Fourier transform spectroscopy of BaO: New ground-state constants from the $A\,^1\Sigma^+ - X\,^1\Sigma^+$ chemiluminescence

Hongzhi Li, Cristian Focsa,[a] Bernard Pinchemel,[a] Robert J. Le Roy,[b] and P. F. Bernath[c]
Guelph-Waterloo Centre for Graduate Work in Chemistry and Biochemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

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The $A\,^1\Sigma^+ - X\,^1\Sigma^+$ emission spectrum of BaO excited in a Broida-type oven was revisited using a Fourier transform spectrometer. Chemiluminescence was observed from excited BaO molecules generated from the $Ba+N_2O$ reaction, and 82 vibrational bands of ^{138}BaO were measured in the range 8900–21 000 cm^{-1} at a resolution of 0.04 cm^{-1}. Vibrational levels were observed up to $v''=20$ of the ground state and up to $v'=11$ for the excited state. In addition, 72 bands from the minor isotopomers ^{137}BaO, ^{136}BaO, and ^{135}BaO were detected with v'' up to 14 and v' up to 4. Over 15 500 lines with J'' up to 119 were measured with a precision of about 0.005 cm^{-1}, which shows that the Broida oven is an excellent source for high-resolution emission spectroscopy. Our main goal here is to obtain an optimum set of molecular constants for the ground electronic state. To avoid complications due to the well-known perturbations for $v'_A \geqslant 1$ of the $A\,^1\Sigma^+$ state, our unified combined-isotopomer analysis used a novel combination of a Dunham expansion description of the ground state with independent band-constants for data involving A-state level $v'_A=0$, while fitting to an independent term value for each observed A-state $v'_A \geqslant 1$ vibration–rotation level of each isotopomer. Significantly improved ground-state constants and A-state $v'_A=0$ band constants are obtained, together with term values for some 1372 higher-v' A-state levels. © *2000 American Institute of Physics.* [S0021-9606(00)01732-3]

I. INTRODUCTION

The spectrum of barium oxide has been studied by various methods for a long time. Mecke and Guillery reported the emission spectrum in 1928,[1] while Mahanti measured bands between 12 000 and 23 000 cm^{-1} in 1934.[2] The high-resolution spectrum of the $A\,^1\Sigma^+ - X\,^1\Sigma^+$ transition in the range 14 300–20 000 cm^{-1} was studied by Lagerqvist *et al.*[3] in 1950, who corrected the rotational analysis of Mahanti. They analyzed 11 bands in which the ground-state vibrational quantum number ranged from $v''=0-4$, and that of the A state from $v'=0-5$. These experiments were performed by producing BaO in an acetylene–air flame fed with a $BaCl_2$ solution.

Wharton and Klemperer detected pure rotational $J=1 \leftarrow 0$ transition for several vibrational levels of the ground state in 1962.[4,5] They used the molecular beam electronic resonance method, taking advantage of the large dipole moment (7.955 D for $v''=0$) of BaO,[4] with BaO vapor produced by heating solid BaO to 2200 K. Subsequently, several other groups obtained additional microwave data for both the ground state and the A state. Tiemann and co-workers[6,7] measured the microwave absorption spectrum of the ground state, employing a high-temperature oven. Field *et al.*[8] studied the microwave optical double resonance spectra of both X and A states, using a Broida-type oven[9–11] to generate high-temperature molecules at relatively low temperatures. Hocking *et al.*[12] obtained the millimeter wave spectra of the three alkaline earth metal oxides, CaO, SrO, and BaO; for BaO they observed rotational transitions for J up to 10 of the ground state. In 1992 Blom *et al.*[13] performed new microwave measurements using laser ablation to produce BaO, and combined their results with other data to obtain the most recent set of Dunham constants for the ground state.

In 1990 Hedderich and Blom[14] observed the first high-resolution infrared spectrum, between 641 and 701 cm^{-1}, using a tunable diode laser spectrometer and a Broida oven source. A total of 140 rovibrational transitions of the five most abundant isotopomers were measured for v'' up to 6. Somewhat earlier Field *et al.*[15] had measured optical–optical double resonance (OODR) photoluminescence progressions generated using two continuous wave (cw) laser to excite BaO to ~38 000 cm^{-1} above the ground state. They observed two photoluminescence progressions into ground-state vibrational levels ranging up to $v''=34$, but only at low resolution.

Besides the work on the $X\,^1\Sigma^+$ state mentioned above, many studies have also been carried out on the excited states of BaO. Exothermic reactions, such as[16] $Ba+N_2O$ and[17] $Ba+O_3$ played an important role in producing the visible and ultraviolet chemiluminescence for these studies. The ''many-line'' visible spectrum produced at pressures below 10 mTorr (with no argon bath gas present) results from highly

[a]Permanent address: Laboratoire de Physique des Lasers, Atomes et Molécules, UMR CNRS 8523, Center d'Etudes et de Recherches Lasers et Applications, Université des Sciences et Technologies de Lille, 59 655 Villeneuve d'Ascq cedex—France.
[b]Electronic mail: leroy@UWaterloo.ca
[c]Electronic mail: bernath@UWaterloo.ca

excited $A\,^1\Sigma^+$ and $A'\,^1\Pi$ emission to the ground state. The intense and rotationally hot part is from the $A\,^1\Sigma^+ \rightarrow X\,^1\Sigma^+$ transition, and the weaker and partially rotationally relaxed part is from the $A'\,^1\Pi \rightarrow X\,^1\Sigma^+$ transition.[18] At pressures between 0.01 and 0.2 Torr (using an argon bath gas) the $A-X$ bands become increasingly strong and eventually dominate the spectrum. $A'-X$ bands in the 23 000–30 000 cm^{-1} region were also observed by Hsu *et al.*[19] at various pressures. Later, Wyss and Broida[20] performed a vibrational analysis of the $A'-X$ transition using the ^{16}O and ^{18}O isotopomers. Using a direct current (dc) arc with barium electrodes in an oxygen atmosphere, Kolman *et al.*[21] studied $B\,^1\Sigma^+-X\,^1\Sigma^+$ transitions and rotationally analyzed the 0–6, 0–7, and 0–8 bands.

