracavity laser technique, electronic spectra, monoxides of molybdenum and tungsten, molecular constants.

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ABSTRACT

Absorption electronic spectra of MoO and WO molecules have been investigated by a intracavity laser technique in the region 550-800 nm. New features have been discovered.

As for MoO molecule the rotational analysis of the four bands have been carried out for the first time. Two of these bands were referred to 0-0 transitions arisen from the new (probable triplet) low-lying electronic state, two other bands were referred to transitions arisen from excited components of $X^5\Pi$ ground state.

As for WO molecule the rotational analysis of 0-0 and 1-0 bands represented A-X and B-X systems have been carried out for the first time. The new band has been discovered which has been referred to new electronic transition.

Molecular constants of new states of both molecules studied have been evaluated.

INTRODUCTION

Progress in the studying complex electronic molecular spectra is speeded up by improving experimental technique.

The laser intracavity spectroscopic technique is of modern one which has been developed over the past years. This technique has been theoretically substantiated and experimentally validated in [21, 22]. This technique is based on a depression of the intensity in the spectrum of the laser generation at the wavelengths corresponding the absorption spectrum of the substance which is inserted into the cavity. Nowadays this technique is the most sensitive one for the absorption measurements.

This intracavity spectroscopic technique has been successfully used at department of chemistry of Moscow State University since 1983 for obtaining additional bands in spectra of some mononitrides of the transient metals. These additional bands allowed us to evaluate the new molecular constants for TiN [11,12], ZrN [13], NbN [14,15], MoN [16,17] molecules.

The purpose of the present work is to study electronic spectra monoxides of molybdenum and tungsten by intracavity technique.

EXPERIMENT

The experimental set-up used in the current studies has been described in detail elsewhere [11].

Diatomic MoO and WO were produced by an electric discharge of the capacitor (C=0.5 μF, V=10 kV) through mixture of vapor of molybdenum or tungsten carbonyl and of argon at 1-2 torr. The tube of quartz used as a discharge cell was 30 cm long and 2 cm in diameter. Carbonyls were placed into the tube, and the tube was located in the cavity of a dye laser. The tube could be heated to increase pressure of the carbonyl's vapor.

The spectra in the region 18000-13000 cm^{-1} were photographed in the 25-27 orders of 4 m grating-mounted spectrograph at a reciprocal dispersion of about 0,1 nm/mm.

To detect the correct molecular spectra, the time resolved technique was employed to suppress an appearance of atomic lines of transient metal in spectra studied. The time delay between the dye-laser and discharge pulses could be changed within 10-2000 ms and was controlled with the help of a photomultiplier

and oscillograph. Optimum condition for recording the best MoO and WO molecular spectra were delayed about 50 ms between pulses.

The accuracy of the measurements of the sharp unblended rotational lines in molecular spectra is of the order of 0.03 cm^{-1}.

RESULTS

MoO molecule

The first electronic spectrum of the MoO molecules were discovered in 1933 [1]. Afterwards spectrum of this molecule has been studied many times [2-8]. There are a lot of bands in the spectrum. Each band has a lot of lines of the rotational structure. The rotational structure of adjacent bands overlap strongly, and the spectrum seems to be structureless on the whole. The partial analysis of the structure of the observable spectrum has become reliable only in the last years, due to development of modern spectroscopic technique which allowed to decrease number of rotational line for each band [9] of molecules under very low temperature condition.

In comparison with research previously reported in literature we obtained absorption spectrum which belongs to molecules under high temperature. Several intense new bands over those previously reported in emission spectrum have been identified in visible region. These bands are red degraded.

Each band recorded has the broad, overlapped rotational structure, and we was able to separate only the four bands which are suitable for analysis.

One would expect isotopic effects to be displayed because molybdenum has seven stable isotopes four of which have almost equal abandons. However we did not detect any vibrational isotopic shifts in these bands. Therefore it would be proposed that all these bands are (0-0) bands.

