A Simple Derivation of the Formula of the Doppler Broadened 478 keV γ-Ray Lineshape from ^{7}*Li and Its Analytical Application

Michael K. Kubo*,[a] and Yoichi Sakai[b]

[a]*Department of Chemistry, School of Science, the University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*
[b]*Department of Chemistry, Daido Institute of Technology, Hakusui-cho, Minami-ku, Nagoya 457-8532, Japan*

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A simple and intuitive derivation of the formula describing the Doppler broadened (± 7.6 keV wide) γ-ray shape at 478 keV of ^{7}*Li was developed. In application to analysis of PGA spectra of multi-elemental targets, a computer code based on the formula efficiently deconvoluted the 472 keV γ-ray from ^{24}Na superposed on the ^{7}*Li line. The code also provided peak areas and the degradation constants of ^{7}*Li in the spectra of samples.

Introduction

Neutron activation analysis (NAA) is a sensitive and versatile analytical technique especially in multielemental quantitative trace analysis of environmental, industrial, biological samples *etc*. With the advent of the prompt γ-ray analysis method (PGA) very short-lived nuclides have been coming into general use in NAA. Improved sensitivity and the range of applicable elements have opened a wide window of utility.[1] One of the elements which PGA has an ultimate sensitivity is boron by using the ^{10}B (n, α)^{7}*Li reaction (σ = 3838 barn for thermal neutrons[2]). Since the halflife of ^{7}*Li (73 fs) is of a comparable order of the thermalization time of the recoiling ^{7}*Li in condensed materials, the 478 keV γ-ray is emitted by fairly rapid ^{7}*Li, leading to Doppler broadening of the γ-ray whose detailed shape reflects the deceleration rate of the ^{7}*Li in the medium. From a practical point of view the broadening sometimes causes serious overlapping of the γ-ray from ^{7}*Li with the ones from ^{24}Na (472 keV), ^{80}Br (469 keV), ^{60}Co (484 keV) *etc.* Since ^{7}*Li does not emit other γ-rays, it is essential to deconvolute the complex spectrum to each component in quantitative analysis of boron in PGA. Deconvolution also provides the information about the deceleration rate of ^{7}*Li in a sample which we define a degradation constant *D* (Ref. 3) to be the averaged stopping power of the environment of sub micrometer vicinity of the boron atoms.

Conventional methods have been adopted to decompose the overlapped peaks in a spectrum into components and to estimate the contribution of each nuclide,[4] no fitting method had been applied to simultaneous extraction of both the peak area and the degradation constant from a γ-ray spectrum before the proposal of Sakai et al.[3] in PGA. While Sakai's method is useful to obtaining degradation constants in materials, its calculation time requirement is not adequate for multielemental analysis of many samples required in practical use. Sometimes an apporximate lineshape formula has been used to fit the spectrum.[5] In this study we reexamined the formulation and succeeded in reducing the multiplicity of numerical integration and computation time. Although similar formulae have been obtained by other authors based on different approaches[6,7] and a pure mathematical procedure leads to the identical formula starting from distributed δ functions within the Doppler shift range,[8] in this NOTE we present a more simple and intuitively understandable derivation of the formula describing the Doppler boradened lineshape with emphasizing physical meanings.

*Corresponding author. E-mail:kubo@chem.s.u-tokyo.ac.jp. FAX: +81-3-5841-8324.

Formulation

The Doppler energy shift is determined by the projected velocity (v_z) of ^{7}*Li along the measurement axis, the detecor-sample line (Figure 1). A γ-ray spectrum reflects the velocity distribution of ^{7}*Li when it emits a γ quantum integrated over its lifetime. Since the velocity of ^{7}*Li relative to the detector does not exceed the initial recoil velocity v_0, 4.8×10^6 ms^{-1}, which is negligibly small compared with the speed of light, everything is treated non-relativistically. The distribution of the projected velocity $f(v_z)$ is easily converted to a γ-ray energy spectrum *g(E)* by variable transformation $E = E_0 (1 + \frac{v}{c}) = E_0 + \Delta E$, where E_0 is the unshifted γ-ray energy, *c* is the speed of light, ΔE is the Dopper shift (for ^{7}*Li ΔE_{max} = 7.6 keV).