Laser techniques have made it much more convenient to study the excited states of BaO.[15,22–30] For example, Pruett and Zare[23] excited the overlapping $A-X$ and $A'-X$ transitions of BaO produced by the $Ba+CO_2$ reaction using a tunable pulsed dye laser. The weak, long-lifetime ($\sim$9 μs) $A'-X$ fluorescence was separated from the strong, short-lifetime ($\sim$356 ns) $A-X$ fluorescence[22] by delaying the observation of the $A'-X$ emission until the $A-X$ emission had decayed away. Using the OODR technique, Gottscho and Field and co-workers[15,24,25,27] studied the low-lying states such as $a\,^3\Sigma^+$, $A\,^1\Sigma^+$, $b\,^3\Pi$, and $A'\,^1\Pi$ by laser-induced fluorescence. Bender *et al.*[28] studied the perturbed states in the region above 32 000 cm^{-1}, using a frequency-doubled pulsed dye laser to excite the BaO molecules.

Strong local perturbations have been found to occur for all observed excited-state vibrational levels except $v'=0$ of the A state,[3,27,29–31] due to interactions among the $A\,^1\Sigma^+$, $b\,^3\Pi$, and $A'\,^1\Pi$ states. This would make a complete analysis of $A-X$ transition quite challenging. Perturbations also occurred between the $A'\,^1\Pi$ state and vibrationally highly excited ground state,[30] and between the $A'\,^1\Pi$ and the $a\,^3\Sigma^+$ states.[27]

The present work re-examines the $A-X$ transition between 8900 and 21 000 cm^{-1} at a resolution of 0.04 cm^{-1}, using a Fourier transform spectrometer. The BaO chemiluminescence was excited by the reaction of Ba with N_2O in a Broida-type oven. This paper is the first in a series on the infrared and near infrared spectroscopy of BaO, CaO, and SrO, and it shows that the Broida oven is indeed an excellent source for high-resolution emission spectroscopy. Note that the technique of infrared and near-infrared emission spectroscopy has recently been reviewed in Ref. 32.

The major objective of this work is to determine improved molecular constants for the ground state. Because of the strong local perturbations of most vibrational levels of the upper state, our combined-isotopomer fit to determine new ground-state spectral constants used an Åslund-type term-value representation[33,34] for $v'_A \geqslant 1$ levels of the A state and independent sets of band constants (one for each isotopomer) for the $v'_A=0$ level. Over 15 500 rovibrational lines from the four isotopomers, involving v'' up to 20 and v' up to 11, together with microwave data and infrared data from literature, and the earlier low resolution OODR photoluminescence data[15] (which extend to $v''=34$), were considered in this analysis.

II. EXPERIMENT

A detailed description of the Broida-type oven we used to generate BaO chemiluminescence has been published elsewhere.[35,36] In our experiment, BaO was produced in a low-pressure reaction of Ba with N_2O with an argon carrier gas. About 10 g of barium metal (granules, 99.7% pure, from Johnson Matthey) in a crucible was heated by a tungsten wire basket to generate barium vapor. The vaporized barium was entrained in a flow of Ar gas, and then mixed with N_2O (99.9% pure, from Praxair) to produce a low-pressure chemiluminescent flame. The partial pressures of N_2O and Ar in the reaction chamber were adjusted separately to obtain the most intense flame, normally with a total of pressure of between 0.5 and 1 Torr. It was found that the vibrational population of the excited BaO varied strongly with different pressure combinations.

The chemiluminescence was collected with a 5 cm in diameter, $f=15$ cm focusing lens and sent to a Bruker IFS 120 HR Fourier transform spectrometer which has been modified to record double-sided interferograms. A spherical mirror was set on the opposite side of the collection lens to enhance the collection efficiency. A notch filter with a blocking range from 15 500 to 15 850 cm^{-1} was used to reduce the strong He–Ne laser signal ($\sim$15 798 cm^{-1}) from the spectrometer. No other color filter was chosen, in order to maximize the signal. A photomultiplier tube (PMT, Hamamatsu, R636-10) was employed to measure the spectrum above 13 500 cm^{-1} and a silicon photodiode detector was used to record the spectrum between 8900 and 15 800 cm^{-1}. Because of the wide spectral range involved (requiring a PMT detector from 10 532 to 21 064 cm^{-1} and a Si photodiode from 7899 to 15 798 cm^{-1}), careful adjustment of the pressure to obtain suitable vibrational populations was necessary to avoid aliasing.[37] Thus very little folding-back of lines, due to out-of-band emissions, was observed in the spectrum. The resolution was set to 0.04 cm^{-1}. Normally, about 2 hours was needed to co-add about 30 scans to obtain a good signal-to-noise-ratio.

