PHYSICAL REVIEW VOLUME 180, NUMBER 2 10 APRIL 1969

Interference of Electronic and Nuclear Resonance Absorption for Mössbauer $E1$ Gamma Rays*

G. T. TRAMMELL†
Physik-Department der Technischen Hochschule München, München, Germany

AND

J. P. HANNON
Physics Department, Rice University, Houston, Texas 77001

(Received 2 December 1968)

The large dispersion term in the absorption spectrum of the 6.25-keV Ta^{181} γ ray which was found by Sauer, Matthias, and Mössbauer is interpreted as arising from the interference between nuclear absorption followed by internal conversion and photoelectric absorption. The interference is large because the nuclear transition is $E1$.

I. INTRODUCTION

A LARGE "dispersion" term in the absorption spectrum of the 6.25-keV Ta^{181} Mössbauer line has been obtained by Sauer, Matthias, and Mössbauer.[1] Their measurements indicate that the average atomic cross section is given by

$$\sigma=[\sigma_0/(1+x^2)](1-2\xi x)+\sigma_e, \qquad (1)$$

where $2\xi\approx-0.16$. No such dispersion term has been noticed in previous Mössbauer absorption spectra.

In Eq. (1), σ_e represents the nonresonant contribution to the atomic cross section; $\sigma_0(1+x^2)^{-1}$, where x is the deviation of the energy of the incident γ ray from the resonance value in units of the half-width, represents the resonance nuclear absorption; and the term proportional to ξ represents the interference between resonant and nonresonant absorption.

The reason why the interference term is so large comes from the fact that the nuclear transition is $E1$ with a large internal conversion coefficient ($\alpha\approx50$). This leads to a large interference between nulcear absorption followed by internal conversion and photoelectric absorption by the atomic electrons (which in this energy region is also large and predominantly $E1$ in character). It is simple to establish (see below) that

$$\xi=\epsilon(\alpha\sigma_e'/6\pi\lambda\!\!\!^{-})^{1/2}\equiv\epsilon\xi_m \qquad (2)$$

represents the contribution of these interfering processes to ξ, where α is the internal conversion coefficient, λ is the wavelength of the incident γ ray, and σ_e' is the partial cross section for $E1$ photoelectric absorption ($\sigma_e'=\sigma_e$ to within a few percent for the cases which are considered). ϵ is a real number which has an absolute value somewhat less than one. It differs from one because both the internal conversion coefficient and σ_e' are the sum of squares of amplitudes for excitation of the atom to various final states (corresponding, e.g., to various atomic shells from which the electron may be ejected), whereas ξ is proportional to the sum of the products of these amplitudes [the expression for ξ is given in Eq. (15) of Ref. 2].

Inserting $\alpha\approx50$, $\sigma_e\approx10^5$ b,[3] $\lambda\!\!\!^{-}\approx\pi^{-1}$ Å, for the Ta^{181} 6.25-keV γ ray into the expression (2), we obtain $\xi_m\approx0.16$. The measured value of $\xi=-0.08$ gives $\epsilon\approx-0.5$, a not unreasonable result. The interference between the electronic Rayleigh scattering ($\sigma_R\approx4\times10^3$ b)[3] and the resonance nuclear scattering is somewhat less than $(\sigma_R/\alpha\sigma_e)^{1/2}\xi_m=0.03\ \xi_m$, and thus contributes only about 6% of the interference term.

For the two other $E1$ Mössbauer γ rays, the 26-keV Dy^{161} ($\alpha=2.5$, $\sigma_e\approx5\times10^3$ b, and $\lambda\approx0.5$ Å) and the 81-keV Gd^{155} ($\alpha=0.5$, $\sigma_e=5\times10^2$ b, and $\lambda=0.14$ Å) γ rays, which have been studied,[4] we obtain values of $2\xi_m=6\times10^{-2}$ and 3×10^{-2}, respectively. These represent interference terms only $\frac{1}{5}$ and $\frac{1}{10}$ as large as for Ta^{181}, and one cannot make a comparison between theory and experiment on the basis of the published data.

An interesting feature of (1) is that for $x<(2\xi)^{-1}$ (assuming $\xi<0$), the atomic cross section becomes less than that due to the electronic absorption alone, and the material becomes more transparent than it is far off resonance.