We start with the special case when ^{7}*Li experiences no velocity degradation. We observe γ-rays emitted from ^{7}*Li recoiling isotropically with a mean lifetime $\tau = 1/\lambda$. The velocity distribution of ^{7}*Li which emit a γ quantum at time *t* is the product of the disintegration rate and the solid angle fraction of ^{7}*Li with v_z,

$$f(v_z)\,dv_z = (\lambda N dt)\frac{2\pi v \sin\theta\,(-v d\theta)}{4\pi v^2} \quad (1)$$

$$= -\frac{1}{2}\lambda N dt \sin\theta\, d\theta \quad (2)$$

where θ is the angle between the motion of ^{7}*Li and the measurement axis, *N* is the number of ^{7}*Li at time *t*, *v* is the velocity of ^{7}*Li. Since *v* remains constant by assumption,

$$v_z = v\cos\theta = v_0\cos\theta \quad (3)$$

$$d(v_z) = d(v_0\cos\theta) = -v_0\sin\theta\, d\theta. \quad (4)$$

Combining eqs. 2 and 4, we obtain

$$f(v_z)\,dv_z = \frac{\lambda N}{2v_0} dt\, dv_z. \quad (5)$$

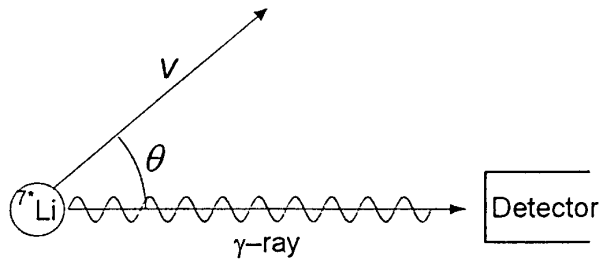

Figure 1. Detection of a γ-ray emitted from ^{7}*Li in flight. The angle between the velocity vector of ^{7}*Li and the observed γ-ray is θ.

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This means that $f(v_z)$ is independent of v_z, or the velocity distribution is constant over the range $(-v_0, +v_0)$, leading to a rectangular shaped γ-ray energy spectrum,

$$g(E)\,dE = g(E_0 + \Delta E)\,dE = \frac{c}{E_0}\frac{\lambda N}{2v_0}dt\,dE. \quad (6)$$

The overall spectrum can be obtained by summing up the time-sliced spectrum obtained above, or integrating eq 6 with respect to t. This process is stacking up the rectangles with area $dS = \varepsilon\,\lambda\,N\,dt$, the number of emitted γ quanta times detection efficiency ε (hereafter we put $\varepsilon = 1$ for simplicity) (Figure 2). Because N decreases with time as $N = N_0 \exp(-\lambda t)$ but the width of the rectangle which is equal to the Doppler shift range keeps constant value of $2E_0 v_0 / c$, the height of the rectangle diminishes with time as

$$dh = \frac{dS}{2E_0 v_0/c} = \frac{c\lambda N_0 \exp(-\lambda t)\,dt}{2E_0 v_0} \quad (7)$$

$$g(E) = \int_{t=0}^{t=\infty} dh = \frac{cN_0}{2E_0 v_0} \qquad (|\Delta E| \le \Delta E_{\max}). \quad (8)$$

All the γ quanta (N_0) are distributed equally over the range $(E_0\text{-}\Delta E_{\max}, E_0 + \Delta E_{\max})$.

Next, let us consider the γ-rays emitted from ^{7}*Li produced in condensed materials where ^{7}*Li experiences deceleration within its lifetime. In such a case the shape of the γ-ray energy spectrum is obtainable by substituting v_0 in eq 7 with time dependent v. For ^{7}*Li the time dependence of v is well described as

$$v = v_0 \exp(-Dt), \quad (9)$$

where D is the degradation constant characterizing the deceleration process of ^{7}*Li in the material.[3] The height of the rectangle dh is larger in this case than the one in no deceleration case (Figure 2) compared at the same timing, because the Doppler shift range, the width of the rectangle, is smaller in this case but the area of the rectangle which is proportional to the γ-ray emission rate $\lambda\,N\,dt$ is same in both the cases. The overall spectrum is given by

$$g(E) = \int_{t=0}^{t=t_E} dh = \int_0^{t_E} \frac{c\lambda N_0 \exp(-\lambda t)}{2E_0 v_0 \exp(-Dt)}\,dt. \quad (10)$$