A program named ''*Spectra*'' provided by Dr. Michel R. Carleer (Université Libre de Bruxelles, Belgium) was used to measure the line positions. The peak positions were determined by fitting Voigt lineshape functions to the lines in a nonlinear least-squares procedure. The air-to-vacuum conversion of the wave numbers was performed with an equation provided by Dr. Tsuyoshi Hirao of this laboratory.[38] His equation was derived from Edlén's formula[39,40] for the refractive index of air. The converted line positions were then calibrated using barium atomic lines that accompanied the BaO emission. The line positions of the Ba atomic emission was provided by Dr. Ulf Litzén (Lund University, Sweden),[41] and have an uncertainty of about 0.002 cm^{-1}. Ten atomic lines between 8800 and 14 200 cm^{-1} common to both spectra were used to determine a calibration factor of 1.000 001 563 2 for the spectrum from the photodiode detector. The spectrum from the PMT was then calibrated by multiplying the wavenumbers by the factor of 1.000 001 546 2, which was determined using more than 100 common lines from the (0,4), (0,3), (1,3), and (0,2) bands common to both spectra, covering a range from 13 850 to 15 400 cm^{-1}. The

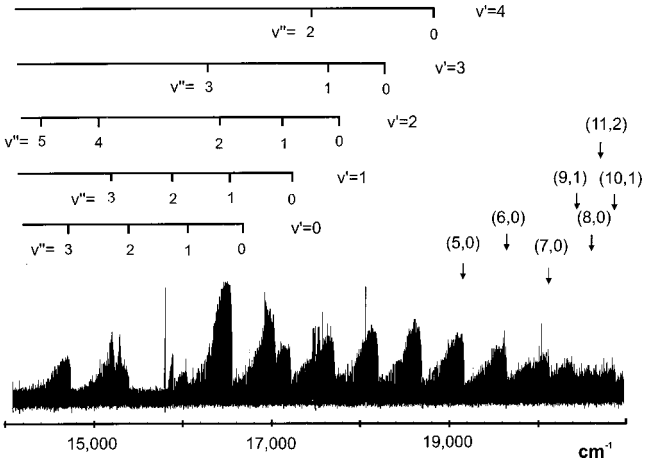

FIG. 1. The $A\,^1\Sigma^+-X\,^1\Sigma^+$ emission spectrum of BaO recorded using a PMT detector; *A*-state vibrational levels were observed up to $v'=11$. A notch filter at $\sim$15 650 cm^{-1} was used to reduce the He–Ne laser light inside the Fourier transform spectrometer.

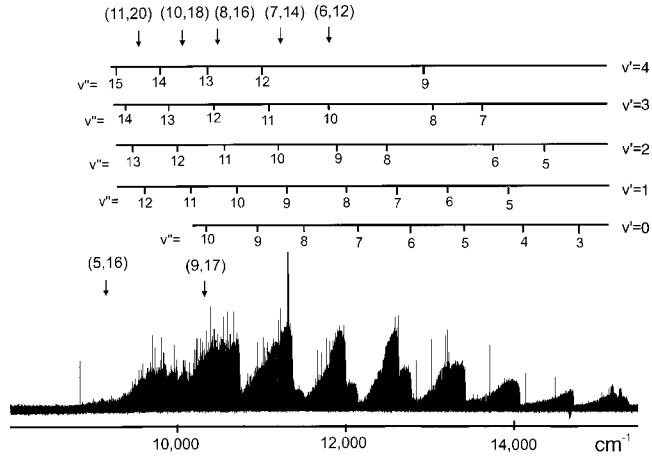

FIG. 2. The $A-X$ emission spectrum of BaO observed using a Si photodiode detector; *X*-state vibrational levels were observed up to $v''=20$. Barium atomic emission lines were used to calibrate this spectrum.

precision of our final measurements was estimated to be about 0.005 cm^{-1} for medium-strength, unblended lines.

III. EXPERIMENTAL RESULTS AND ASSIGNMENTS

The chemiluminescence spectra we obtained were mainly from the $A\,^1\Sigma^+-X\,^1\Sigma^+$ transition of BaO. Some atomic emission lines of barium were also observed and used for calibration. So far we have not found any lines due to the $A'\,^1\Pi-X\,^1\Sigma^+$ transition, mainly because most of the $A'-X$ lines appear above 22 000 cm^{-1}, which is beyond our observation range, and partially because of their low intensity.[18] The relatively high pressure we used in the reaction chamber also does not favor the $A'-X$ transition.[19]

The BaO spectrum obtained from the PMT detector between 14 000 and 21 000 cm^{-1} is shown in Fig. 1. A notch filter at $\sim$15 650 cm^{-1} used to reduce the He–Ne laser intensity eliminated a large number of lines from the (1,2) band and parts of the (0,1) band. The PMT we used has a very low sensitivity below 14 000 cm^{-1}, and only a weak signal from the (0,5) band ($\sim$13 436 cm^{-1}) was seen in the low wave number region (not shown in this figure). In the high wave number region there were some weak lines above 21 064 cm^{-1} from aliasing.[37] For example, some lines from the (12,2) band, whose band head lies near 21 162 cm^{-1}, were found to be folded back to the 20 966 cm^{-1} region. None of the aliased lines were included in the present analysis.

The spectrum measured with the photodiode detector is displayed in Fig. 2. Barium atomic emission lines can be seen throughout the whole range. Signals disappear around 8900 cm^{-1} because of the very low sensitivity of the detector. We tried to use an InSb detector to extend our observation range to the near infrared, but without success. As discussed previously, no aliasing of signals originally above 15 798 cm^{-1} was observed. A small distortion of lines from the (0,3) band occurs near 14 700 cm^{-1} for unknown reasons, and these lines were not included in our analysis.