It is also of some interest that the rather large dispersion term in the total cross section implies an appreciable phase shift of the waves scattered by the nucleus because of induced electronic currents.[2] It follows from Ref. 2 or directly from the optical theorem that the atomic coherent elastic scattering amplitude will have the form

$$f=-f_N(1+2i\xi)(x+i)^{-1}+f_e, \qquad (3)$$

where in (3), f_N is the usual product of nuclear excitation and deexcitation matrix elements [see, for example,

---

* Research supported in part by the U. S. Department of Defense under Project THEMIS.

† On leave from Rice University, Houston, Texas.

[1] C. Sauer, E. Matthias, and R. L. Mössbauer, Phys. Rev. Letters 21, 961 (1968).

[2] J. P. Hannon and G. T. Trammell, Phys. Rev. Letters 21, 726 (1968).

[3] G. White-Grodstein, Natl. Bur. Std. (U.S.) Circ. 853, 1957 (unpublished).

[4] For data and references see A. H. Muir, Jr., K. J. Ando, and H. M. Coogan, in *Mössbauer Effect Data Index 1958–1965*, edited by Arthur H. Muir, Jr., K. J. Ando, and Helen M. Coogan (Wiley-Interscience, Inc., New York, 1966).

Eq. (19) of Ref. 2], and ξ represents the effect of the induced electronic currents. f_e represents the direct electronic contribution to the coherent scattering. The effect of the atomic electrons is to advance the phase of the resonance scattering amplitude by 2ξ. [What one may detect in a scattering experiment, however, is only the relative phase between the waves scattered by various systems, and for the case at hand we should notice that the phase of f_e differs significantly from π. We may take for f_e, $f_e=\hat{e}_f\cdot\hat{e}_0[-r_0F(\theta)+i\sigma_e/4\pi\bar{\lambda}]$, where $\hat{e}_f$ and $\hat{e}_0$ are the final and initial polarizations of the photon, r_0 is the classical radius of the electron, and $F(\theta)$ is the atomic form factor (we approximate the real part of the scattering amplitude by the Rayleigh scattering expression) and σ_e is, as in (1), the atomic cross section. Inserting $F(\theta)\approx 73$, $\sigma_e\approx 10^5$ b, $\lambda\approx 2$ Å we obtain $f_e=-2(1\text{-}0.1i)10^{-3}\hat{e}_f\cdot\hat{e}_0$ Å.]

II. THEORY AND DISCUSSION

In a previous paper[2] we discussed the dynamic effects of the atomic electrons (to second order in e^2) on the emission, absorption, and scattering of nuclear resonance radiation. From Eq. (26) of that paper we obtain for the average atomic absorption cross section involving an $E1$ transition

$$\begin{aligned}\sigma(\mathbf{k}_0,\hat{e}_0)=f\sum g(m_0,E(m_1)-E(m_0))(4\pi\bar{\lambda}_0)^2\\ \times|\hat{e}_0\cdot\mathbf{Y}_{1M}{}^{(1)}(\hat{k}_0)|^2\cdot|C(j_11j_0;\,m_1-Mm_0)|^2\\ \times[(1+\alpha)(1+x^2)]^{-1}(1-2\xi x)+\sigma_e.\quad(4)\end{aligned}$$

In (4), f is the Mössbauer factor, g is the probability that a given atom is originally in spin state with $J_z=m_0$, and with a (j_1,m_1), (j_0,m_0) energy difference $E(m_1)-E(m_0)$, $x=[\hbar ck_0-E(m_0)+E(m_1)]2/\Gamma$, and the other symbols have been previously defined. The summation is over m_0, m_1, M, and $E(m_1)-E(m_0)$ [the summation over $E(m_1)-E(m_0)$ is to allow for the possibility of different hyperfine and quadrupolar splittings for the atoms of the sample]. As pointed out in Sec. I, the term proportional to ξ gives the effect of the interference between conversion and photoelectric absorption. It is noteworthy that ξ is independent of $\hat{e}_0$, $\hat{k}_0$, j_1, m_1, j_0, and m_0 (so long as only closed atomic shells may be taken as contributing appreciably to the photoelectric absorption and internal conversion).

