the electron energy spectrum resulting from collisions of I⁻ with various noble gases. He observed the production of two groups of electrons—one at 2–3 eV and the second at 6–7 eV. The first group he attributes to the usual detachment process, while the second group he explains by assuming the existence of a highly excited, autodetaching state of the I⁻ ion. In addition, Cunningham and Edwards[9] have observed peaks in the energy spectrum of electrons emitted in collisions of Cl⁻ with helium. They have reported a prominent doublet peak at 9.99 and 9.88 eV, which they attribute to the autodetaching, doubly excited state $3p^4(^1D)4s^2\,^1D$, and a second weaker and broader peak at 12.04 eV associated with the state $3p^4(^1S)4s^2\,^1S$. In these ion-atom collisional excitations, it is, of course, not necessary for the autodetaching state to be optically connected to the ground state, as in the photodetachment case.

It should pointed out that this is the first direct spectroscopic observation of a negative-ion excited state. However, it would be interesting to verify independently the resonance reported here in an experiment of the Cunningham and Edwards[9] type for the iodine negative ion.

[1] R. S. Berry, T. Cernoch, M. Coplan, and J. J. Ewing, J. Chem. Phys. 49, 127 (1968).

[2] J. J. Ewing, R. M. Stein, and R. S. Berry, in Proceedings of the Seventh Shock Tube Symposium, Toronto, Canada, 1969 (unpublished).

[3] J. J. Ewing, R. Milstein, and R. S. Berry, J. Chem. Phys. 54, 1752 (1971).

[4] E. J. Robinson and S. Geltman, Phys. Rev. 153, 4 (1967).

[5] A. Mandl, Phys. Rev. A 3, 251 (1971).

[6] K. Codling and R. P. Madden, Phys. Rev. A 4, 2261 (1971).

[7] R. J. W. Henry, private communication.

[8] Yu. F. Bydin, Zh. Eksp. Teor. Fiz., Pis'ma Red. 6, 857 (1967) [JETP Lett. 6, 297 (1967)].

[9] D. L. Cunningham and A. K. Edwards, Bull. Amer. Phys. Soc. 17, 1137 (1972).

Absorber-Thickness Effect Versus Goldanskii-Karyagin Effect in ¹²¹Sb Mössbauer Quadrupole Patterns

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From a detailed analysis of the Mössbauer quadrupole spectra of Sb(CH₃)₃Br₂ measured using the 37.15-keV γ ray of ¹²¹Sb, it is shown that the large Goldanskii-Karyagin effect reported in this compound is not conclusive; the spectra are well accounted for by a transmission integral to include the absorber-thickness effects. Such an analysis also yields an $e^2q_{zz}Q$ in agreement with nuclear-quadrupole-resonance measurements.

With a few exceptions, the Goldanskii-Karyagin effect (GKE) has been reported mainly in the quadrupole patterns of the $\frac{1}{2} \to \frac{3}{2}$ Mössbauer transitions.[1] The intensities of the different hyperfine transitions in a quadrupole spectrum of a powder sample are affected to different extents because of anisotropic lattice vibrations. In a $\frac{1}{2} \to \frac{3}{2}$ Mössbauer transition, for example, an integral asymmetry is induced in the components of the quadrupole doublet of otherwise equal intensities. Recently, Stevens and Ruby[2] have reported

the Mössbauer spectra of the 37.15-keV ($\frac{5}{2} \to \frac{7}{2}$, $M1$) transition of ¹²¹Sb in a number of chemical systems of antimony with large quadrupole interactions. They observed deviations in the intensities of certain hyperfine components from those predicted by the Clebsch-Gordan coefficients and attributed this effect to the existence of a rather large GKE. The purpose of this Letter is (1) to point out that the above-mentioned intensity anomalies in the spectra of antimony compounds are *not* due to the GKE, but arise primarily from ab-
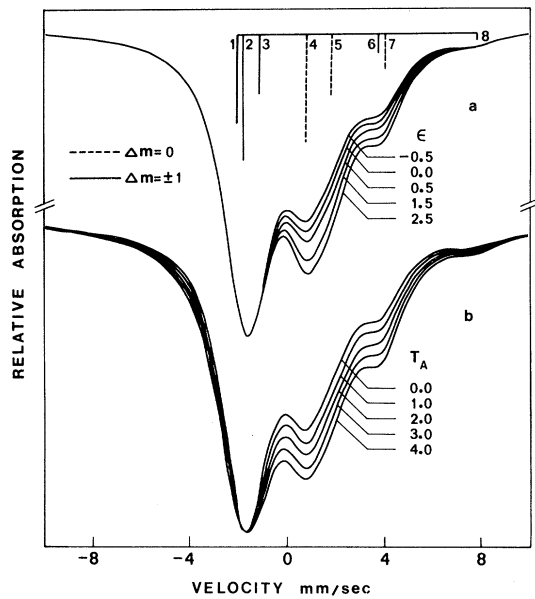
FIG. 1. Simulated Mössbauer spectra for $e^2 q_z Q = -20$ mm/sec and $\eta = 0$. In (a) the curves represent a sum-of-Lorentzians function for various values of the GKE parameter ϵ. In (b) the curves represent Eq. (2) for various absorber thicknesses T_A. In all the calculations the natural value of the linewidth is used.

