PHYSICAL REVIEW VOLUME 164, NUMBER 2 10 DECEMBER 1967

# Mössbauer-Effect Studies on $Kr^{83}$ in Bromide and Bromate Crystals

M. PASTERNAK AND T. SONNINO
*Nuclear Physics Department, Soreq Nuclear Research Centre, Israel Atomic Energy Commission, Yavne, Israel*

(Received 19 April 1967)

Mössbauer-effect studies have been performed using $Kr^{83}$ sources produced by the $\beta^-$ decay of $Br^{83}$ ($T_{1/2}=2.4$h) in various bromine compounds. Experiments were done with LiBr, NaBr, KBr, CsBr, $NH_4Br$, $KBrO_3$, and Kr-$\beta$-hydroquinone sources at 90°K using solid krypton absorber at 22°K. No isomer shift was observed for any of the sources, indicating that the Kr outer configuration is not perturbed by the induced dipole interaction with its neighbors. No "$KrO_3$" species was detected as a result of the $\beta^-$ decay of Br in $KBrO_3$. Broad and symmetric emission lines were observed for the Kr-hydroquinone, the bromides, and the bromate, increasing in broadening in that order. This broadening has been explained on the basis of the formation of a local distorted crystalline field, as a consequence of the internal-conversion process of $Kr^{83m}$. From the fact that a symmetric line is observed, it has been concluded that at least two modes of distortion are formed in such a way as to produce opposite signs of the electric field gradient. The Debye temperature calculated for the alkali-bromide sources was found to be 60°K in average, and for that of $HN_4Br$ a value of 90°K was derived. The techniques of source preparation and of the krypton absorber deposition are described.

## INTRODUCTION

THE Mössbauer effect (M.E.) with the 9.3-keV ($T_{1/2}=147\times10^{-9}$ sec) level of $Kr^{83}$ was first observed by Hazony *et al.*[1] with both source and absorber of krypton-$\beta$-hydroquinone clathrate. Recently, measurements on this nuclide were made with a $KrF_2$ absorber and a $Rb^{83}Cl$ source,[2] and with a solid krypton absorber and a clathrate source.[3]

The 9.3-keV level is directly populated by the internally converted $Kr^{83m}$ ($T_{1/2}=1.86$ h) decay[4] (see Fig. 1). This metastable state can be formed by one of the following processes: (a) pile ($n$, $\gamma$) irradiation of $Kr^{82}$ (11% natural abundance); (b) electron-capture decay of $Rb^{83}$ ($T_{1/2}=83$ d), in which a small fraction decays directly to the 9.3-keV level[5]; (c) $\beta$ decay of $Br^{83}$ ($T_{1/2}=2.4$ h).[6] This work deals with studies performed with sources produced by the last process.

The two main motivations for the present research were: (a) to learn about the influence of the environment on the Kr atom situated at $Br^-$ positions in various alkali-bromide crystals. Mössbauer-effect studies with such sources against solid krypton absorbers could tell us directly about the effect of the electrostatic perturbation on the krypton ground-state electronic configuration, the origin of which is the induced dipole interaction produced by the alkali-bromide-Kr system on the Kr atoms. Configuration changes of the outer Kr shell would be directly revealed through the isomer shift. The 9.3-keV natural linewidth ($2\Gamma=0.2$ mm/sec)[4] and the relatively large value[2] of $\Delta R/R$ ($=4\times10^{-4}$) are extremely favorable to the detection of very slight changes in $|\psi_s(0)|$.[2] Since the Kr atom sits in a cubic symmetry environment, we were expecting narrow emission lines and no appreciable distortions due to the slight change of the $Br^-$-ion radius ($r=1.95$ A[7]) to the atomic Kr ($r=1.98$°A [8]) one;

(b) to investigate whether "$KrO_3$" species could be formed from the $\beta^-$ decay of $Br^{83}$ in $(BrO_3)^-$. Since the Br atom is in a relatively high ionic state, a $KrO_3$ molecule might be produced as in the case of the isomorphous $(I^{129}O_3)^-$ ion decay to $Xe^{129}O_3$,[9] in which case a quadrupole split spectrum would be observed.

## 1. EXPERIMENTAL PROCEDURE

### Source Preparation

Natural $SeO_2$ was irradiated for a period of 0.5 to 1 h in a flux of $2\times10^{13}$ $n$ cm$^{-2}$ sec$^{-2}$ in the Soreq research reactor IRR-I. Radioisotopes of Se are produced which then decay to Br isotopes.

