Microwave Spectrum of BaO

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Observation of the $J=1 \rightarrow 2$ rotational transition of BaO in a microwave absorption spectrometer at 1700 °C is described. For ^{135}BaO and ^{137}BaO the nuclear electric quadrupole constants, $e\,q_0\,Q$, in the ground vibrational state are reported.

A large group of diatomic molecules has eluded microwave absorption spectroscopy principally because the vaporization temperature is higher than 1000 °C. The group II a and transition metal monochalcogenides are good examples of such high temperature molecules. Measurements of rotational spectra of several of these have been obtained by the molecular beam electric resonance method. The rotational spectra of BaO [1] and SrO [2] and the dipole moments of BaS [3], GeO [4] and SiO [4] have been measured by this technique. Unfortunately, molecular beam surface ionization detection is rather selective and electron bombardment detection is relatively inefficient. Due to the lack of an efficient general purpose detector, systematic studies of these high temperature species by electric resonance is still not possible. Aside from the basic interest in studying molecular properties, knowledge of the rotational spectra of molecules like MgO and SiO is of great interest to infrared and microwave astronomers who are attempting to determine the composition of stars and interstellar matter. In order to study such high temperature species we employ a molecular beam-microwave absorption spectrometer with a water cooled absorption cell. The advantage of this spectrometer over the electric resonance type lies in the use of microwave absorption detection instead of molecular ionization detection. In addition, this cold cell spectrometer is not limited to 1000 °C like the typical hot cell microwave spectrometer. In this report we hope to demonstrate the utility of the molecular beam-absorption technique for studies of molecules requiring up to 2000 °C for vaporization.

The spectrometer employed in the present study had been successful in the past up to about 1300 °C for the study of SiO [5]. Subsequent investigations of species requiring temperatures higher than about 1500 °C were hampered by the disturbance of the Stark modulation field and microwave transmission by electrons and ions emitted from the oven into the absorption cell. These difficulties have now been overcome by the use of a novel superheterodyne detection scheme and high power Stark generator. These problems and the techniques used to eliminate them are described in detail in a recent report [6].

Barium oxide is a good candidate for this initial high temperature study since its rotational spectrum has been measured [1] and because its vaporization temperature is about 1700 °C. In addition, it was possible to obtain some new information, i. e. measurement of the nuclear quadrupole coupling constants of ^{135}BaO and ^{137}BaO. The $J=1 \rightarrow 2$ rotational transitions of ^{135}BaO, ^{136}BaO, ^{137}BaO and ^{138}BaO were observed by heating reagent grade BaO in a molybdenum oven to 1700 °C. The line widths at half maximum were approximately 300 kHz. The best signal-to-noise ratio obtained for ^{138}BaO, $v=0$ was about 30 using a 1 sec time constant.

The observed transition frequencies are listed in Table 1. The rotational constants listed in Table 2 were derived from the ^{138}BaO lines. The ^{136}BaO, $v=0$ transition frequency was calculated by isotope relations from the ^{138}BaO rotational constants. Only the strongest hyperfine transition component in the ^{135}BaO and ^{137}BaO could be observed. The nuclear quadrupole coupling constants for the Ba nuclei were obtained by using the isotope relations to calculate the hypothetical unperturbed rotational transition frequencies. The differences between these and the observed frequencies allowed the determination of the $e\,q_0\,Q$ constants for ^{135}Ba and ^{137}Ba shown in Table 2. For this reason we give no $\Delta\nu$ for the ^{135}BaO and ^{137}BaO transitions in Table 1. The rotational constants from the earlier electric resonance study are shown for comparison.

$F \rightarrow F'$	v	$J=1 \rightarrow 2$ ν (MHz)	$\Delta\nu$ (MHz)
		^{138}Ba^{16}O	(70.41%)
	0	37 403.880 (50)	0.000
	1	37 235.911 (50)	−0.016
	2	37 066.887 (70)	0.000
	3	36 896.853 (70)	0.002
		^{137}Ba^{16}O	(11.87%)
$5/2 \rightarrow 7/2$ $5/2 \rightarrow 5/2$	0	37 432.595 (50)	
		^{136}Ba^{16}O	(8.07%)
	0	37 461.055 (70)	−0.013
		^{135}Ba^{16}O	(6.73%)
$5/2 \rightarrow 7/2$ $5/2 \rightarrow 5/2$	0	37 490.426 (90)	

Table 1. The $J=1 \rightarrow 2$ transition frequencies for ^{138}Ba^{16}O, ^{137}Ba^{16}O, ^{136}Ba^{16}O and ^{135}Ba^{16}O. The difference between calculated and observed transition frequencies are listed under $\Delta\nu$.