sorber-thickness effects,[3] and (2) to demonstrate that the often-mentioned discrepancy[4] between nuclear-quadrupole-resonance and Mössbauer-resonance determinations of the quadrupole coupling constant disappears if the Mössbauer spectra are analyzed taking into account the absorber-thickness effects.

We shall consider *an axially symmetric* situation in describing the quadrupole pattern of [121]Sb. In Fig. 1(a) we have used a bar diagram to indi-

cate the line positions and their ideal intensities in a quadrupole pattern with $e^2 q_z Q = -20$ mm/sec. It has to be pointed out that *all* the $\Delta m = 0$ transitions are located in one region of the spectrum, and that all of them *do not* have the same angular distribution. In the presence of a GKE the Clebsch-Gordan intensities are modified by certain factors, which for a harmonic solid are written as[5]

$$
\begin{aligned}
I^0 &= \int_{-1}^{1}(1 - u^2)\exp(-\epsilon u^2)\,du, \\
I^1 &= \tfrac{1}{2}\int_{-1}^{1}(1 + u^2)\exp(-\epsilon u^2)\,du, \\
I^{1/2} &= \tfrac{1}{2}\int_{-1}^{1}(\tfrac{5}{3} - u^2)\exp(-\epsilon u^2)\,du.
\end{aligned}
\tag{1}
$$

Here I^0, I^1, and $I^{1/2}$ are the intensity-modifying factors for the $\Delta m = 0$, $\Delta m = \pm 1$, and $\Delta m = 0$ ($\pm \tfrac{1}{2} \to \pm \tfrac{1}{2}$) transitions, respectively; $u = \cos\theta$, and $\epsilon = (\langle z^2 \rangle - \langle x^2 \rangle)k^2$. The mean-square displacements parallel and perpendicular to the principal symmetry axis are denoted by $\langle z^2 \rangle$ and $\langle x^2 \rangle$, respectively, and k is the absolute value of the wave vector for the 37.15-keV γ radiation. When $\epsilon = 0$, the GKE vanishes and all the above factors become equal, so that the relative intensities of the components of a spectrum are described by the Clebsch-Gordan coefficients. To illustrate the influence of the GKE on the intensities of a [121]Sb quadrupole pattern, we have given in Fig. 1(a) spectra for different values of ϵ. All the $\Delta m = 0$ transitions have more intensity relative to the $\Delta m = \pm 1$ transitions for the positive values of ϵ (i.e., $\langle z^2 \rangle > \langle x^2 \rangle$).

In order to describe the influence of the absorber thickness on the quadrupole spectra of [121]Sb we use the formalism of Margulies and Ehrman.[3] The transmission integral for a single-line source and a split absorber is written as

$$
I(v) = I_0 \left\{ (1 - f_s) + \frac{f_s}{\pi} \int_{-\infty}^{\infty} \frac{(\Gamma_0/2)\,dE}{(E + vE_0/c)^2 + (\Gamma_0/2)^2} \exp\left[-\sum_k W(k) T_A \frac{(\Gamma_0/2)^2}{[E - E_A(k)]^2 + (\Gamma_0/2)^2} \right] \right\}.
\tag{2}
$$

Here, f_s is the resonance fraction for the source, Γ_0 is the full width at half-maximum, assumed to be the same for both the source and the absorber, $W(k)$ is the Clebsch-Gordan intensity for the kth line located at $E_A(k)$, $E_0 = 37.15$ keV, c is the velocity of light, v is the relative velocity between the source and the absorber, and T_A is the effective thickness of the absorber. We have numerically integrated this function[6] on a Univac 1108 computer for various values of T_A, and the calculated spectra are shown in Fig. 1(b). Comparing this with Fig. 1(a), one realizes that both the GKE and the absorber-thickness effects (ATE)

