# LETTER TO THE EDITOR

## First Observation of the BaI $A'$ $^2\Delta$ Electronic State: The $\Omega = 3/2$ Component

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Alkaline–earth monohalides have been the theme of a number of studies. Several experimental works on the spectroscopic properties of these molecules have made possible the testing of the theoretical ionic bonding models (*1–6*) developed to represent the electronic structure of these compounds and, especially, the location of the first excited metastable $A'$ $^2\Delta$ state.

The BaI molecule was first identified in 1928 by Walters and Barratt (*7*), who observed the $C^2\Pi - X^2\Sigma^+$ band system. The same band system was studied later by Mesnage (*8*), Patel and Shah (*9*), and Rao *et al.* (*10*). Patel and Shah (*9*) have also identified two other electronic band systems: $E^2\Sigma^+ - X^2\Sigma^+$ at about 374 nm and $D^2\Sigma^+ - X^2\Sigma^+$ at about 388 nm. Bradford *et al.* (*11*) have observed the chemiluminescence reaction Ba + I$_2$ and determined that the infrared emission was issued from two unobserved electronic transitions: $A^2\Pi - X^2\Sigma^+$ and $B^2\Pi - X^2\Sigma^+$. The rovibrational structure of seven subbands ($v = 0, 1, 2, 3, 4, 8, 12$, with $\Delta v = 0$) of the $C^2\Pi - X^2\Sigma^+$ band system has been largely and accurately studied after 1981 (*12–17*). More recently Gutterres *et al.* have observed and analyzed several rovibrational transitions of the $B^2\Sigma^+ - X^2\Sigma^+$ band system (*18*) as well as of the $A^2\Pi - X^2\Sigma^+$, $C^2\Pi - X^2\Sigma^+$, $C^2\Pi - A^2\Pi$, and $C^2\Pi - B^2\Sigma^+$ band systems (*19*).

In this work a spectroscopic study of the $A'$ $^2\Delta_{3/2}$ electronic component of the BaI molecule is presented. The $C^2\Pi_{1/2} - A'$ $^2\Delta_{3/2}$ subband system was investigated using laser-induced fluorescence (LIF) and Fourier transform spectroscopy (FTS). The near-infrared LIF spectra were obtained from dye single-mode laser excitations and from a Kr$^+$ multimode ion laser excitation. Resolved rotational data were added to previously recorded data (*17–19*) and a set of molecular constants for the $A'$ $^2\Delta_{3/2}$ component could be derived from a simultaneous treatment of the whole data set.

BaI molecules were produced in a heat-pipe oven in which a mixture of a few grams of Ba metal and BaI$_2$ powder was heated to 850°C in the presence of 12 mbar of argon buffer gas. The obtained fluorescence was focused onto the entrance iris of a 2-m optical path length Fourier transform spectrometer. The experimental configuration and techniques used in this work were similar to those previously reported (*18, 19*).

The excitation of the BaI molecules was done by using three laser lines provided by a dye single-mode laser (Coherent 599-21, Rh 6G) and one laser line provided by a Kr$^+$ (Coherent Innova K 3000) multimode ion laser. Each laser line of the dye and Kr$^+$ lasers excited several and successive rotational levels of the $C^2\Pi_{1/2}$ state, and always the vibrational levels $v'$ of the upper state were excited from a $v'' = v' + 2$ vibrational level of the $X^2\Sigma^+$ ground state. The classical triplet pattern ($P, Q, R$), in which the $Q$ lines have about two times the intensities of the $P$ and $R$ lines, was observed in the obtained spectra. The observed fluorescence progressions are given in Table 1, which summarizes the quantum numbers $J'$, $v'$, and the term energy value $E'$ of the

involved $C^2\Pi_{1/2}$ level together with the quantum numbers $J''$, $v''$, and the term energy value $E''$ of the lower level in the ground $X^2\Sigma^+$ state. Table 1 shows also the range of observed vibrational levels in the $A'$ $^2\Delta_{3/2}$ component. A short portion of the studied fluorescence spectra, induced after excitation with the Kr$^+$ 568.2-nm radiation, is depicted in Fig. 1.

