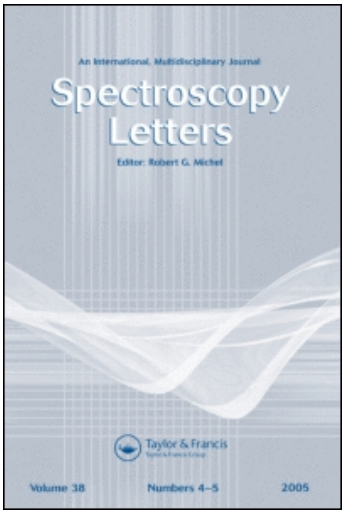

Spectroscopy Letters

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

Electronic Bands of the BeOH and BeOD

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To cite this Article Antić-jovanović, A. , Bojović, V. and Pesić, D.(1988) 'Electronic Bands of the BeOH and BeOD', Spectroscopy Letters, 21: 8, 757 — 765
To link to this Article: DOI: 10.1080/00387018808082339
URL: http://dx.doi.org/10.1080/00387018808082339

SPECTROSCOPY LETTERS, 21(8), 757-765 (1988)

ELECTRONIC BANDS OF THE BeOH AND BeOD

Key Words: electronic bands, beryllium monohydroxide, isotope shift

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ABSTRACT

The electronic bands appearing in the region 300-330 nm were produced in a low-pressure DC arc with beryllium electrodes. The bands were obtained in the atmosphere of ordinary water vapour and heavy water vapour. From isotope shift studies, experimental conditions and the similarity with the bands of isoelectronic BeF, the emitting molecules were identified as BeOH and BeOD, respectrively.

INTRODUCTION

The electronic spectra of monohydroxide of magnesium, calcium, strontium and barium have been the subject of numerous studies[1-10]. These triatomic molecules have recently atracted considerable attention from spectroscopists[11-17]. This activity is partly due to the fact that

laser excitation technique greately simplified the interpretation of their electronic spectra which are very complex.

Although the BeOH molecule, as a part of monovalent alkaline-earth compounds, is of spectrochemical interest, its electronic spectrum was not observed up to now. There is only one spectroscopic work on the BeOH concerning the ESR spectrum of the radical[18], and a few theoretical studies [19-21].

The results of ESR study were interpreted by Brom and Weltner[18] as arising from high ionic linear molecule. The ab initio calculations, made by Hinchliffe[19] and Abashkin and Dement'ev[20], support such interpretation. Recently, Palke and Kirtman[21] have presented the results of an additional theoretical work, which predicts BeOH as a quasilinear molecule.

We have surveyed the emission spectrum of low-pressure beryllium arc in the near ultraviolet region. Using the conventional spectrographic technique, we have attempted to locate and identify all prominent bands of BeOH. The spectrum of isoelectronic BeF molecule[22-26] served as a guide to the BeOH spectrum. In the present paper a general description of the bands of BeOH and BeOD in the 300-330 nm region is given. The electronic spectra of these molecular species were observed for the first time, and the emitter has been established on experimental grounds.

EXPERIMENTAL

The emission spectra of the BeOH and BeOD molecules were obtained in a low-pressure arc, which was modified version of that used elsewhere[27,28].

Due to toxicity of beryllium compounds, the arc was run in a closed system to prevent the contamination. The arc, maintained by 1 kV DC supply at a current of 1.0-1.5 A, was run between water-cooled beryllium electrodes in the atmosphere of water vapour and started by axiliary Tesla coil.

Since the examined spectral region has strong OH transitions and less intense BeO transitions[9], an extra efforts were made to remove these contaminants. The working pressure of ordinary (H_2O) and heavy water (D_2O) vapour of 120-140 Torr was selected as the most appropriate. Before the experiments,the arc chamber was evacuated up to 10^{-5} Torr. During this evacuation water was frozen in a small side tube. After pumping out, the chamber was filled with the water vapour at the working pressure. The latter was adjusted by keeping this tube at the required temperature. During exposure, the chamber was slowly evacuated in order to remove the decomposition products.

The spectral region between 200-400 nm was investigated in the first and second order of a 600 lines/mm plane grating, at dispersion of 0.7 nm/mm, 0.35 nm/mm and 0.18 nm/mm. Exposure times of 5 to 20 minutes were needed on Ilford HP5 film. The lines from an iron arc were used as the reference spectrum. The wavelengths of the band-heads were obtained by means a third order interpolative polynomial using a computer program. Uncertainty of measurements for well deffined heads is estimated to be within ± 0.02 nm, but it was about 0.05 nm for weak and diffuse heads.

RESULTS AND DISCUSSION

Description of the Spectrum

The first observation of the spectra emitted either in ordinary water vapour or heavy water vapour was done at low dispersion of 0.7 nm/mm. Apart from shifts in positions of recorded bands, the resemblance between general appearence of both spectra is very marked. Each spectrum consists of a number rather weak and diffuse bands divided into three groups, which are revealed apparently on Fig. 1, representing the microphotometer tracings of the spectra emitted in H_2O- vapour (a) and D_2O-vapour (b).