Two of the bands (15510.68 cm^{-1} and 155365.03 cm^{-1}) are of very simple structure consisting of a single P and R branch. The rotational analysis has been performed and rotational constants of lower and upper states have been derived. Figure 1 shows microphotometer tracing of the 15510.68 cm^{-1} band and the assignment of lines. The wave numbers of the branch lines were fitted by least-squares methods to the standard formula $\nu=\nu(0)+B'x'-Dx'^2-B''x''+D''^2$, where $x=J(J+1)$ and the absolute J-numbering was established by J variation to minimize the overall standard deviation. It should be recognized that when the rotational

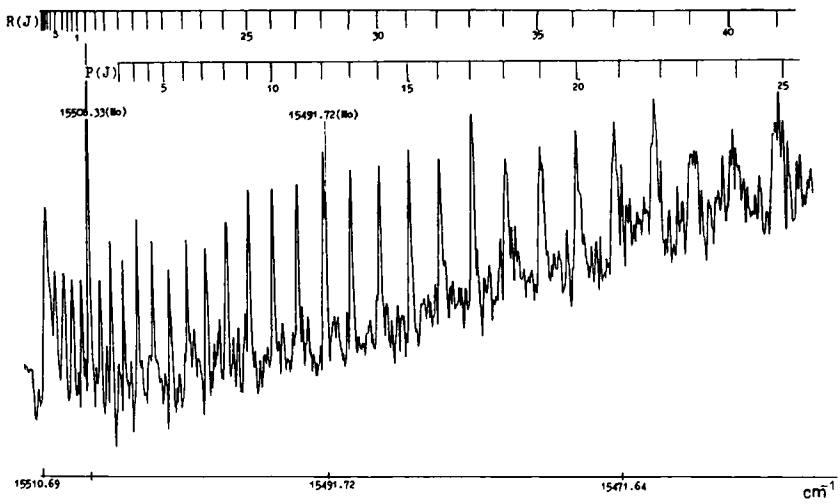

Fig. 1. Microphotometer trace of the intracavity dye laser absorption spectrum of the MoO (0,0) band in the region 15510-15450 cm^{-1}.

constants are obtained in this manner, the values $\Delta B=B'-B''$ and $\Delta D=D'-D''$ are much reliable determined then the individual upper and lower state rotational constants, which may be strongly correlated. The rotational constants derived in such a manner from each band are given in Table 1.

The rotational constant obtained for lower state is not in agreement with that (0.4175 cm^{-1}) of ground $X^5\Pi$ state calculated in [9]. That is way, we assume that the bands recorded belong to a new electronic transition between triplet states, one of which, namely lower state, lays about 2000 cm^{-1} above the ground MoO molecular state. The position of the triplet state has been predicted by ab-initio calculation [20].

Our assignment of these bands to the transition between triplet states based on the fact that the initial triplet state is well populated under the high temperature condition used in the present study. In the another study of absorption spectra of MoO molecule [9] authors used the MoO molecules which have been cool off until very low temperature. Therefore the population of the triplet state had to be very little, and these bands had no opportunity to be recorded. The alone band 15365.03 cm^{-1} has been recorded with extremely low intensity.

Table 1. Heads of the bands and rotational constants (in cm^{-1}) derived from the isolated bands of the MoO molecule.

head of band	B"	B'	D"*10^7	D'*10^7
15510.78	0.40605(5)	0.36161(18)	6.96(1)	9.42(5)
15365.03	0.40776(9)	0.36417(15)	5.12(5)	7.42(8)
15053.39	0.40630(7)	0.38227(9)	1.56(3)	2.3(3)
14811.84	0.40413(9)	0.38171(6)	2.22(6)	1.96(3)

On the base of rotational constants evaluated, it was estimated that a rotational isotopic shift should be manifested by broadening (or splitting) of these rotational lines at values of rotational quantum numbers being equal to 35-40 or more. Really, the line of R branch with J equal to 34, becomes broader and the lines with J equal more then 39 are diffuse (see Fig.1).

It may be concluded from the absence of Q lines that the transition has $\Delta\Omega=0$. However, without information regarding J assignments of the first members in the branches, the value of Ω cannot be established.

Two other bands (15053.39 cm^{-1} and 14811.84 cm^{-1}) consist of group of lines which have been assigned to R, Q, and P branches. The rotational analysis has been performed for each band and rotational constants of lower and upper electronic states have been derived. These constants are shown in Table 1. Figure 2 shows microphotometer tracing of the 15053.39 cm^{-1} band and the assignment of lines.