We obtain the expression for ξ_m as given in (2) as follows: If in internal conversion and in the photoelectron absorption the atom is left in the same state, then the total cross section takes the form

$$\sigma\approx(\sigma_0/1+x^2)[1+2x(\sigma_0'\sigma_e/\sigma_0^2)^{1/2}]+\sigma_e.\quad(5)$$

Here σ_0' is the partial cross section for the nucleus to have "internally converted" and returned to the same state m_0 from which it was initially excited:

$$\sigma_0'=\sigma_0\alpha(1+\alpha)^{-1}C^2(j_11j_0;\,m_1-Mm_0).$$

We must ensure that only a single M value [see Eq. (4)] is allowed for the incident photon; this may be achieved, e.g., if we take $\hat{e}_0\|\hat{z}$, $\hat{k}_0\perp\hat{z}$, in which case we have

$$\hat{e}_0\cdot\mathbf{Y}_{10}{}^{(1)}(\hat{k}_0)=\surd(3/8\pi),$$

$$\surd\sigma_0=4\pi\bar{\lambda}_0|\hat{e}_0\cdot\mathbf{Y}_{10}{}^{(1)}(\hat{k}_0)|C(j_11j_0;\,m_1-Mm_0)(1+\alpha)^{-1/2}.$$

Inserting these values into the formula $\xi_m=(\sigma_0'\sigma_e/\sigma_0^2)^{1/2}$, we obtain

$$\xi_m=(\alpha\sigma_e/6\pi\bar{\lambda}^2)^{1/2},\quad(6)$$

as in Eq. (2).

In Eq. (4) we may take

$$g=(2j_0+1)^{-1}g(E(m_1)-E(m_0)).$$

If we also consider unpolarized incident radiation and suppose that the absorber is unmagnetized, the factor $|\hat{e}_0\cdot\mathbf{Y}_{1M}{}^{(1)}(\hat{k}_0)|^2$ may be replaced by $\frac{1}{3}$. If, furthermore, the lines are unsplit, the function g becomes independent of m_1 and m_0, and the summation of the square of the Wigner coefficient over m_1, M, and m_0 gives a factor of $(2j_1+1)$. Making these replacements we obtain

$$\begin{aligned}\sigma(x)=\int g(y)\sigma_0[1+(x-y)^2]^{-1}\\ \times[1-2\xi(x-y)]dy+\sigma_e,\quad(7)\end{aligned}$$

where $\sigma_0=\frac{1}{3}(4\pi\bar{\lambda})^2(2j_1+1)/(2j_0+1)(1+\alpha)$, y is the deviation of the resonance energy from its average value (measured in natural half-widths), and x is the deviation of the energy of the incident γ ray from the average resonance energy, also measured in natural half-widths.

Now we have shown in this paper that we expect a dispersion curve of the form (1) for an unsplit line,[5] and that the value of ξ appearing in these formulas should be somewhat less than ξ_m which is given in (6) or (2). Furthermore, the value of ξ found by fitting the experimental data for the Ta^{181} 6.25-keV resonance to the form (1) was reasonably close to and less than ξ_m. However, the width of the experimental curve was some eleven times the natural linewidth. It now remains to be shown that if the experimental width is larger than the natural width, because of a range of environments of the resonant nuclei, then the value of ξ in Eq. (1) is still roughly that which we have estimated theoretically.

The width enhancement in the Ta^{181} experiment[1] was presumably due to a range of quadrupole splittings, arising from inhomogeneous distortions. Individual (quadrupole) lines were not resolved, but a small asymmetry in the absorption spectrum which may be taken to be indicative of an underlying unresolved quadrupole spectrum was observed.

We now approximate the experimental line shape by the form (7), taking $g(y)$ to have a range $\approx\pm a$, which

---

[5] Or, more generally, of the form (4) if the line is split and broadened by inhomogeneous environments of the resonant nuclei.

should then produce a "resonance curve" with a range $x \approx \pm(1+a)$. If for simplicity we take

$$g(y) = (a/\pi)(a^2+y^2)^{-1}, \tag{8}$$

and substitute in (7) we obtain

$$\sigma(x_a) = \sigma_0'(1+x_a^2)^{-1}(1-2\xi x_a)+\sigma_e, \tag{9}$$

where $\sigma_0' = \sigma_0/(1+a)$, $x_a = x/(1+a)$.

Finally, it goes without saying that the dispersion term does not appear in the emission spectrum of the source.

ACKNOWLEDGMENTS

The authors would like to thank C. Sauer, E. Matthias, and R. L. Mössbauer for an advance copy of their paper. One of us (GT) wishes to acknowledge most helpful discussions with C. Sauer and Dr. Mössbauer concerning the interpretation of their experiment.

