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The *E*2 admixture in mixed multipole line 647.6 nm in the spectrum of Bi I

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A study of the hyperfine structure of mixed multipole line 646.7 nm of Bi I is reported. A special computer program was designed to obtain the predicted contour of the hyperfine structure of the line for different values of the electric-quadrupole admixture. By variation of free parameters, describing the line shape and the electric-quadrupole admixture D, defined as the ratio of the magnetic-dipole and electric-quadrupole decay rates $D = A^{E2}/(A^{M1} + A^{E2})$, the calculated profiles were fitted into the recorded spectra. The D value of the best fit found is (17.8 ± 1.0)%. Our result is compared with recent theories and other experiments.

Keywords: hyperfine structure, forbidden transitions, transition probability.

1. Introduction

The $6s^26p^3$ ground configuration of bismuth gives rise to five levels $^4S_{3/2}$, $^2P_{3/2,\,1/2}$ and $^2D_{5/2,\,3/2}$. Since electric-dipole ($E1$) transitions between the states of the same parity are forbidden, all the levels of the $6s^26p^3$ configuration are metastable. Weak: magnetic-dipole ($M1$), electric-quadrupole ($E2$) or mixed type (*i.e.*, those permitted for both $M1$ and $E2$ types of radiation) transitions between these levels are permitted in the second-order radiation theory.

Usually decay rates calculated for strong $E1$ transitions, are in reasonable agreement with experiments, but in the case of weak forbidden transitions the predictions often disagree with the experimental data. It results from the fact that multipole transition rates are particularly sensitive to even small modifications of the wave functions and a careful choice of the theoretical method is required.

A complete list of $M1$ and $E2$ transition probabilities calculated for the $6s^26p^3$ configuration of Bi I has been presented in [1]. However, the obtained data disagree with experiments [2, 3] mainly because of very rough estimate of the adopted value for the radial integral s_q determining the $E2$ contributions in forbidden transitions. Improved semiempirical single-configuration calculations presented in [4] better agree with experiment.

The most extensive multiconfiguration calculations of multipole transition rates for states within the $6s^2 6p^3$ configuration of Bi I have been performed by BIÉMONT and QUINET [5], using the HFR method. In this method the transition rates are computed in intermediate coupling with basis functions obtained in the framework of the Slater–Condon theory, where electrostatic and spin-orbit integrals are evaluated so as to fit to the observed energy levels. The HFR energies obtained in [5] appear in very good agreement with the observed structure, but the agreement with the experimental data concerning multipole transition rates is not that satisfactory. For instance, the experimental transition probability $A(^2D_{3/2} - {}^4S_{3/2}) = 22.5 \pm 1.4\ \mathrm{s}^{-1}$ [6] is almost by 50% lower than the corresponding theoretical result.

The measurements of the $E2$ admixture in the mixed type transitions are one of the most sensitive methods verifying the calculations for multipole transitions. Because of large discrepancy between experimental ant theoretical predictions for $E2$ admixture in 647.6 nm line of Bi I we reexamined this line with the aid of our computer modeling technique.

2. Experiment

The experimental arrangement used in the experiment was similar to that described in [7–9].

In brief, the light source was a quartz discharge tube connected to the vacuum system. Helium was used as a buffer gas. The discharge was excited by rf oscillator (55 MHz) connected to the discharge tube by external electrodes. The high resolution spectral apparatus consisted of a silver-coated Fabry–Perot etalon (with 5.9 and 6.3 mm spacers) and a Carl Zeiss PGS-2 grating spectrograph. The spectra were recorded by the CCD detector (Hamamatsu model C7041 with head device model S7031-1006).

3. Theory

The theory of forbidden lines is presented in many papers and monographs [10–14].

The spontaneous transition probability for a single photon emission A_{ab} for mixed $M1$+$E2$ transition is given by:

$$\sum_{M',\,M} a_{ab}^{\mathrm{Total}}(M \to M') = \sum_{M',\,M} \left[\sum_{q=-1}^{1} \left| \mathbf{e}^* \cdot \mathbf{Y}_{1q}^{(0)}(\mathbf{n}) \right|^2 a_{ab}^{M1}(q) + \sum_{q=-2}^{2} \left| \mathbf{e}^* \cdot \mathbf{Y}_{2q}^{(1)}(\mathbf{n}) \right|^2 a_{ab}^{E2}(q) \right] \tag{1}$$

where $a_{ab}^{M1}(q)$, $a_{ab}^{E2}(q)$ are well known pure multipole transition probabilities of electric and magnetic type defined as:

$$a_{ab}^{M1}(q) = \frac{4}{3\hbar}\left(\frac{\omega}{c}\right)^3 \left|\langle b|\mu_{1q}|a\rangle\right|^2 \tag{2}$$

$$a_{ab}^{E2}(q) = \frac{1}{15\hbar}\left(\frac{\omega}{c}\right)^5 \left|\langle b|Q_{2q}|a\rangle\right|^2 \tag{3}$$

The spherical vector $\mathbf{Y}_{Jq}^{(\lambda)}(\mathbf{n})$ characterizes a photon with angular momentum J, its $\hat{z}$ component q and parity $P = (1)^{J+\lambda+1}$ (λ may assume values 1 or 0 for electric or magnetic multipoles) and **n**, **e** are unit propagation and polarization vectors, respectively.