The rotational constants of lower state studied are close to rotational constants of ground electronic state of MoO molecule from [9].

Because the values of these rotational constants are close to those of $X^5\Pi$ state, we assign 15053.39 cm^{-1} and 14811.84 cm^{-1} bands to transition arisen from excited components of manifold $X^5\Pi$ state. Lambda doubling in the first lines of rotational structure of the bands studied has not been observed as it should for this transition.

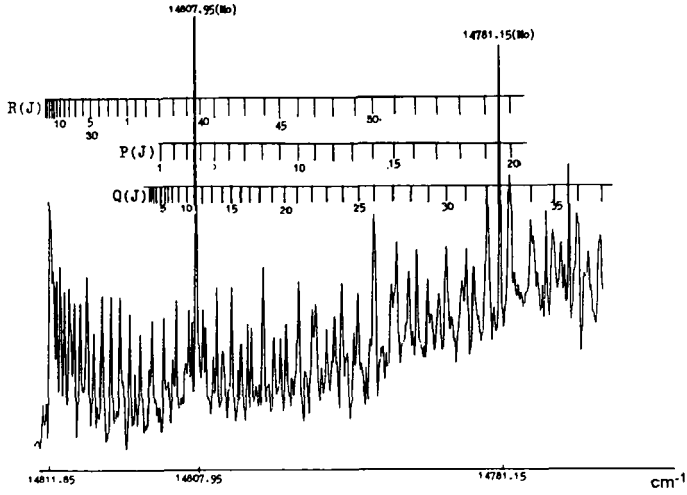

Fig.2. Microphotometer trace of the intracavity dye laser absorption spectrum of the MoO (0,0) band in the region 14811 - 14770 cm^{-1}.

WO molecule

The most extensive analysis of the WO electronic spectrum has been carried out in [10]. Ten electronic states have bee identified. Rotational constants of ground and excited states have been derived from analysis of 14 bands. However, rotational analysis of bands assigned to A-X and B-X transitions has not been performed because these bands have the very low intensity.

More then 20 bands, which have not been observed previously, have been recorded. The next new bands have been assigned to transition related earlier to A-X and B-X electronic systems.

It has been discovered that the assignment of 17172.32 cm^{-1} and 16114.91 cm^{-1} bands to 3-0 and 3-1 vibrational transitions of A-X systems [10, 19] is wrong.

Namely, the vibrational isotopic shifts, which have been calculated using the vibrational molecular constants taken from [10] do not coincide with these experimental values measured by us. On the basis of the isotopic shifts studied in the present research, we assign the 16114.91 cm^{-1} band, with zero isotopic shift, and the 17172.32 cm^{-1} band with isotopic shift equal -0.8 cm^{-1}. In this connection they can be regarded as 0-0 and 1-0 bands.

The structure of these red-degraded bands consists of a single P,R, and Q branch. Figure 3 shows microphotometer tracing of the 16114.91 cm^{-1} band and the assignment of lines. The rotational constants of the upper and lower electronic state have been derived. The rotational constants of the lower state are the same in values with that of the vibrational state v=0 of X electronic state {B0($X0^+$)=0.415349 cm^{-1}, B1($X0^+$)=0.413028 cm^{-1}}. We came to the conclusion that these bands belong to the transition started from the ground state. The rotational constants of the new excited state are given in Table 2.

For the first time, the 0-0 and 0-1 bands (17250.92cm^{-1} 16193.84 cm^{-1}) of B-X system have time been rotationaly analyzed.

The rotational constants for B-state are given in Table 2.

The new band of 15499.35 cm^{-1} degraded to the red has been discovered. The band has isotopic shift equal to zero. The structure of this band is similar to that of 16114.91 cm^{-1}. It is likely that this band belongs to new (A') electronic transition. There is not enough information to make the more correct conclusion. The absolute J numbering was determined in the usual way, independently from plots of $\Delta_2F'(J)$, $\Delta_2F''(J)$, and Q(J) first differences. The consistency of these results suggests an uncertainty of these in the absolute J numbering of ± one unit. Figure 4 shows microphotometer tracing of the 15499.35 cm^{-1} band and the assignment of lines.