have similar influences on the shape of the spectra, and *an experimentally measured spectrum* (even with $T_A < 1$) could always be mistaken to provide evidence for the presence of GKE (with $\epsilon > 0$). Noteworthy is the fact that preferred orientation of the crystallites in the absorber, a situation often discussed in the case of $\tfrac{1}{2} \to \tfrac{3}{2}$ transitions,[7] can in an identical way interfere with any unique interpretation. In view of above remarks, we have taken unusual care[8] in all the experiments to avoid any preferred orientation and to produce absorbers of uniform thickness. In a
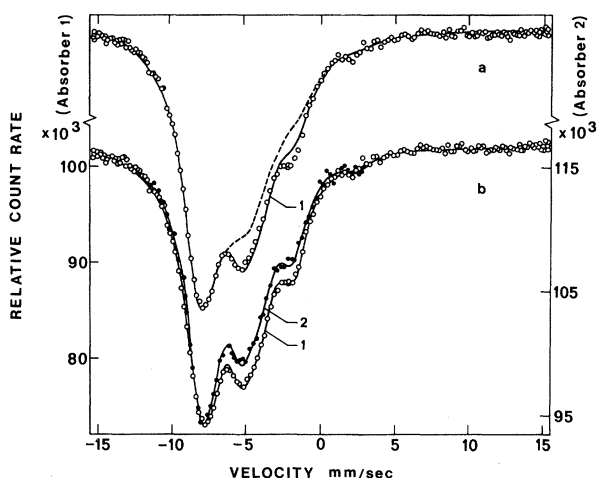
FIG. 2. Mössbauer spectra of $Sb(CH_3)_3Br_2$ against a $Ba^{121m}SnO_3$ source, both at 4.2 K, for two absorber thicknesses: (1) 12 mg/cm² and (2) 7 mg/cm² of Sb. In (a) the solid curve represents the SOL analysis including the GKE; the dashed curve, without the GKE. In (b) the data for the two absorbers are fitted by TI without any GKE.

few absorbers, the spectra were recorded every time after grinding the sample mixed with glass powder, and this procedure was repeated till they showed no noticeable change.

The spectra of $Sb(CH_3)_3Br_2$ were measured for two absorber thicknesses against a $Ba^{121m}SnO_3$ source, both at 4.2 K (Fig. 2). A further measurement was done at 77 K. In this compound, the Sb ions are located in the sites of axial symmetry (D_{3h}).[9] The dashed curve in Fig. 2(a) is the best fit obtained by assuming $T_A = 0$ and $\epsilon = 0$. The intensity anomalies in the neighborhood of the $\Delta m = 0$ transitions are identical to the ones reported earlier.[2] The solid curve in Fig. 2(a)

represents the analysis as a sum of Lorentzians including the GKE.[10] In Fig. 2(b) we give the data for two absorber thicknesses least-squares fitted with Eq. (2).[11] With the thinner absorber, the relative intensity of the peaks in the $\Delta m = 0$ region is reduced compared to those stronger absorption peaks corresponding to $\Delta m = 1$, as would be expected from saturation effects. Thus it is clear that the major contribution to the excess intensities arises out of the ATE rather than the GKE. The results of the different analyses with and without the ATE and the GKE are given in Table I.

We note from Table I that the intensity discrepancies that come up in the analysis of the spectra as a sum of Lorentzians are rather easily accounted for by Eq. (2), and the GKE appears to be very small if not zero. We would like to make the following additional remarks:

(1) The value of χ^2, the goodness-of-fit parameter, improves significantly between the fit with $T_A = 0$, $\epsilon \neq 0$ and the one with $T_A \neq 0$, $\epsilon = 0$. Inclusion of T_A increases, in particular, the intensities of both the transitions 6 and 7 [Fig. 1(a)], while the presence of GKE would only increase (or decrease) the intensity of transition 7 relative to that of 6. This can clearly be seen by comparing the experimental data with the best fit considering only the GKE in Fig. 2(a).

(2) The ratio of the absorber thicknesses yielded by the analysis that assumes $T_A \neq 0$ and $\epsilon = 0$ (Table I) for the two absorbers is in good agreement with the ratio of the weights of material used in these absorbers.

(3) The value of ϵ deduced for the two absorber thicknesses in the analysis with $T_A = 0$ and $\epsilon \neq 0$ (Table I) would yield ($\langle z^2 \rangle - \langle x^2 \rangle$) of the order of 10^{-2} Å². This is physically unreasonable at 4.2

TABLE I. Results of the sum-of-Lorentzians (SOL) and the transmission-integral (TI) analysis for two different thicknesses of $Sb(CH_3)_3Br_2$ measured at 4.2 K.