A. Vibrational assignments

Using the best available spectral constants for the ground state[13] and deperturbed spectral constants for the $A\,^1\Sigma^+$ state from Ref. 27, most of the relatively isolated vibrational bands could be assigned. However, the ground-state constants from Ref. 13 are not good for high v''. In particular, their G_v expression does not reproduce the band origins for $v''>10$, with the offset growing to 1.2 cm^{-1} by $v''=20$. For the weak and blended vibrational bands, the assignment was performed through detailed analysis of the rotational lines.

Some of the vibrational assignments are shown in both Figs. 1 and 2. In Fig. 1 the vibrational quantum number of the *A* state can be seen up to $v'=11$ for the (11,2) band with its head around 20 697 cm^{-1}. On the low wave number side, transitions were observed into ground-state vibrational levels up to $v''=20$ for the (11,20) band, which can be seen in Fig. 2 at around 9521 cm^{-1}. For the unperturbed bands with $v'=0$, all of those from (0,0) to (0,10) were observed. No significant rotational lines from the unperturbed (0,11) band were detected, because of the small Franck–Condon factor.

Some 82 vibrational bands from ^{138}BaO, 27 bands from ^{137}BaO, 25 bands from ^{136}BaO, and 20 bands from ^{135}BaO were assigned and analyzed, and are distributed as shown in Table I. A normal Condon parabola[42] due to the Franck–Condon principle can be seen in Table I for the observed ^{138}BaO bands. For the minor isotopomers, only bands with $v'<5$ were assigned. A small number of lines in the (5,0) band from the minor isotopomers were observed, but not analyzed here. Coincidentally, a large number of bands appear in a narrow region around 10 000 cm^{-1}. There are about 33 bands from ^{138}BaO observed in the range between 9300 and 11 500 cm^{-1}, which caused great deal of spectral congestion. All of our data are for isotopomers formed from the ^{16}O isotope.

B. Rotational assignment of ^{138}BaO

A program called ''*Loomis*,'' written by Dr. C. Jarman, based on the method developed by Loomis and Wood,[43] is the very powerful tool we used for picking out rotational

TABLE I. Observed and assigned vibrational bands from chemiluminescence spectra of BaO, including 82 bands from $^{138}Ba^{16}O$, 27 bands from $^{137}Ba^{16}O$, 25 bands from $^{136}Ba^{16}O$, and 20 bands from $^{135}Ba^{16}O$. *a*: observed band of ^{138}BaO. *b*: observed band of ^{137}BaO. *c*: observed band of ^{136}BaO. *d*: observed band of ^{135}BaO.

	$v''=0$	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
$v'=0$	*a*	*a*	*a*	*abcd*	*abcd*	*abcd*	*abcd*	*ab*	*a*	*a*	*a*										
1	*abcd*	*abcd*	*abc*	*ab*		*a*	*abcd*	*abcd*	*abcd*	*abcd*	*abcd*	*abc*	*a*								
2	*a*	*abcd*	*a*		*a*	*a*	*a*		*a*	*abc*	*abcd*	*abcd*	*abcd*	*a*							
3	*abcd*	*a*		*a*				*a*	*a*		*a*	*abc*	*abcd*	*abcd*	*a*						
4	*abc*									*a*			*a*	*abcd*	*abcd*	*a*					
5	*a*		*a*												*a*	*a*	*a*				
6	*a*	*a*	*a*										*a*	*a*			*a*				
7	*a*	*a*													*a*			*a*			
8	*a*	*a*														*a*	*a*		*a*		
9	*a*	*a*															*a*	*a*			
10		*a*	*a*																*a*	*a*	
11			*a*																	*a*	*a*

branches of unperturbed bands. With the help of *Loomis* we can easily pick out the branches of the unperturbed $(0,v'')$ bands from their dense background. Even for the perturbed bands, *Loomis* is still valuable. In that case, it can be used to pick out the lines from the unperturbed or weakly perturbed parts of the band. For lines in the perturbed regions, other methods, such as the checking of combination differences, have to be used.

Different methods were used to perform the rotational assignment of the branches picked out by *Loomis*. Lagerqvist *et al.*[3] rotationally assigned the (0,2), (0,3), (0,4), (1,1), (1,2), (2,0), (2,1), (3,0), (3,1), (4,0), (5,0) bands of ^{138}BaO. The maximum J'' they observed was 118. The line positions they published are very close to our data, with an average discrepancy of about 0.05 cm^{-1}, and the maximum deviation was only about 0.1 cm^{-1}. We assigned these bands by following the assignments of Lagerqvist *et al.*, and double-checked them by methods described below.

Due to the uncertainties in the spectral constants for the perturbed *A* state, it is impossible for us to assign the dense rotational lines by calculations using the reported spectral constants of the *A* and *X* states. Fortunately, the ground state is not perturbed, and the spectral constants from Blom *et al.*[13] are very good for $v''<10$. In this case, checking the combination differences of ground state $R(J-1)-P(J+1)=\Delta_2F''(J)$, which bypasses the perturbed upper state, is a useful method for assignment, with

$$\Delta_2F''(J)=F_v(J+1)-F_v(J-1)\approx 4B_v(J+\tfrac{1}{2})-8D_v(J+\tfrac{1}{2})^3. \quad (1)$$

Using this relationship, we assigned most of the low v'' bands with $v'>5$. Equation (1) is also helpful for predicting the line positions of a branch if the other branch has been assigned by another method. Furthermore, it is also a powerful method for checking assignments. However, for a very dense spectrum, such as the region around 10 000 cm^{-1} in Fig. 2, the method of rotational combination differences fails. There are too many potential *P*-*R* doublet pairs that satisfy Eq. (1), and it is very hard to pick out the correct assignments from the numerous candidates.