Energy dependence is included in the upper limit of the integral t_E as follows. Because of the deceleration ^{7}*Li is so slow at $t = t_E$ that the maximum Doppler shift can not exceed $|E - E_0| = |\Delta E|$. Hence the emitted γ quanta after t_E do not contribute to the spectrum region where Doppler shift is larger than ΔE (Figure 2). Since $|\Delta E| = E_0 v_0 \exp(-Dt_E) / c$ at $t = t_E$, the limit t_E is written as

$$t_E = \frac{1}{D}\ln\left(\frac{E_0 v_0}{c|\Delta E|}\right). \quad (11)$$

By integrating eq 10 one comes to the final form,

$$g(E) = \frac{cN_0}{2E_0 v_0}\;\lambda\;\left[1 - \left(\frac{c|E-E_0|}{E_0 v_0}\right)^{\frac{\lambda - D}{D}}\right] \quad (|\Delta E| \le \Delta E_{\max}). \quad (12)$$

A real spectrum is obtained by convoluting eq 12 with an instrumental response function, usually assumed to be Gaussian, by one step numerical integration. It has reduced computing time compared with our previous method[3] which required double numerical integration. From the exponent of eq 12 we can derive a new characteristic of the spectrum which eluded us before. The spectrum is upward concave and bell-shaped when the degradation is slow, $(\lambda - D)/D \ge 1$, or $2D \le \lambda$, and downward concave when ^{7}*Li decelerates rapidly, $(\lambda - D)/D \le 1$, or $2D \ge \lambda$ (Figure 3). In our derivation this is clearly shown through a consideration about the shape of the rectangles. As the width of a spectrum-building rectangle at time t is $\frac{E_0 v_0}{c}\exp(-Dt)$ and its height is described as $\frac{c\lambda N_0 \exp(-\lambda t)\,dt}{2E_0 v_0 \exp(-Dt)}$ from eq 7, the time dependence of the horizontal to vertical ratio of the rectangle is proportional to $\frac{\exp(-2Dt)}{\exp(-\lambda t)}$. Therefore the skewness of the lineshape is determined by the balance between $2D$ and λ as mentioned above. As far as we know, no material has ever shown a downward concave spectrum for ^{7}*Li case.

Analytical Application

Experimental details were published previously.[3] Gamma-ray spectra were obtained with the PGA system by using the thermal neutron beam guide at JRR-3M in Japan Atomic Energy Research Institute.[1] Typical thermal neutron flux was 2×10^7 cm^{-2} s^{-1}, and cold neutron flux was 2×10^6 cm^{-2} s^{-1}. Measuring time varied from 10 minutes to 2 hours depending on the boron content of the samples.

A usual procedure to fit a γ-ray spectrum obtained with a

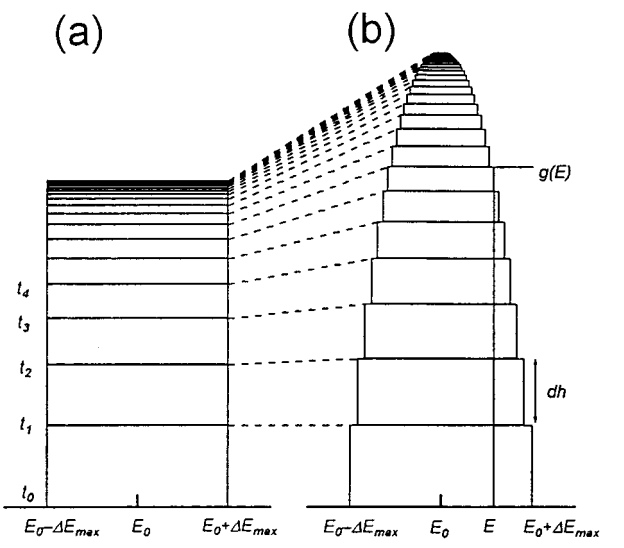

Figure 2. Doppler broadened γ-ray spectra from ^{7}*Li: (a) without deceleration; (b) with deceleration. The spectra can be obtained by stacking rectangles whose areas correspond to the sum of γ quanta emitted during dt distributed over the region $(E_0(1 - v/c), E_0(1 + v/c))$.