Thickness (mg/cm² of Sb)	Analysis	$e^2 q_z Q$ (mm/sec)	IS [a] (mm/sec)	ϵ	T_A	χ^2 [b]
7	SOL	−22.07(38)	−5.96(4)	⋯	⋯	1.77
7	SOL	−21.86(30)	−6.11(4)	1.67(17)	⋯	1.02
7	TI	−21.42(24)	−6.12(4)	⋯	3.5(5)	1.00
7	TI	−21.43(26)	−6.12(4)	−0.01(20)	3.4(5)	0.99
12	SOL	−22.52(22)	−5.87(3)	⋯	⋯	7.19
12	SOL	−22.27(20)	−6.10(3)	3.06(14)	⋯	1.85
12	TI	−21.43(15)	−6.11(4)	⋯	5.6(4)	1.24
12	TI	−21.44(15)	−6.12(3)	0.29(20)	5.3(4)	1.21

[a] Relative to a $Ba^{121m}SnO_3$ source.   [b] Per degree of freedom.

K, especially in view of the fact that the antimony compounds we are concerned with in this Letter are not polymers.[8] Furthermore the two values of ϵ thus deduced differ considerably, which reveals the weakness of the GKE analysis.

(4) We notice that the quadrupole coupling constant yielded by the TI analysis is smaller by about 3% than that obtained from a SOL analysis (Table I). The TI value for e^2q_zQ at 77 K is $-20.89(40)$ mm/sec. With the usual temperature dependence of e^2q_zQ observed in such compounds, these results are in good agreement with the nuclear-quadrupole-resonance value of 20.02 mm/sec reported at 300 K.[9] The ratio of the nuclear quadrupole moments of the $\frac{7}{2}$ and the $\frac{5}{2}$ levels in ^{121}Sb agrees well with the previous determination (1.34 ± 0.01).[2]

In conclusion we would like to express our concern regarding the analysis of Mössbauer spectra without accounting for T_A when the components are unresolved. In addition to ^{121}Sb, similar situations also arise in ^{127}I and ^{151}Eu. An analysis to correct for the exponential absorption would help to report more reliable hyperfine interaction parameters[12] and avoid predicting physically unreasonable effects.

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[1]V. I. Goldanskii, E. F. Makarov, and V. V. Khrapov, Phys. Lett. 3, 344 (1963); S. V. Kariagin, Dokl. Akad. Nauk SSSR 148, 1102 (1963); I. P. Suzdalev and E. F. Makarov, in *Proceedings of the Conference on the Application of the Mössbauer Effect, Tihany, Hungary, June 1969*, edited by I. Dézsi (Akademiai Kiado, Budapest, 1971), p. 201.

[2]J. G. Stevens and S. L. Ruby, Phys. Lett. 32A, 91 (1970).

[3]S. Margulies and J. R. Ehrman, Nucl. Instrum. Methods 12, 131 (1961).

[4]J. G. Stevens and L. H. Bowen, in *Mössbauer Effect Methodology*, edited by I. J. Gruverman (Plenum, New York, 1970), Vol. 5, p. 27; G. G. Long, J. G. Stevens, R. J. Tullbane, and L. H. Bowen, J. Amer. Chem. Soc. 92, 4230 (1970).

[5]M. Pasternak and T. Sonnino, J. Chem. Phys. 48, 2004 (1968).

[6]G. K. Shenoy and J. M. Friedt, to be published.

[7]H. D. Pfannes and U. Gonser, Appl. Phys. 1, 93 (1973).

[8]R. H. Herber and S. Chandra, J. Chem. Phys. 52, 6045 (1970).

[9]T. B. Brill and G. G. Long, Inorg. Chem. 9, 1980 (1970).

[10]It appears that in a similar analysis in Ref. 2, different angular distributions of the $\Delta m = 0$ transitions were not considered.

[11]The time required for the fitting is of the order of 15 min for a spectrum with 200 data points.

[12]E. Gerdau, W. Räth, and H. Winkler, Z. Phys. 257, 29 (1972).

Observation of Self-Steepening of Optical Pulses with Possible Shock Formation

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Near-resonant light pulses were steepened by passage through Rb vapor. The rise time changed from typically 4 nsec to less than 1 nsec, and complicated envelopes developed. The self-steepening, well described by adiabatic following, results from (i) an intensity-dependent pulse velocity, (ii) self-phase modulation combined with strong group-velocity dispersion. Numerical integration gives quantitative agreement with observations and indicates shock formation on the leading edge.

The possibility of observing self-steepening of optical pulses and the formation of shocks has been extensively discussed.[1-9] An early problem was that of pulse propagation in a medium with an intensity-dependent refractive index but no dispersion.[2,3] The resulting pulse reshaping is entirely caused by the intensity-dependent pulse velocity. This steepening effect has remained unobserved because either the propagation distances and input powers required are unattainable, or

dispersion cannot be rightly neglected. With dispersion included in the analysis,[1,4,7,8] self-steepening was predicted to occur over much shorter distances. It is then mainly caused by self-phase modulation, which modifies the instantaneous frequency along the pulse, thereby producing reshaping due to group-velocity dispersion. Even though the conditions required to observe this type of self-steepening are more favorable, experimental verification has not been obtained.