By proper chemical separation one can extract only the bromine isotopes, namely, $Br^{79}$, $Br^{81}$, and $Br^{83}$, the first two being stable. The following procedure was carried out[10]: The radioactive $SeO_2$ was dissolved in $HNO_3$ and 1–2 mg of $BrO_3^-$ and $Br^-$ were added to "milk" the bromine out in the form of $Br_2$. The vessel was heated up to 70°C and a slow stream of air allowed to bubble through the solution to carry out the $Br_2$

---

[1] Y. Hazony, P. Hillman, M. Pasternak, and S. Ruby, Phys. Letters **2**, 337 (1962).

[2] S. L. Ruby and H. Selig. Phys. Rev. **147**, 349 (1966).

[3] M. Pasternak, A. Simopoulos, S. Bukshpan, and T. Sonnino, Phys. Letters **22**, 52 (1966).

[4] S. L. Ruby, Y. Hazony, and M. Pasternak, Phys. Rev. **129**, 826 (1963).

[5] I. Dostrovsky, S. Katcoff, and R. W. Stoermer, Phys. Rev. **136**, B44 (1964).

[6] M. Pasternak and T. Sonnino, Nucl. Phys. **45**, 336(1963).

[7] L. Pauling, *Nature of the Chemical Bond and the Structure of Molecules and Crystals: an Introduction to Modern Structural Chemistry* (Cornell University Press, Ithaca, New York), 3rd ed., p. 521.

[8] This value refers to the crystal-lattice radius [*Argon Helium and the Rare Gases*, edited by G. A. Cook (Interscience Publishers, Inc., New York, 1961), p. 13].

[9] G. J. Perlow and M. R. Perlow, Rev. Mod. Phys. **36**, 353 (1964).

[10] T. Sonnino and M. Pasternak, Intern. J. Appl. Radiation Isotopes (to be published).

gas to a receiver kept at ice temperature. To produce alkali bromide, the proper stoichiometric quantity of hydroxide was placed in the receiver and reduced with $H_2O_2$. To prepare $BrO_3^-$ a stream of $Cl_2$ was passed through the receiver to oxidize the $Br_2$. After drying, the source was encapsulated in a lucite holder and cooled to liquid-nitrogen temperature. The activity of $Br^{83}$ depended on the Se mass and the neutron flux. For instance, 100-mg Se irradiated for 1 h produced a total activity of the 9.3-keV x ray of $3\times10^8$ disintegrations per sec (d.p.s.). We found that the chemical extraction efficiency was very high. One should bear in mind that the high activity is necessary for M.E. spectroscopy with $Kr^{83}$ mainly because of the high absorption of the 9.3-keV level and the high background of its $K$ x rays, and, in our case, the relatively short working period of 6–7 h. The sources produced in this way have advantages over the $Rb^{83}$ and $Kr^{83m}$ sources for the following reasons: (a) Higher specific activities can be produced. (b) The electron-capture decay of $Rb^{83}$ results in high-activity $K$ x rays, which severely interfere with the relevant $\gamma$ rays. Also, as a result of the $Rb^{83}$ production method $[Br^{81}(\alpha, 2n)Rb^{83}]$, the isotope $Rb^{84}$ ($T_{1/2}=33$ d) is formed by the reaction $Br^{83}(\alpha, n)Rb^{84}$. This isotope contributes to the x-ray background. (c) No resonant self-absorption is present in the source as in the $Kr^{83m}$ case. The intense $\beta^-$ rays in $Br^{83}$ decay are reduced with a beryllium window. A typical case of $Kr^{83m}$ activity growing from $Br^{83}$ is shown in Fig. 2. From the activity-time behavior of the 9.3 keV, we found that no $Kr^{83m}$ escapes from the bromide and bromate samples at room or liquid-nitrogen temperature. For some experiments, clathrate sources were used and their preparation details are described elsewhere.[3]

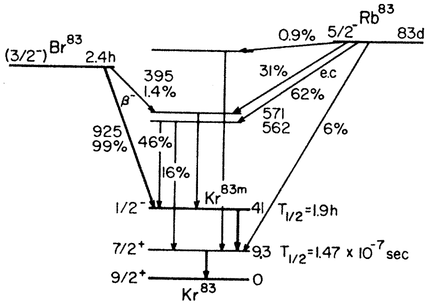


FIG. 1. Decay scheme of $Kr^{83}$, $Br^{83}$, and $Rb^{83}$ as from Ref. 4–6.