For a vibrational progression (v',v'') from a given excited state v', if one of the bands for a particular $v''=v''_{ass}$ has been assigned, then the line positions of the other bands of that progression can be predicted by taking advantage of the well-known spectral constants of the ground state. In particular, the positions of the other (v',v'') bands can be calculated from that of the known band (v',v''_{ass}) using the relationship

$$F_{v''}(J)-F_{v''_{ass}}(J)=G_{v''}-G_{v''_{ass}}+(B_{v''}-B_{v''_{ass}})J(J+1)-(D_{v''}-D_{v''_{ass}})[J(J+1)]^2. \quad (2)$$

This method proved to be very effective in this work, and all of the weak, blended bands seen in Fig. 2 were found and assigned in this way. For the bands with $v''>10$ an offset needs to be added to the $G_{v''}$ term predicted from Blom's constants[13] when using Eq. (2) to perform the assignment. The offset increases strongly with v'' from about 0.03 cm^{-1} at $v''=11$ to about 1.2 cm^{-1} at $v''=20$. An alternate way to correct for this offset is to gradually revise the spectral constants obtained from the assigned lower v'' bands by stepwise inclusion of the higher-v'' data to obtain new constants, until the entire data set up to $v''=20$ is included.

Another method was also used to help make the assignments. When two bands belong to the same progression with about the same signal-to-noise ratio, such as the (1,9) and (1,10) bands of Fig. 2, and neither of them is assigned, a combination of Eqs. (1) and (2) can be helpful. First, we analyze the first band to obtain a number of possible *P*-*R* doublet pairs that satisfy Eq. (1). Then for these candidates Eq. (2) allows us to determine whether a similar pair of lines with the same combination differences exists in the second band. If it does, this candidate is much more likely to be the correct assignment.

Figure 3 shows a small part of the dense spectrum near 9500 cm^{-1} for the rotational assignment of ^{138}BaO. The five observed bands (1,12), (4,14), (5,15), (6,16), and (11,20) all lie in this congested region. Using the above techniques, ~11 400 rovibrational lines from 82 bands of ^{138}BaO were assigned, with maximum J'' values up to 119. These data and

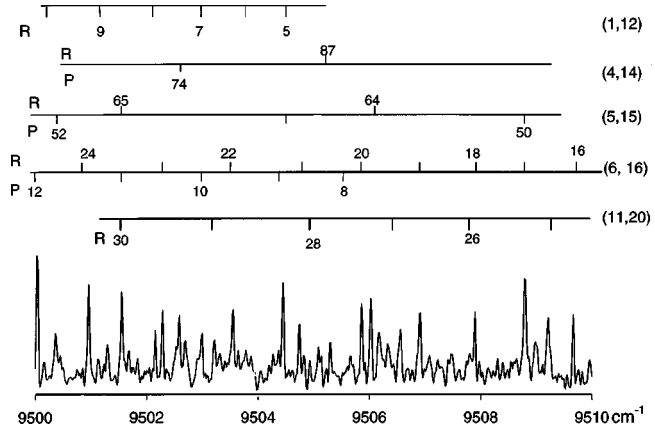

FIG. 3. A portion of the $A\,^1\Sigma^+-X\,^1\Sigma^+$ spectrum illustrating rotational assignments of the (1,12), (4,14), (5,15), (6,16), and (11,20) bands.

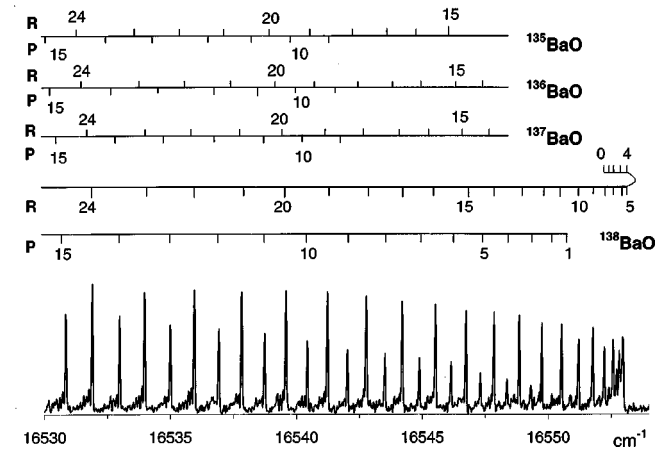

FIG. 4. Part of the (1,1) band of the $A-X$ emission spectra of ^{138}BaO, ^{137}BaO, ^{136}BaO, and ^{135}BaO, illustrating the rotational assignments.

assignments, together with over 4000 lines from the minor isotopomers, are available electronically (EPAPS).[44]