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[1] L. WHARTON, M. KAUFMAN, and W. KLEMPERER, J. Chem. Phys. **37**, 621 [1962]. — L. WHARTON and W. KLEMPERER, J. Chem. Phys. **38**, 2705 [1963].

[2] M. KAUFMAN, L. WHARTON, and W. KLEMPERER, J. Chem. Phys. **43**, 943 [1965].

[3] C. A. MELENDRES, A. J. HEBERT, and K. STREET, JR., J. Chem. Phys. **51**, 855 [1969].

[4] JOHN W. RAYMONDA, JOHN S. MUENTER, and WILLIAM A. KLEMPERER, J. Chem. Phys. **52**, 3458 [1970].

[5] T. TÖRRING, Z. Naturforsch. **23 a**, 777 [1968].

[6] J. HOEFT, F. J. LOVAS, E. TIEMANN, and T. TÖRRING, to be published.

	Present		Previous [1]	
$^{138}Ba^{16}O$	(10.41%)			
Y_{01}	9371.937 (15)	MHz	9371.952 (10)	MHz
Y_{11}	−41.740 (15)	MHz	−41.776 (10)	MHz
Y_{21}	− 0.128 (10)	MHz	− 0.120 (5)	MHz
μ_r	14.332 553	amu		
Y_{02} [a]	−8.165	kHz	− 8.165	kHz
$^{137}Ba^{16}O$	(11.87%)			
$e\,q_0\,Q$	−17.5 (25)	MHz		
μ_r	14.321 687	amu		
$^{136}Ba^{16}O$	(8.07%)			
μ_r	14.310 658	amu		
$^{135}Ba^{16}O$	(6.73%)			
$e\,q_0\,Q$	−10.1 (25)	MHz		
μ_r	14.299 511	amu		

Table 2. Rotational and hyperfine structure constants for BaO. Isotope relations and the ^{138}BaO constants were used to calculate the hypothetical pure rotational transitions of ^{137}BaO and ^{135}BaO, and the $e\,q\,Q$ constants were derived from the differences between these calculated line positions and the observed transitions shown in Table 1.

[a] Calculated from $Y_{02} = -4\,B_e^3/\omega_e^2$ with $\omega_e = 669.81\ \mathrm{cm}^{-1}$.

The slight discrepancies might be due to the fact that our line shapes were slightly asymmetric since the background disturbances from the emitted electrons and ions could not be suppressed completely. We hope to eliminate this problem with an improved cell design and detection system.

The ratio of the quadrupole moments

$$e\,q_0\,Q\,(^{137}\mathrm{Ba})/e\,q_0\,Q\,(^{135}\mathrm{Ba}) = 1.73\,(43)$$

agrees well within the estimated error with the ratio obtained from the 6s 6p : $^3P_1$ atomic states [7]:

$$Q_{137}/Q_{135} = 1.537\,(2)\,.$$

The hyperfine structure of the $^3P_2$ atomic state of Ba has not been measured. However, to a good approximation [8] the nuclear quadrupole coupling constants, B, for the Ba 6s 6p : $^3P_2$ state may be given as $B\,(^3P_2) = -1.83\,B\,(^3P_1)$.

For comparison to the molecular hyperfine structure, one derives the axial component of this constant for the atomic state as [9]:

$$e\,q_{n10}\,Q = -\quad 2\,B\,(^3P_2)$$

One obtains then,

$$e\,q_{610}\,Q\,(^{135}\mathrm{Ba}) = -\ \ 99\ \mathrm{MHz}\,,$$
$$e\,q_{610}\,Q\,(^{137}\mathrm{Ba}) = -153\ \mathrm{MHz}\,.$$

Thus, the BaO quadrupole coupling constants are identical in sign and about one-tenth in magnitude of the atomic values.

Since the dipole moment [1] of BaO is about 85% of $e\,r_e$ and small hybridization is indicated by the small quadrupole coupling constant, it seems quite plausible that BaO bonding is basically ionic with an additional σ bond arising from an orbital with small sp-hybridization.

[7] GISBERT ZU PUTLITZ, Ann. Phys. **11**, 248 [1963].

[9] C. H. TOWNES and A. L. SCHAWLOW, Microwave Spectroscopy, McGraw-Hill Book Co., Inc., New York 1955.

[8] The ratio of the field gradients of the $^3P_2$ and $^3P_1$ states were obtained from the $[(3\cos^2\Theta-1)/r^3]_{JJ}$ terms listed by CASIMIR [H. B. G. CASIMIR, On the Interaction Between Atomic Nuclei and Electrons, Teyler's Tweede Genootschap, Harlem (Holland) 1936] using the relativistic corrections tabulated by KOPFERMANN [H. KOPFERMANN, Kernmomente, Akademische Verlagsges. m.b.H., Frankfurt 1956].