The first group of bands, positioned in the 300-307 nm region, is the most intense in recorded spectra. In the largest part, these bands

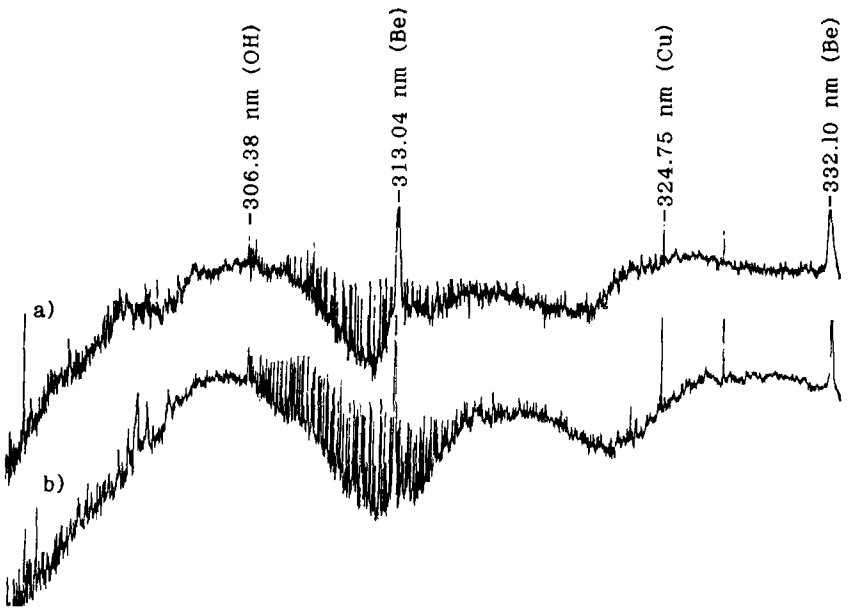

FIG.1. Microphotometer tracings of the spectrograms obtained in the atmosphere of H_2O-vapour (a) and D_2O-vapour (b) at dispersion of 0.7 nm/mm.

are free from overlapping structure of strong OH bands, which were considerably weakened under experimental conditions.

The second group of the bands lies in the region of the 1,1 and 2,2 $A^2\Sigma^+ - X^2\Pi$ bands of OH, and the 0,0 and 1,1 BeO bands of Bengtsson's system[9]. Although all these bands were minimised in intensity, the traces of their structures hindered apparent revealment of new bands. Because of that and its inherent diffuse structure, the second group of bands were observed on low dispersion spectrograms as prominent continuous background ranging from 313-318 nm.

The bands of third group, situated between 322-330 nm,are free from overlapping impurities but largely masked by continuous emission.

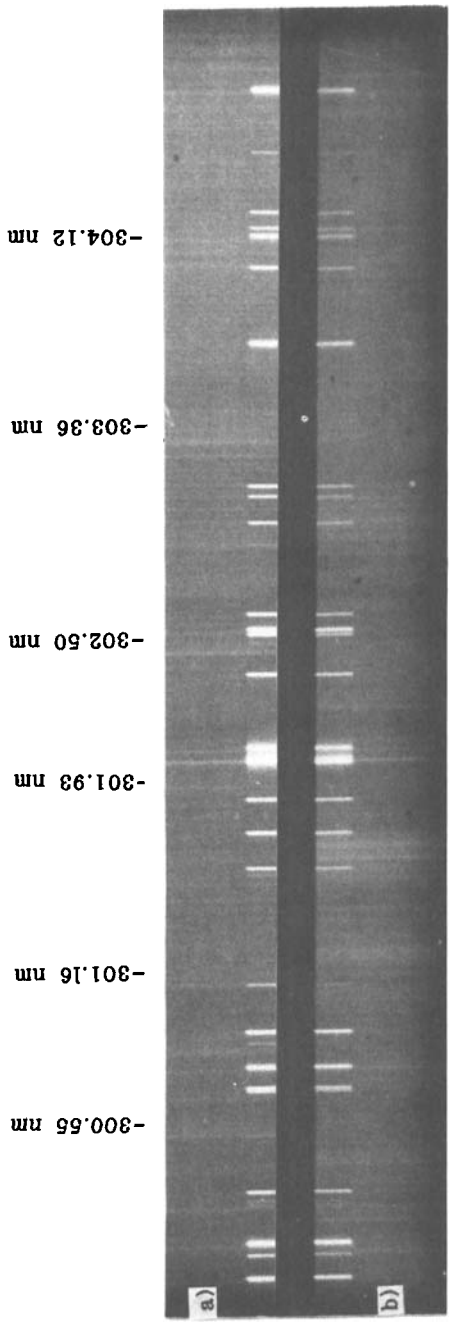

FIG. 2. A portion of the spectra obtained in the atmosphere of H_2O-vapour (a) and D_2O-vapour (b) at dispersion of 0.35 nm/mm.