C. Rotational assignment of ^{137}BaO, ^{136}BaO, and ^{135}BaO

Of the seven isotopes of barium found in nature, we observed transitions for $Ba^{16}O$ formed by the four most abundant ones, with natural abundances of 71.70% for ^{138}Ba, 11.23% for ^{137}Ba, 7.854% for ^{136}Ba, and 6.592% for ^{135}Ba. When the assignment of ^{138}BaO was finished, it was relatively easy to find and assign the other isotopomers, with the help of the *Loomis* program. The unperturbed lines from minor isotopomers are shifted from those corresponding to ^{138}BaO by the offset $\Delta T^{\alpha}_{v,J}$, where α is a label identifying a particular isotopomer

$$\Delta T^{\alpha}_{v,J}=T^{\alpha}_{v,J}-T^{138}_{v,J}=G^{\alpha}_{v}-G^{138}_{v}+F^{\alpha}_{v}(J)-F^{138}_{v}(J)$$
$$=\Delta G^{\alpha}_{v}+\Delta F^{\alpha}_{v}(J), \tag{3}$$

where $\Delta G^{\alpha}_{v}\equiv G^{\alpha}_{v}-G^{138}_{v}$ is a constant for a given band and $\Delta F^{\alpha}_{v}(J)\equiv F^{\alpha}_{v}(J)-F^{138}_{v}(J)$ varies with J. Because BaO is a relatively heavy molecule, the rotational constants of the various Ba isotopomers are very close to one another. Compared to the value of ΔG^{α}_{v}, ΔF^{α}_{v} is very small for the low-J lines, so the offset is almost a constant, $\Delta T^{\alpha}_{v,J}\approx\Delta G^{\alpha}_{v}$. As a result, with the graphical *Loomis* program the branch from isotopomer-α is clearly seen as a parallel line lying near the line associated with the assigned ^{138}BaO branch. All the lines from the isotopomers in this work were found and assigned in this way.

Figure 4 shows a portion of the rotational assignments for the (1,1) bands of ^{138}BaO, ^{137}BaO, ^{136}BaO, and ^{135}BaO. Lines from the minor isotopomers can be clearly distinguished near the base of the ^{138}BaO lines. The position offset $\Delta T^{\alpha}_{v,J}$ of the ^{137}BaO lines from the ^{138}BaO lines is about 0.13 cm^{-1} towards lower wave numbers. The offset between ^{137}BaO and ^{136}BaO is about 0.12 cm^{-1}, and that between ^{137}BaO and ^{136}BaO is about 0.11 cm^{-1}. This offset will increase for the higher v'' bands in a progression. For example, in the (1,11) band, the lines from ^{137}BaO shift to lower wave numbers by about 1.5 cm^{-1}. On the other hand, the lines from ^{137}BaO eventually shift to higher wave numbers when v' is large enough. For example, in the (2,1) band the line positions for ^{137}BaO are about 0.04 cm^{-1} to the blue of those for ^{138}BaO, while in the (4,0) band the blue shift is increased to 0.66 cm^{-1}. This change of the isotopomer shift reflects the change of ΔG^{α}_{v} value in Eq. (3).

Approximately 2000 lines from 27 bands of ^{137}BaO, 1300 lines from 25 bands of ^{136}BaO, and 800 lines from 20 bands of ^{135}BaO were assigned, and are available electronically.[44] The maximum J'' observed for ^{137}BaO goes as high as 88; for ^{136}BaO this maximum J'' is 77, and for ^{135}BaO it is 59. It is interesting to note that the percentage of lines observed and assigned for a particular isotopomer is close to the natural abundance of the Ba isotopes (i.e., ~73% of the assigned lines are for ^{138}BaO, ~13% from ^{137}BaO, ~9% from ^{136}BaO, and ~5% from ^{135}BaO).

D. Perturbations

Several new perturbations due to the interaction of the $A\,^1\Sigma^+$ state with the $b\,^3\Pi$ state were observed in our experiment. A strong perturbation from the interaction of A-state level $v_A=6$ with the 0^+ spin component of b-state level $v_b=5$ was seen around $J\approx 0$. Another perturbation at around $J\approx 80$ of $v_A=9$ was observed, which should be due to the interaction with the 0^+ spin component for $v_b=9$. Two other weak perturbations were also newly determined, which involve $J\approx 77$ of $v_A=6$ coupling with the $^3\Pi_2$ spin component of $v_b=6$ and $J\approx 70$ of $v_A=8$ coupling with the $^3\Pi_1$ spin component of $v_b=8$. Besides these new perturbations, we also observed most of the other perturbations reported in literature for $v_A<12$.[3,27,29–31] However, we have postponed their analysis to a forthcoming comprehensive deperturbation analysis for the A-state.

IV. DETERMINING NEW DUNHAM CONSTANTS FOR THE $X\,^1\Sigma^+$ STATE

Our objective here is to determine the best possible Dunham expansion constants for the ground state of BaO. Since the upper vibrational levels of the $A\,^1\Sigma^+$ state are known to be heavily perturbed, for $v'_A\geqslant 1$ the term value of each ob-

served upper-state level of each isotopomer $\{T^{\alpha}_{v',J'}\}$ was, therefore, treated as an independent parameter in our analysis, while for $v'_A=0$ the term values were represented by a separate set of band constants $\{T^{\alpha}_{v',0},B^{\alpha}_{v'},D^{\alpha}_{v'},\ldots\}$, and all ground-state term values were represented by the usual mass-scaled double polynomial expansion in $(v+\frac{1}{2})$ and $[J(J+1)]$. This term-value treatment of the upper A-state levels is a type of procedure suggested by Åslund in 1974.[34] However, it may also be thought of as a sorting of the electronic vibrational band data into groups of lines associated with distinct upper-state levels, followed by an analysis which treats those groups as fluorescence series. For the data set used in our final analysis (see below), this involves a total of 1372 ''fluorescence series'' associated with 878 levels of A-state ^{138}BaO, 215 levels of ^{137}BaO, 178 of ^{138}BaO, and 101 of ^{138}BaO. This approach allows the electronic data to be used directly, without first converting it into a set of combination differences, and allows the estimated experimental line position uncertainties of 0.005 cm^{-1} to be used to weight the data.