In the present work the rovibrational levels of the $C^2\Pi$ state excited by the mentioned laser lines were the same as the ones previously analyzed in (*19*) ($C^2\Pi - X^2\Sigma^+$, $C^2\Pi - A^2\Pi$, and $C^2\Pi - B^2\Sigma^+$ band systems) facilitating the assignment of the observed transitions. The obtained available spectroscopic data of the $C^2\Pi_{1/2} - A'$ $^2\Delta_{3/2}$ subband system were combined with previous results (*17–19*) and reduced by using a nonlinear least-squares method. All term values of the involved electronic states were described by standard Hamiltonian representations (see, for example, (*20*)); spin–orbit interaction could naturally not be determined. Vibrational dependence of parameters was taken into account by a "Dunham-type" variation.

There was no significant change between the molecular constants calculated for the $X^2\Sigma^+$, $A^2\Pi$, $B^2\Sigma^+$, and $C^2\Pi$ states and the ones previously reported (*19*). Table 2 summarizes the final values of the recommended effective molecular constants for the $A'$ $^2\Delta_{3/2}$ component derived from the global analysis described above. The theoretical energy origin values derived from the model of *ligand field approach* (*21*), from the model of *electrostatic polar-*

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**TABLE 1**

**Dye Single-Mode Laser and Kr$^+$ Multimode Ion Laser Vacuum Wavenumbers $\sigma$, Quantum Numbers $v'$, $J'$, and Energy $E'$ for the $C^2\Pi_{1/2}$ Excited Levels, Quantum Numbers $v''$, $J''$, and Energy $E''$ of the Lower Levels in the Ground $X^2\Sigma^+$ State and Range of Observed $v$ Values in the $A'$ $^2\Delta_{3/2}$ State**

| $\sigma(cm^{-1})$ | $v'$ | $J'$ | $E'(cm^{-1})$ | $v''$ | $J''$ | $E''(cm^{-1})$ | $v$ |
|---|---|---|---|---|---|---|---|
| 17507.51 | 0 | 165.5–201.5 | 18771.12–19121.13 | 2 | 166.5–202.5 | 1263.61–1613.62 | 0 |
| 17514.27 | 1 | 168.5–197.5 | 18804.48–19085.69 | 3 | 169.5–198.5 | 1290.21–1571.42 | 0–2 |
| 17521.00 | 2 | 165.5–190.5 | 18924.02–19158.09 | 4 | 166.5–191.5 | 1403.02–1637.09 | 1–3 |
| 17594.91 | 10 | 199.5–200.5 | 20494.15–20504.48 | 12 | 200.5–201.5 | 2899.24–2909.57 | 7–12 |
| | 11 | 133.5–137.5 | 20061.01–20088.98 | 13 | 134.5–138.5 | 2466.10–2494.07 | 8–13 |
| | 11 | 231.5–232.5 | 20979.05–20990.90 | 13 | 230.5–231.5 | 3384.14–3395.99 | 8–16 |
| | 12 | 120.5–130.5 | 20119.21–20183.82 | 14 | 119.5–129.5 | 2524.30–2588.91 | 9–17 |
| | 13 | 203.5–210.5 | 20961.59–21035.54 | 15 | 204.5–211.5 | 3366.68–3440.63 | 9–18 |
| | 13 | 228.5–233.5 | 21237.95–21296.94 | 15 | 229.5–234.5 | 3643.04–3702.03 | 10–16 |
| | 14 | 130.5–133.5 | 20469.36–20489.63 | 16 | 129.5–132.5 | 2874.45–2894.72 | 11–18 |
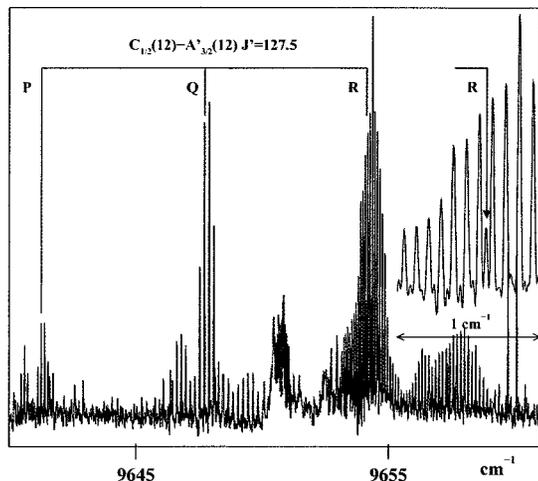
**FIG. 1.** Part of the $C^2\Pi_{1/2}$ ($v = 12$) $\rightarrow A'$ $^2\Delta_{3/2}$ ($v = 12$) fluorescence spectrum obtained after 568.35-nm Kr$^+$ laser line excitation. The $P$, $Q$, and $R$ structure is shown for $J' = 127.5$. The inset clarifies the $R$ line position, among another fluorescence structure due to the $C$–$A$ transition.