Using standard vector coupling technique [15], the matrix elements of operators $a_{kq}(\mathbf{k}, \mathbf{e})$ for electric and magnetic multipole transitions can be written in terms of 3-*j* and 6-*j* symbols as

$$\langle \gamma' J' I F' M_F' | a_{kq}(\mathbf{k}, \mathbf{e}) | \gamma J I F M_F \rangle = S_{qF'F}^{(k)} \langle \gamma' J' \| a_k \| \gamma J \rangle \tag{4}$$

where

$$S_{qF'F}^{(k)} = (-1)^{F' - M_F' + J' + I + F + k} \sqrt{(2F'+1)(2F+1)} \begin{pmatrix} F' & k & F \\ -M_F' & q & M_F \end{pmatrix} \begin{Bmatrix} J' & F' & I \\ F & J & k \end{Bmatrix} \tag{5}$$

Then, the relative transition probability after summing over M_F', M_F can be expressed as

$$a_{F',F}^{\text{Total}} = (2F'+1)(2F+1)\left\{ A_{J'J}^{M1} \begin{Bmatrix} J' & F' & I \\ F & J & 1 \end{Bmatrix}^2 + A_{J'J}^{E2} \begin{Bmatrix} J' & F' & I \\ F & J & 2 \end{Bmatrix}^2 \right\} \tag{6}$$

where transition probabilities $A_{J'J}^{M1}$, $A_{J'J}^{E2}$ are expressed by reduced matrix elements: $A_{J'J}^{M1} = \left|\langle \gamma' J' \| a_1 \| \gamma J \rangle\right|^2$ and $A_{J'J}^{E2} = \left|\langle \gamma' J' \| a_2 \| \gamma J \rangle\right|^2$.

Let us define the electric-quadrupole admixture in mixed transition as:

$$D = \frac{A_{J'J}^{E2}}{A_{J'J}^{M1} + A_{J'J}^{E2}} \tag{7}$$

As a final step one may express the relative transition probability $\tilde{a}_{F',F}^{\text{Total}}$ defined as $\tilde{a}_{F',F}^{\text{Total}} = a_{F',F}^{\text{Total}} / (A_{J'J}^{M1} + A_{J'J}^{E2})$ as follows:

$$\tilde{a}^{\,\mathrm{Total}}_{F',F} = (2F'+1)(2F+1)\left\{(1-D)\begin{Bmatrix} J' & F' & I \\ F & J & 1 \end{Bmatrix}^2 + D\begin{Bmatrix} J' & F' & I \\ F & J & 2 \end{Bmatrix}^2\right\} \tag{8}$$

The relative intensities of hyperfine structure patterns observed in the experiment are directly proportional to the relative transition probabilities $\tilde{a}^{\,\mathrm{Total}}_{F',F}$.

4. Computer analysis

The first step in the computer analysis involves finding the position and the relative intensities of all the individual hfs components. This procedure accepts the required atomic data of the investigated line: hyperfine structure constants A and B (see Tab. 1), and quantum numbers I and J for the two energy levels involved. The next procedure sorts all the components according to the wave numbers. Then the following intensity distribution function

$$I(\nu) = I_0(\nu) + \sum \frac{I_i}{1 + \alpha_1^2(\nu - \tilde{\nu}_i)^2 + \alpha_2^4(\nu - \tilde{\nu}_i)^4} \tag{9}$$

is employed to calculate the sum of intensities at each point of the final pattern. In (9) the $I_0(\nu)$ describes the background noise, $I_i(\nu)$ is the intensity of the i-th hfs component directly proportional to the transition probability (8), $\tilde{\nu}_i = \nu_i + \nu_0$ is the position of the component on the frequency axis (ν_0 shifts the whole contour to either left or right), and parameters α_1, α_2 describe the shape of the line. The function (9) is a convolution of Cauchy, Gauss and approximate Airy functions [18, 19]. The Cauchy and Gauss functions describe the radiative and Doppler broadenings of the atomic line whereas the Airy profile is connected with instrumental broadening.

In the next step, the least-square-fitting procedure is used. The simulated structure by variations of the estimated D values and line shape parameters is fitted into the experimental curve recorded in the digital form. In order to avoid difficulty the experimental profile is linearized. This is because the recorded Fabry–Perot patterns have a variable dispersions, especially near the center of the fringe system, but the simulated structure is calculated with a linear dispersion. In this procedure care is taken to keep the area under the interferometric curve constant.