Because of the density of our electronic spectrum, over 2100 of the assigned transitions were actually blended lines with duplicate assignments; they were omitted from our analysis. Moreover, since $v'_A\geqslant 1$ levels of the A-state are each represented by an independently fitted term value, if only one chemiluminescence transition originated in one of those levels it was also omitted from the present analysis, as it could not contribute to our knowledge of the ground state and the uncertainty associated with a $T^{\alpha}_{v',j'}$ value obtained in this way would be undefined.

The present analysis also utilized 37 microwave data[6,7,12,13] and 124 high-resolution infrared data[14] for the ground state and 1 microwave measurement for the A-state[8] taken from the literature, each weighted by the inverse square of the reported experimental uncertainty. Although they are of distinctly lower resolution, the OODR photoluminescence data of Ref. 15 were also included since they extend to $v''=34$, far beyond the range (up to $v''=20$) of our high-resolution data. Again, their weights were defined as the inverse square of the experimental uncertainties, which are ~2.4 cm^{-1} for the absolute frequencies defining the vibrational spacings, and 0.94 cm^{-1} for the P/R branch splittings. This left a total of 13 683 data in our analysis, consisting of our 13 402 chemiluminescence data plus 38 microwave data,[5,6,8,7,12,13] 124 infrared data,[14] and the 59 fluorescence R-lines and 60 P/R splittings from the low resolution OORD study of Ref. 15 for the P-R splittings.[15]

Our analysis was performed using computer program DSPARFIT.[45] This code allows various kinds of data for multiple isotopomers to be treated in a combined analysis which can use different types of representations for data associated with different electronic states. When conventional Dunham expansions are selected, it automatically implements the normal first-order semiclassical scaling

$$Y^{\alpha}_{l,m}=Y^{\beta}_{l,m}(\mu_{\beta}/\mu_{\alpha})^{m+l/2}, \tag{4}$$

where μ_{α} and μ_{β} are the reduced masses of isotopomers α and β, and treats the expansion parameters $\{Y^1_{l,m}\}$ of a selected reference isotopomer ($\alpha=1$) as free parameters, with those for other isotopomers being defined by Eq. (4). DSPARFIT also allows for the inclusion of atomic-mass-dependent Born–Oppenheimer breakdown correction terms,[46] but such correction terms were not required here.

The observed $A-X$ electronic transition frequencies for $v'\geqslant 1$ level of isotopomer-α of BaO were fitted to the expression

$$\nu_{\alpha}(v',J';v'',J'')=T^{\alpha}_{v',J'}-\sum_{l=0}^{l_{\max}(m)}\sum_{m=0}^{m_{\max}}Y^1_{l,m}(\mu_1/\mu_{\alpha})^{m+l/2}\times(v+1/2)^l[J(J+1)]^m, \tag{5}$$

where $T^{\alpha}_{v',J'}$ are the individual A-state term values being fitted to, and $Y^1_{l,m}$ are the normal Dunham constants of the species ($\alpha=1$) selected as the reference isotopomer. For A-state levels with $v'=0$, the term values were represented by a separate set of band constants for each isotopomer,

$$\begin{aligned}T^{\alpha}_{0,J'}&=T^{\alpha}_{0,0}+\sum_{m=1}K_m(0)[J'(J'+1)]^m\\&=T^{\alpha}_{0,0}+B^{\alpha}_0[J'(J'+1)]-D^{\alpha}_0[J'(J'+1)]^2\\&\quad+H^{\alpha}_0[J'(J'+1)]^3+\cdots.\end{aligned} \tag{6}$$

The present analysis used ^{138}BaO as the reference isotopomer ($\alpha=1$), while the atomic masses used to determine the various reduced masses were taken from Ref. 47. Note that the masses of all stable atomic isotopes are included in data subroutine MASSES which is part of the DSPARFIT program package.[45]

After some experimentation it was found that an optimum fit was obtained when the Dunham expansion for the ground state was defined by $m_{\max}=2$ and $l_{\max}(m)=5$, 3, and 2 for $m=0$, 1, and 2, respectively. The 1400 determined parameters consisted of the 12 Dunham constants for ^{138}Ba^{16}O, 14 band constants for $v'_A=0$, plus 1372 independent A-state $T^{\alpha}_{v',J'}$ values and 2 fluorescence series origins associated with the low resolution OODR-excited data. The resulting dimensionless standard error[48] of $\overline{\sigma_f}=1.27$ suggests that our estimated experimental uncertainty of 0.005 cm^{-1} may have been slightly (~25%) optimistic. The final fit was performed using the ''sequential rounding and refitting'' scheme described in Ref. 48 (and incorporated in program DSPARFIT[45]) which minimizes the number of significant digits in the fitted parameters required to accurately represent the input data.

The resulting Dunham parameters for ^{138}Ba^{16}O, and their 95% confidence limit uncertainties are presented in Table II, together with the A-state $v'_A=0$ band constants for the four observed isotopomers. Although readily generated from Eq. (2), for the reader's convenience the X-state Dunham parameters for the minor isotopomers are also listed there. The fact that more significant digits are required for the latter than for the constants of the reference isotopomer ^{138}Ba^{16}O simply reflects the fact that the simplification yielded by the sequential rounding and refitting procedure only applies to parameters directly determined by the fit, so these derived quantities may only be rounded off at the first digit of the parameter sensitivity.[48]

TABLE II. Recommended molecular constants for BaO determined from our combined-isotopomer fit. The numbers in parentheses are the 95% confidence limit uncertainties in the last significant digits shown, and the Dunham constants for the minority isotopomers were rounded at the first significant digit of the parameter sensitivity (Ref. 48).