TABLE 1. Head Positions of the BeOH Bands

λ, nm	I	λ, nm	I	λ, nm	I
300.41	2	306.28	2	322.65	2
300.55	2	306.34	2	322.82	2
300.70	2	306.69	2	323.27	2
300.89	2	307.08	2	323.69	3
301.16	2			324.07	2
301.57	1	313.30	2	324.39	2
301.93	3	313.50	2	324.63	3
302.25	2	314.76	3	325.04	2
302.30	2	314.99	2	325.22	2
302.50	3	315.15	3	325.72	1
302.74	2	315.48	3	326.30	1
302.78	2	316.10	2	326.70	1
302.94	3	316.33	2	327.22	1
303.36	3	316.79	2	327.27	2
303.68	2	317.00	2	327.99	1
304.12	3	317.12	2	328.29	2
304.38	2	317.19	2	328.69	2
304.48	3	317.25	3	328.91	2
304.86	3	317.71	1	329.32	1
304.90	3			329.69	2
305.37	1	321.92	1	330.00	2
305.48	2	322.25	2	330.77	2
305.66	2	322.47	2	331.16	2
305.76	2	322.53	2		

With larger dispersion of 0.35 nm/mm and 0.18 nm/mm, however, the structure of many bands emitted in ordinary water vapour atmosphere was found to be rich and very complex with heads apparently degraded to the red. The spectrum emitted in heavy water vapour atmosphere is less resolved and, in general, less intense.

Figure 2 contains the portion of spectrograms photographed at dispersion of 0.35 nm/mm. Displacements of band heads on spectrograms (a) and (b) relative to one another are clearly seen.

The positions of prominent heads in both isotopic spectra with visual intensities estimated on a scale of 0–3, are listed in Tables 1 and 2. The bands of second group emitted in the atmosphere of D_2O–vapor

TABLE 2. Head Positions of the BeOD Bands

λ,nm	I	λ,nm	I	λ,nm	I
300.42	2	305.47	2	325.79	1
300.81	2	305.92	2	325.89	2
301.26	3	306.59	2	326.65	2
301.65	3	306,85	2	327.61	1
302.28	3	306.92	2	327.87	1
302.68	2			328.05	1
302.77	2	323.68	2	328.30	0
302.89	2	324.15	0	328.47	1
303.36	1	324.25	0	329.26	0
303.60	1	324.54	2	329.33	0
303.78	1	324.92	2	329.92	0
304.01	2	325.23	1		
304.67	1	325.63	2		

could not be measured with any certainty due to their inherent weak intensity and overlapping background.

Assignment of the Spectrum

In view of the resemblance of the position of the new bands and those of isoelectronic BeF, it seemed likely to assign them to BeOH molecule, by analogy with corresponding spectra observed for other alkaline-earth metals. In the present paper we have verified this conjucture on experimental grounds, as follows.

The fact that the new bands occur only in discharge between beryllium electrodes implies that beryllium is necessary to produce them.

The isotope shifts, resulting upon substituting H_2O for D_2O in the arc atmosphere, unequivocaly prove the hydrogen in emitter which could be, therefore, BeH, BeH^+ or BeH_2. However, all these possibilities were ruled out by the fact that discharge in hydrogen atnosphere with beryllium electrodes failed to show new bands. Hence, the conclusion consistent with general appearence and with the conditions in the arc source, is that emitting molecule involves the Be, H and O atoms.

In the spectra taken in discharge running in the H_2O- and D_2O-vapour mixture in about equal ratio, both the hydroxide and deuteroxide feature were observable, but no extra features were found. The absence of new bands is interpreted as an evidence that there is only one hydrogen, i.e. only one OH radical per molecul-emitter, supporting the assignment of new bands to triatomic BeOH.

From the appearence of monohydroxide spectrum in the same region as the halid spectra can be deduced that bonding in the molecule is Be-O-H, and it is probably a quasilinear, as suggested by Palke and Kirtman[21]. In this case the substitution of hydrogen for deuterium the three normal modes of vibrations will be differently affected by the isotope shift what can be reason for complicated isotope displacements.

Based on similarity of electronic properties of isoelectronic species and their optical spectra, the observed monohydroxide bands are assumed to arise in perpendicular transition corresponding to the $A^2\Pi - X^2\Sigma$ system of BeF.

The spectrograms obtained did not allow an analysis of the spectrum. For this purpose additional experimental work on the spectrum at high resolution and new source is needed. The study of the spectra produced by hollow cathode or by microwave should be very useful because the rotational excitation in these sources is very low compared with the arc.

ACKNOWLEDGEMENT

We thank Professor D.O.Harris for bringing this problem to our attention.

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Date Received: 05/18/88
Date Accepted: 07/20/88