about 330 cm$^{-1}$ leading to an energy origin around 8369.04 + 330 = 8699 cm$^{-1}$. The difference between the obtained experimental transition energy value and the theoretical estimate for this parameter is about 5% for the model of ligand field approach and below 1% for the model of electrostatic polarization. Nevertheless it is important to note that the value for the energy origin obtained in this work represents only the energy origin of the $\Omega = 3/2$ component and fluorescence data involving the $\Omega = 5/2$ component will be necessary to improve the value of $A$, then the $T_e = 8699$ cm$^{-1}$ present determination.

Laser-induced fluorescence (LIF) combined with Fourier transform spectroscopy (FTS) have permitted the first spectroscopic study with rotational resolution of the $\Omega = 3/2$ component of the BaI $A'$ $^2\Delta$ electronic state. A total of 1329 transitions, involving 16 vibrational levels ($0 \leq v \leq 3$ and $7 \leq v \leq 18$) of the $A'$ $^2\Delta_{3/2}$ component, could be assigned. A global analysis including previously reported data (17–19) was done and a set of nine molecular constants for the $A'$ $^2\Delta_{3/2}$ component was determined, the obtained constants describing the analyzed transitions with a standard deviation less than $3 \times 10^{-3}$ cm$^{-1}$.

*ization* (*22*), are shown in the same table. The energy origin derived in the present work ($\Omega = 3/2$ component) is in fact equal to $T$–$A$, if $A$ represents the spin–orbit parameter of the state. This parameter has been calculated (*6*) as

### TABLE 2
**Molecular Constants in cm$^{-1}$ for the $A'$ $^2\Delta_{3/2}$ Electronic Component Determined in the Analysis from a Nonlinear Least-Squares Fit of the Global Data Set**

| Molecular constants | $A'^2\Delta_{3/2}$ |
|---|---|
| $T_{3/2}$ | 8369.0384(127) [this work] |
| $T_e$ | 8699 [$T_{3/2} + A_{calc.}$] |
| [21] | 8273 |
| [22] | 8780 |
| $B_e \times 10^{+2}$ | 2.623369(101) |
| $D_e \times 10^{+9}$ | 5.0805(273) |
| $H_e \times 10^{+15}$ | 9.335(274) |
| $\alpha_B \times 10^{+5}$ | 6.93512(208) |
| $\beta_B \times 10^{+8}$ | 4.4834(872) |
| $\omega_e$ | 142.285903(343) |
| $\omega_e x_e$ | 0.2741060(560) |
| $\omega_e y_e \times 10^{+4}$ | 2.6085(168) |

*Note.* Numbers in parentheses represent two standard deviations in units of the last figure quoted.

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