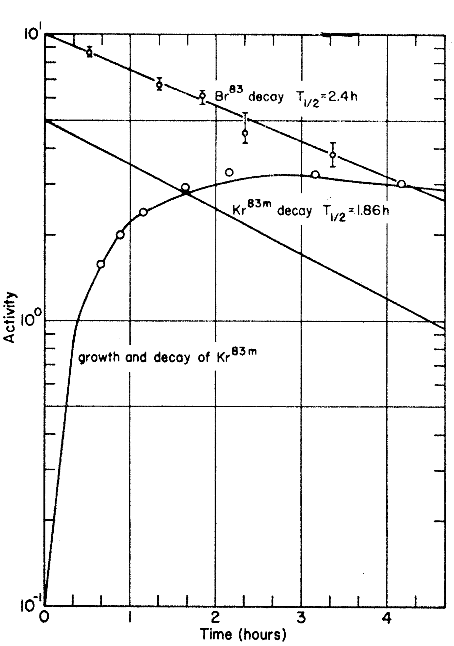


FIG. 2. Growth and decay of $Kr^{83m}$.

## Absorbers and Radiation Detection

The absorbers used in the present investigation were solid krypton and $\beta$-hydroquinone clathrates. The solid krypton absorber was produced by slow injection of gas onto an aluminum backing of 3-mg/cm² thickness kept at 22°K. In this way a uniform krypton layer was formed. Under optimum conditions the efficiency of deposition was found to be 80%. The thickness of the krypton layer was measured by the absorption of the 6.3-keV $K$ x rays of a $Co^{57}$ source.[11] The clathrate absorbers were prepared by mixing pulverized clathrate with sugar.

An argon-methane proportional-flow counter was used to detect the radiation emitted from the $Br^{83}$-$Kr^{83m}$ source. A typical spectrum, indicating the single-channel setting, is shown in Fig. 3. The background contribution to the 9.3-keV peak consisted of the following parts:

(a) the continuous radiation mainly from the bremsstrahlung of the $Br^{83}$. This was greatly reduced by inserting a 3-mm-thick beryllium window between the source and the absorber. This background depends strongly on the $Z$ of the alkali. For LiBr sources the fraction of the counts in the single-channel window was 12%, while for CsBr it reached 17%;

(b) the 12.6-keV escape peak which appears at 9.4 keV. The value of the background fraction due to

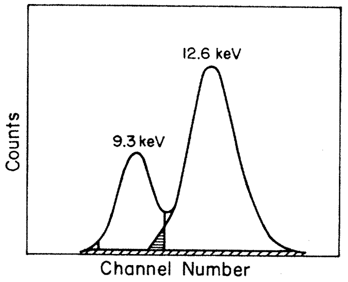
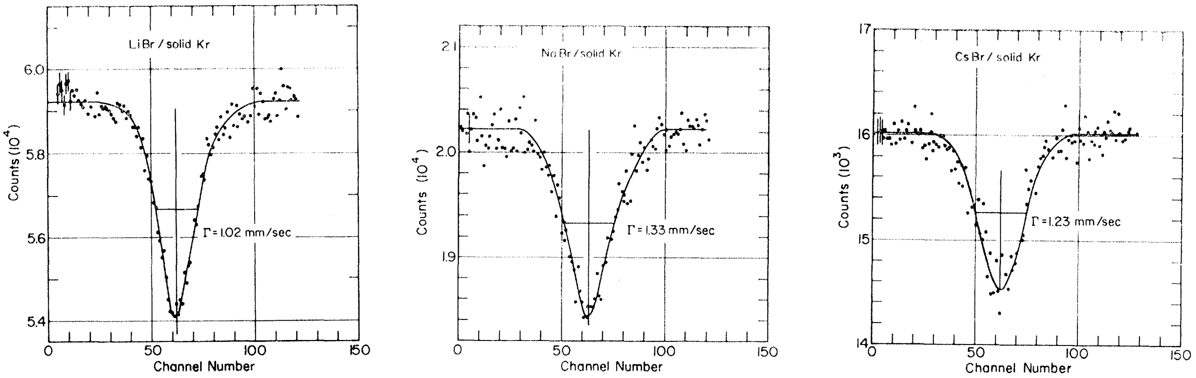


FIG. 3. The energy spectrum of $Kr^{83m}$. The 9.3-keV line is the Mössbauer transition, that of 12.6 keV is the characteristic $K$ x ray of Kr. The position of the single-channel settings are indicated.

---

[11] P. F. Berry, Nucleonics, 19, 62, (1961).



(a) (b) (c)

FIG. 4. Typical Mössbauer spectra of (a) LiBr, (b) NaBr, and CsBr (c), sources against solid Kr absorber.

this effect was evaluated using an "old" Kr source which emitted solely x rays. We found for our counter a value 7.5% of the total 12.6-keV radiation, giving in most cases 30% of the total background;

(c) the 12.6-keV tail interference. The total background was typically 50% of the counting rate. The spectra were measured at the beginning and end of each run and the corrections for background were weighted averages of the backgrounds derived from these data.