5. Results

Reliable $E2$ contribution can be obtained only from spectra made with well separated structures. In our experiment this was achieved by using Fabry–Perot interferometer with spacers 5.9 and 6.3 mm. Unfortunately, under these conditions the interferometer

T a b l e 1. Hyperfine structure constants A and B used in our computations (in mK).

	$^2D_{5/2}$ (ref. [16])	$^4S_{3/2}$ (ref. [17])
A	83.67(3)	–14.92770(3)
B	1.3(6)	–10.18924(7)

orders overlap each other. The computer program was modified to take this into account. One of the results of such an analysis is presented in Fig. 1. The α_1 parameter values obtained in the fitting procedure varied from 0.07 cm^{-1} to 0.10 cm^{-1}, and the values of α_2 varied in the range of 0.1–0.3 cm^{-1}. The weighted mean value from all our experimental results was determined to be $D = (17.8 \pm 1.0)\%$. The error bar represents the standard deviation.

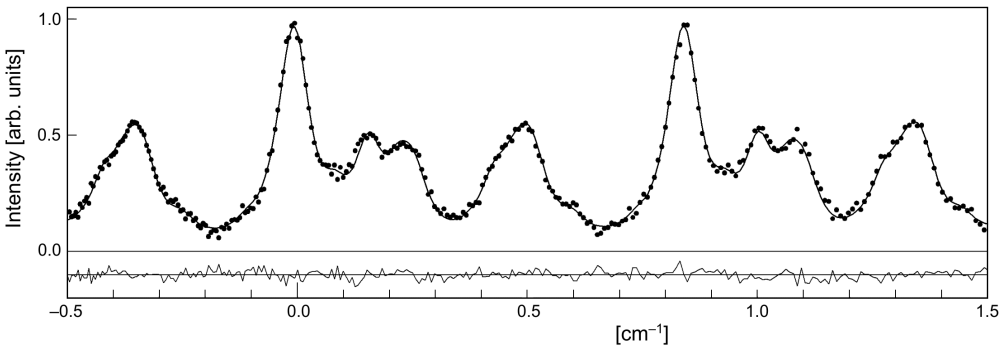

Fig. 1. The recorded hyperfine structure of 647.6 nm line obtained by using the 5.9 mm spacer. Black dots presents experimental profile. Solid line are the computer-generated best fits. At the bottom of the picture the "error" curves present deviations between calculated and experimental profiles.

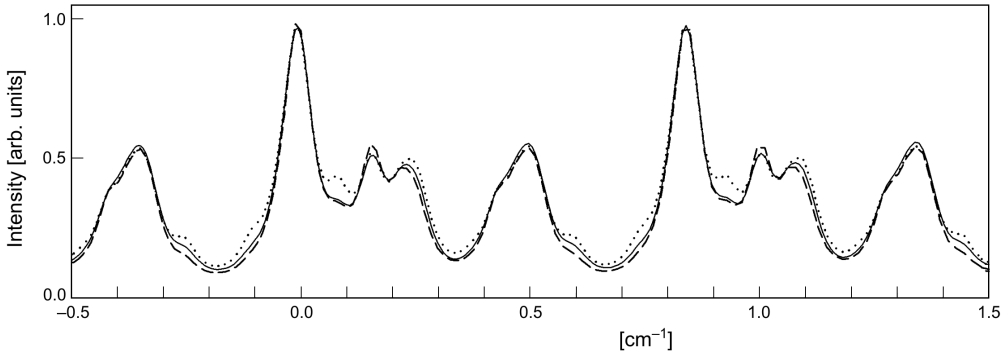

Fig. 2. The computer generated profiles for different values of electric-quadrupole admixture in the observed 647.6 nm line. The solid line presents the best fit to the experimental data obtained for D = 17.8%. The dotted line represents the simulated profile for D = 28% and the dashed line was generated for D = 8%. Comparison between these curves shows sensitivity of our method of analysis.

T a b l e 2. The *E*2 contribution in mixed 647.6 nm line of Bi I.

Experiment	Theory	Method of calculations
18 ± 4.5 [20]	20 [1]	Single configuration approximation
15 ± 5 [21]	35 [5]	Multi-configurational HFR
16 ± 1 [2]	17 [4]	Semiempirical
17.0 ± 1.0 [3]		
19.4 ± 1.3 [16]		
17.8 ± 1.0 present work		

Figure 2 presents the computer simulations of the hyperfine structure pattern for varying values of the electric-quadrupole admixture *D*. The presented figure shows the sensitivity of the shape of the generated structure to the *D* parameter changes.

In Table 2 our result was compared with experimental results of other authors and with theoretical predictions.

6. Conclusions

Our result is consistent with recent experimental data, but in strong disagreement with result of multi-configurational HFR calculations. The comparison between the single- and multi-configurational calculations shows that the configuration mixing for ground configuration of Bi I is very weak and a limited inclusion of admixtures of only several selected configurations into calculations not necessarily gives reliable results for transitions probabilities even if the calculated energy levels agree very well with observation.

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