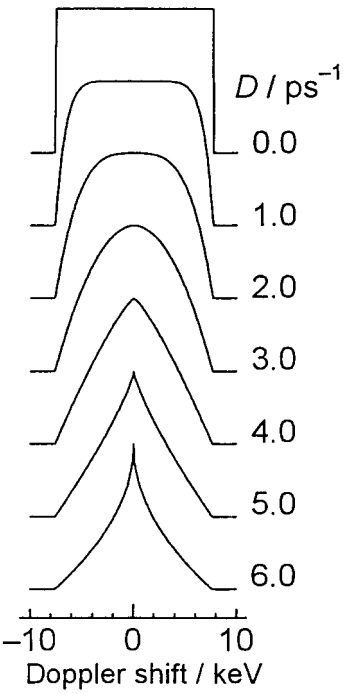

Figure 3. Lineshape dependence on degradation constant D for ^{7}*Li case. D's are 0.0, 1.0, 2.0, 3.0, 4.0, 5.0 and 6.0 ps^{-1} from top to bottom. Lineshape changes from upward concave (bell-shaped) curve to downward concave one as deceleration becomes faster. Instrumental response function is not convoluted.

semiconductor detector is to assume that a γ-ray line is observed as a Gaussian function on a background, which is a combination of a linear function and an arctan type function.[9]

Since in our case eq 12 is interpreted as continuously distributed Gaussian functions in the energy range ($-\Delta E_{max}$, $+\Delta E_{max}$), we can safely assume that the steep arctan type background jump is also distributed over the range and smeared out

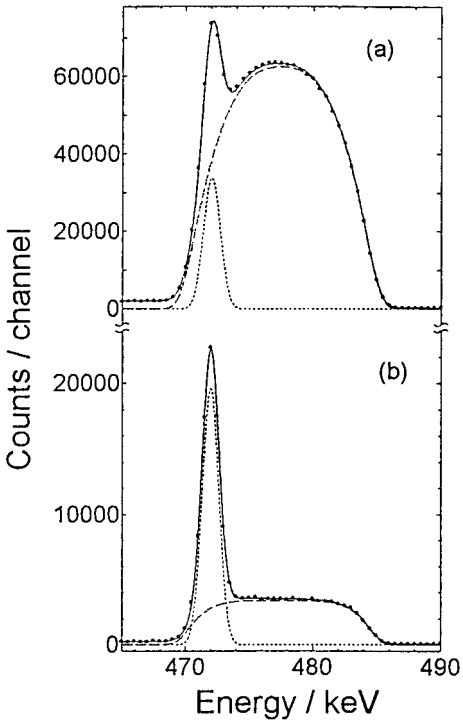

Figure 4. Decomposition of γ-ray spectra: (a) a mixture of elemental boron and Na_2CO_3; (b) a mixture of boric acid and Na_2CO_3. Filled circles are observed data, solid lines are fitted line, dotted Gaussian curves are 472keV γ-ray from ^{24}Na, dashed lines are Doppler broadened 478keV γ-ray from ^{7}*Li (eq 12). For elemental boron and boric acid $D = 2.54 \pm 0.02$ ps^{-1} and $D = 1.52 \pm 0.03$ ps^{-1} were obtained, respectively.

to become a linear gradual change. So we developed a computer code to fit a spectrum as a superposition of the function of eq 12 from ^{7}*Li, several Gaussian type peaks from nuclides other than ^{7}*Li and a background composed of three linear line segments. Decomposition examples are shown in Figure 4. Sharp γ-rays from ^{24}Na and broad lines from ^{7}*Li are clearly separated in both cases. The code also yielded degradation constants, 2.54 ± 0.02 ps^{-1} for elemental boron and 1.52 ± 0.03 ps^{-1} for boric acid, which are good agreement with those for pure substances obtained by using our previous analysis method.[3] The calculation times were less than a few minutes with a personal computer, which clearly proves the effectiveness of the code based on the formulation of the present study.

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