## 2. RESULTS AND ANALYSIS OF DATA

### Bromide Sources

Typical absorption spectra for LiBr, NaBr, and CsBr sources and solid krypton absorber are shown in Fig. 4. The isomer shifts (i.s.) for all the sources were found to be zero within the experimental error. The linewidths observed ($\Gamma_{\text{obs}}$) are more than 10 times the natural linewidth ($\Gamma_{\text{nat}}=0.10$ mm/sec) and symmetrical around zero velocity. No effect is observed which could be interpreted as a static quadrupole splitting. The data were analyzed assuming that (a) the line shape is Lorentzian and (b) the krypton absorber has a natural linewidth at zero thickness. This last assumption is supported by the data of Ruby and Selig[12] and by the results of the following section. The linewidths $\Gamma_s$ of the bromide sources were calculated using the following expression[13]:

$$\Gamma_{\text{obs}}=\Gamma_s+\Gamma_a\ (1+0.27T_a), \tag{1}$$

where $T_a=f_a t_a \sigma_0 n_a$, with $f_a$ the recoilless fraction for the absorber, $t_a$ the absorber thickness, $\sigma_0$ the absorption cross section, and $n_a$ the number of $Kr^{83}$ atoms per cm$^3$. The value of $f_a(=0.50)$ for solid Kr at $T=22$°K was calculated from the $\Theta_D=37$°K obtained in a previous experiment.[3] The values of $\Gamma_s$ are given in Table I.

The absolute source recoilless fraction $f_s$ was calculated by applying the formula derived by O'Connor[13] for the absorption depth $R_m$:

$$R_m=f_s\frac{(1+k)\Gamma_a}{\Gamma_s+\Gamma_a k}F(T_a), \tag{2}$$

where $F(T_a)=1-[\exp(-T_a/2)J_0(iT_a/2)]$ and $k$ depends on the effective thickness $T_a$. The absorber thickness $t_a$ was $1.4\pm0.1$ mg/cm$^2$ of $Kr^{83}$. Because of the high $\sigma_0$, uncertainty in 20% in the $f_a$ will result in an error of 2% in $F(T_a)$, therefore in $f_s$. The values of $f_s$ for all the bromide sources are given in Table I.

### Determination of Kr-Clathrate Linewidth and Absolute Effect

A series of experiments was performed with Kr-clathrates (Kr–Clt) source, absorber, and solid krypton absorber. The purposes of these measurements were: (1) to determine whether the broadening observed in Kr-clathrates experiments[1,3] is intrinsic to both source and absorber or only to the source and (2) to determine the Kr–Clt source linewidth and its absolute effect. The starting assumption was that solid krypton at $T_a=0$ exhibits the natural linewidth. The results of $\Gamma_{\text{obs}}/\Gamma_{\text{nat}}$ and $R_m$ as a function of $T_a/f_a$ of solid krypton is shown in Fig. 5.

TABLE I. Experimental linewidth and absorption depth for the various sources at 90°K and solid krypton absorber (1.4 mg/cm$^2$Kr$^{83}$) at 22°K. The source linewidth $\Gamma_s$ was computed for $T_a=0$ under the assumption that emission and absorption spectra are Lorentzian. The value of $\Gamma_s$ of the clathrate source in parenthesis is for infinitely thin source ($T_s=0$).

| Source | $\Gamma_{\text{obs}}/\Gamma_{\text{nat}}$ | Computed $\Gamma_s$ | $R_m$(%) | $f_s$ |
|---|---|---|---|---|
| LiBr | 10.2±0.5 | 6.5±0.5 | 17.3±0.5 | 0.32±0.03 |
| NaBr | 13.3±0.5 | 9.6±0.5 | 17.9±0.5 | 0.44±0.04 |
| KBr | 11.2±0.5 | 7.5±0.5 | 17.6±0.5 | 0.36±0.04 |
| CsBr | 12.3±0.5 | 8.6±0.5 | 18.8±0.5 | 0.42±0.04 |
| $NH_4Br$ | 12.4±0.5 | 8.7±0.5 | 30.0±1 | 0.68±0.04 |
| Kr clathrate | 8.8±0.4 | 6.1±0.2<br>(3.4±0.3) | ... | 0.52±0.04 |
| $KBrO_3$ | 19.0±1.0 | 16±1 | ... | ... |

---

[12] S. L. Ruby and H. Selig, Argonne National Laboratory Report No. ANL-7108, p. 17 (unpublished).