Constant		$^{138}Ba^{16}O$	$^{137}Ba^{16}O$	$^{136}Ba^{16}O$	$^{135}Ba^{16}O$
$X\,^1\Sigma^+$ State:		From all-isotopomer fit	From the fitted ^{138}BaO constants & Eq. (4)		
$Y_{1,0}$	ω_e	669.736 53(65)	669.990 545 74	670.248 674 43	670.509 910 46
$Y_{2,0}$	$-\omega_e x_e$	−2.0195(2)	−2.021 032 191	−2.022 589 786	−2.024 166 741
$Y_{3,0}$	$\omega_e y_e$	$-4.168(29)\times10^{-3}$	$-4.172\,744\,3\times10^{-3}$	$-4.177\,569\,1\times10^{-3}$	$-4.182\,455\,7\times10^{-3}$
$Y_{4,0}$	$\omega_e z_e$	$-3.56(17)\times10^{-5}$	$-3.565\,404\times10^{-5}$	$-3.570\,902\times10^{-5}$	$-3.576\,472\times10^{-5}$
$Y_{5,0}$	-	$-5.5(4)\times10^{-7}$	$-5.510\,438\times10^{-7}$	$-5.521\,061\times10^{-7}$	$-5.531\,829\times10^{-7}$
$Y_{0,1}$	B_e	0.312 614 64(6)	0.312 851 820 1	0.313 092 932 7	0.313 337 042 4
$Y_{1,1}$	$-\alpha_e$	$-1.39374(8)\times10^{-3}$	$-1.395\,326\,44\times10^{-3}$	$-1.396\,939\,81\times10^{-3}$	$-1.398\,573\,86\times10^{-3}$
$Y_{2,1}$	γ_e	$-3.681(15)\times10^{-6}$	$-3.686\,588\times10^{-6}$	$-3.692\,272\times10^{-6}$	$-3.698\,032\times10^{-6}$
$Y_{3,1}$	-	$-4.60(7)\times10^{-8}$	$-4.608\,73\times10^{-8}$	$-4.617\,61\times10^{-8}$	$-4.626\,62\times10^{-8}$
$Y_{0,2}$	$-D_e$	$-2.7144(12)\times10^{-7}$	$-2.718\,520\,4\times10^{-7}$	$-2.722\,712\,3\times10^{-7}$	$-2.726\,959\,6\times10^{-7}$
$Y_{1,2}$	$-\beta_e$	$-1.11(17)\times10^{-10}$	$-1.112\,11\times10^{-10}$	$-1.114\,25\times10^{-10}$	$-1.116\,42\times10^{-10}$
$Y_{2,2}$	-	$-1.28(12)\times10^{-11}$	$-1.282\,92\times10^{-11}$	$-1.285\,88\times10^{-11}$	$-1.288\,89\times10^{-11}$
$A\,^1\Sigma^+$ State:			Band constants from the all-isotopomer fit		
$K_0(v=0)$[a]	$T_{0,0}$	16 722.2542(8)	16 722.2164(21)	16 722.1826(22)	16 722.1485(26)
$K_1(v=0)$	B_0	0.257 824 6(6)	0.258 020 5(28)	0.258 226 3(19)	0.258 425 1(15)
$K_2(v=0)$	$-D_0$	$-2.7814(18)\times10^{-7}$	$-2.783(10)\times10^{-7}$	$-2.810(3)\times10^{-7}$	$-2.810(2)\times10^{-7}$
$K_3(v=0)$	H_0	$-1.06(7)\times10^{-13}$	$-1.7(10)\times10^{-13}$		

[a]Energy relative to the ground-state $v=0$ level of that isotopomer.

The other key results of this analysis are the 1372 independent *A*-state $T^{\alpha}_{v',J'}$ values for the four observed isotopomers of $Ba^{16}O$. These will be the key input for our planned deperturbation analysis of this state. While too extensive to list here, these term values (and their 95% confidence limit uncertainties) are available electronically from the Journal archive, together with the complete input data set used in this analysis.[44]

V. CONCLUSIONS

The use of a Fourier transform spectrometer to record the $A\,^1\Sigma^+-X\,^1\Sigma^+$ emission spectrum of BaO in a Broida-type oven extends our high-resolution knowledge of the ground state up to $v''=20$. A total of 154 vibrational bands, with over 15 500 rovibrational lines of four isotopomers of BaO were identified, of which 13 402 unblended lines were used in our analysis. Several new perturbations in the $A\,^1\Sigma^+$ state were observed. Our analysis of these results also incorporated existing microwave data, infrared data and low-resolution OODR data which extend the vibrational range covered by our recommended constants to $v''=34$.

Because of the perturbations affecting the upper vibrational levels of the *A*-state, a novel type of combined-isotopomer analysis was performed in which energy levels of the ground state were represented by (mass scaled, for the minor isotopomers) conventional Dunham expansions, the $v'=0$ levels of the *A*-state were represented by independent band constants for each isotopomer, and for higher vibrational levels of the *A*-state, an independent term value was determined for each vibration–rotation level of each isotopomer. In addition to the improved Dunham constants for the ground state and band constants for $v'_A=0$, this yielded 1372 accurate independent term values for the upper levels of the *A*-state which will be the starting point for our forthcoming deperturbation analysis of that state.

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