PHYSICAL REVIEW VOLUME 180, NUMBER 2 10 APRIL 1969

Absorption Spectrum of NpO_2^{2+} in $Cs_2UO_2Cl_4$[†]

O. M. Stafsudd
Department of Engineering, University of California, Los Angeles, California 90024

and

A. F. Leung and Eugene Y. Wong
Department of Physics, University of California, Los Angeles, California 90024

(Received 30 September 1968)

The absorption spectrum of NpO_2^{2+} in $Cs_2UO_2Cl_4$ has been observed. Five pure electronic levels at 6880, 13 277, 15 426, 17 478, and 19 358 cm^{-1} have been identified through the vibronic transitions. The ground state and the energy level at 6880 cm^{-1} belong to the $5f^1$ configuration. However, the rest of the observed energy levels do not belong to the $5f^1$ configuration. Most likely, they come from an excited configuration which has a hole in the Np—O bond and two electrons in the nonbonding $5f$ shell.

INTRODUCTION

Some theoretical work on the energy levels of the NpO_2^{2+} ion was reported in detail by Eisenstein and Pryce in two papers.[1,2] They assumed that the low-lying energy levels came from the $5f^1$ configuration of the Np^{6+} ion, and the effect of the oxygens were treated as a strong crystal field with axial symmetry. The crystal field was parametrized and fitted to the experimental data. The experimental data were based on the EPR results by Bleaney and co-workers[3] and the optical spectra of NpO_2^{2+} in $HClO_4$ solution in the visible and infrared (IR) region by Waggener and others.[4–7] The EPR data seemed to be very reliable, but the optical spectrum showed only a few bands and the identification was rather doubtful. There were no experimental identifications of these bands because Zeeman or polarization effect was impossible in a solution. It was suggested by Eisenstein and Pryce that better spectra should be taken.

We follow their suggestion here. We have studied the absorption spectrum of NpO_2^{2+} doped in $Cs_2UO_2Cl_4$. The spectrum of the host $Cs_2UO_2Cl_4$ is well known and reported in detail by Dieke and Duncan.[8] There is no spectrum from 2000 to 20 000 cm^{-1}, and this provides a window for the spectrum of the NpO_2^{2+} complex ion. The crystal structure of $Cs_2UO_2Cl_4$ has been reported by Hall and co-workers.[9] It has a monoclinic lattice belonging to the space group C_{2h}^3. The cell dimensions are $a = 11.92$ Å, $b = 7.71$ Å, $c = 5.83$ Å, and $\beta = 99°40'$. There are two U^{6+} ions in the unit cell at (0,0,0) and $(0,\frac{1}{2},\frac{1}{2})$. These two U sites are identical and have C_{2h} point symmetry. There are four O^{2-} ions at site i with $x = 0.1168$, $y = 0.0$, and $z = 0.2198$. Each U^{6+} ion has two O^{2-} ions and four Cl^- ions as nearest and second nearest neighbors to form an approximate octahedral complex. The U-O distance is 1.81 Å and the U-Cl distance is 2.62 Å. The crystals always grow from the solution as twins and in the form of a needle plate. This is also reported by Nichols and Howes.[10] The (010) plane which contains the UO_2^{2+} axes was identified according to Nichols and Howes as the largest face of the crystal

---

[†] Research supported in part by grant from National Science Foundation, under Grant No. GP-6183.

[1] J. C. Eisenstein and M. H. L. Pryce, Proc. Roy. Soc. (London) **A229**, 20 (1955); **238**, 31 (1956).

[2] J. C. Eisenstein and M. H. L. Pryce, J. Res. Natl. Bur. Std. Std. (U. S.) **69A**, 217 (1965).

[3] B. Bleaney, P. M. Llewellyn, M. H. L. Pryce, and G. R. Gall, Phil. Mag. **45**, 992 (1954).

[4] R. H. Betts and B. G. Harvey, J. Chem. Phys. **16**, 1089 (1948).

[5] R. Sjoblom and J. C. Hindman, J. Am. Chem. Soc. **73**, 1744 (1951).

[6] L. H. Jones and R. A. Penneman, J. Chem. Phys. **21**, 542 (1953).

[7] W. C. Waggener, J. Phys. Chem. **62**, 382 (1958).

[8] G. H. Dieke and A. B. F. Duncan, Natl. Nucl. Energy Ser. Div. **III** (1949).

[9] D. Hall, A. D. Rae, and T. N. Waters, Acta Cryst. **20**, 160 (1966).

[10] E. L. Nichols and H. L. Howes, *Fluorescence of Uranyl Salts* (Carnegie Institute of Washington, 1919), p. 219.