DISCUSSION

Spectra of MoO and WO molecules are wildly complicated, and there are no comprehensive assignment of each bands observed in spectra. The modern spectroscopic techniques which has been applied for studying spectra recover regular structure of some bands. On the basis of this structure the molecular constants of the ground and of some excited states have been derived for MoO [9] and WO [10] molecules. Nevertheless there still a lot of unclassified bands.

For the first time, the intracavity laser technique has been used to investigate electronic spectra of MoO and WO molecules. This technique allowed us to make next step in understanding these complicated spectra, namely: new bands in the spectrum of MoO has been assigned to transition from triplet electronic state which has been predicted by ab-initio calculations; for the first

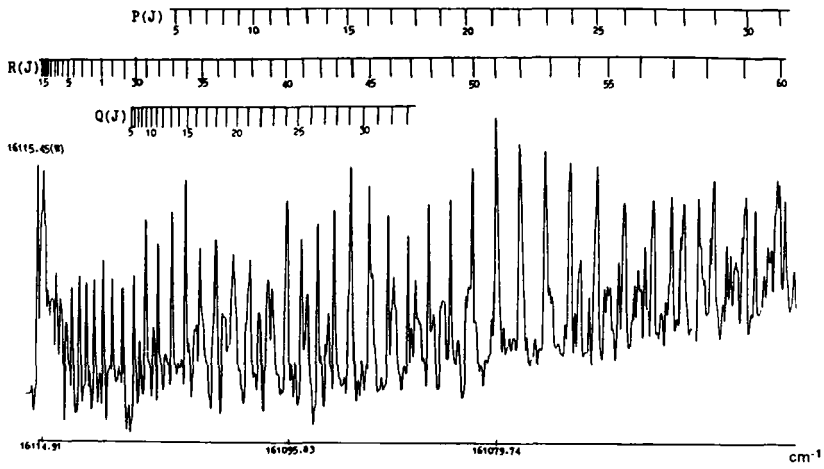

Fig.3. Microphotometer trace of the intracavity dye laser absorption spectrum of the WO A-X (0,0) band, over the spectral range 16115-15950 cm^{-1}.

Table 2. Rotational constants (in cm^{-1}) derived from the spectrum of the WO molecule.

Electronic state	v	Bv	$Dv*10^7$
A'	0	0.38433(15)	3.81(6)
A	0	0.38733(15)	2.70(6)
	1	0.38181(15)	2.64(9)
B	0	0.4013(5)	-
XO^+	1	0.4135(5)	-
	0	0.4153(5)	2.61(8)

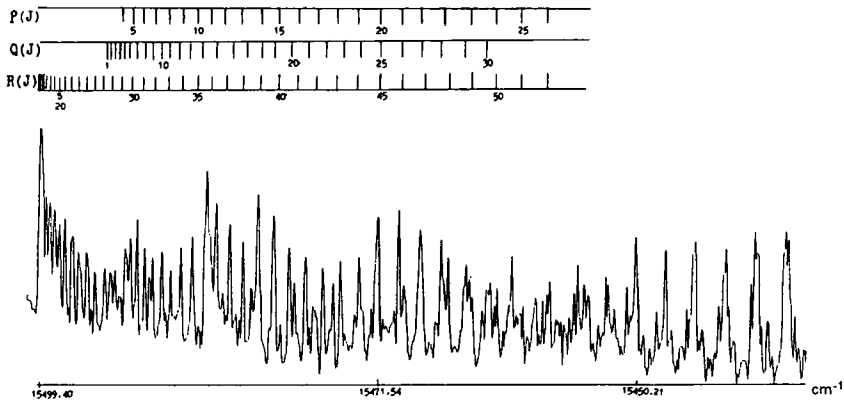

Fig.4. Microphotometer trace of the intracavity dye laser absorption spectrum of the WO A'-XO⁺(0,0) band in the region 15499-15440 cm^{-1}.

time rotational constants of B excited state of WO molecule has been derived, vibrational reassignment of some bands of A-X system of WO molecule has been performed and so on.

These spectra studied remain still too complicated for complete understanding, and new investigations have to be done.

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