[13] O. D. A. O'Connor, Nucl. Instr. Methods 21, 318 (1963).

From a graphical extrapolation at $T=0$, we found that $\Gamma_{\mathrm{obs}}=(7.0\pm0.5)\Gamma_{\mathrm{nat}}$. Assuming, (as stated before) that the absorption curve has a Lorentzian shape, we then found that the Kr–Clt linewidth for a source with $t_s=0.6$ mg/cm$^2$ of $Kr^{83}$ at $T=80°K$ has an emission linewidth of $(6.0\pm0.5)\Gamma_{\mathrm{nat}}$. We note that (a) a fitting of expression (1) to the experimental results was not successful, and it seems that the Kr–Clt source has a mixture of Gaussian and Lorentzian distribution; and (b) if $\Gamma_s=\Gamma_a$, the slope of $\Gamma_{\mathrm{obs}}/\Gamma_{\mathrm{nat}}$ wound be larger than that observed, indicating that the broadening in the solid krypton absorber is significantly less than in the source.

From experiments with "thick" solid krypton absorbers, we calculated the absolute "effective" recoilless fraction $\phi_s$ of the Kr–Clt source. This effective fraction is less than the absolute $f_s$, due to the fact that the source exhibits a self-resonant absorption. The fraction $\phi_s$ is a function of the effective source-resonant thickness $T_s$, and of the electronic absorption $\mu_s t_s$.[14] For a Kr–Clt source at 90°K with 0.6 mg/cm of $Kr^{83}$, we found $\phi_s(\leq f_s)=0.53\pm0.05$. With this value of $\phi_s$, we were able to extrapolate the contribution of the self-absorption to the broadening. The intrinsic linewidth $\Gamma_s$ of Kr–Clt was found to be

$$\Gamma_s=(3.4\pm0.3)\Gamma_{\mathrm{nat}}. \tag{3}$$

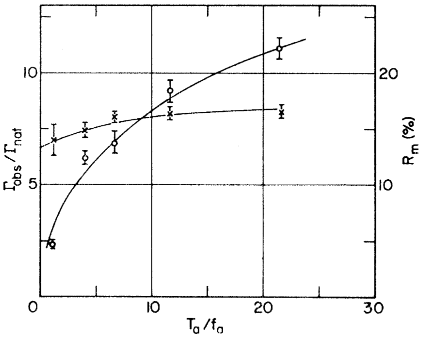


FIG. 5. Dependence of observed linewidth at half-maximum $\Gamma_{\mathrm{obs}}/\Gamma_{\mathrm{nat}}$ (×left scale) and of the absorption depth at zero velocity *Rm* (o right scale) for Kr β-hydroquinone source ($T_s=4.1$) on increasing thickness of solid Kr absorber.

An experiment done with a Kr–Clt source and absorber ($t_a=1.18$ mg/cm$^2$ of $Kr^{83}$) at 90°K revealed a linewidth (see Fig. 6) of 0.89±0.03 mm/sec. By inserting the value calculated for $\phi_s$, we find that the absorber linewidth resulted solely from the resonant self-absorption. The conclusion is that an intrinsic broadening exists in a Kr–Clt source and is absent in the absorber.

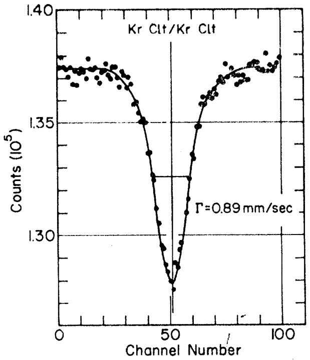


FIG. 6. The Mössbauer spectrum of Kr-β hydroquinone clathrate source ($T_s=4.1$) against Kr-β hydroquinone clathrate absorber ($T_a=7.3$).

### Bromate Source

The spectrum of $Kr^{83}$ embedded in $KBrO_3$ by using a Kr-clathrate absorber is shown in Fig. 7(a). In the same figure (c) we indicate the line positions calculated on the assumption that a $KrO_3$ species forms as a result of the $Br^{83}$ decay. In that case we assumed the electric field gradient (e.f.g.) to be the same as for $BrO_3^-$, and used the ratio $Q(7/2)/Q(9/2)$ found by Ref. 2. The broad line ($\Gamma_{\mathrm{obs}}=0.19$ cm/sec) does not show any sign of a split spectrum.

## 3. DISCUSSION

### The Bromate Decay

From the fact that no quadrupole splitting is observed with the bromate source, we conclude that a

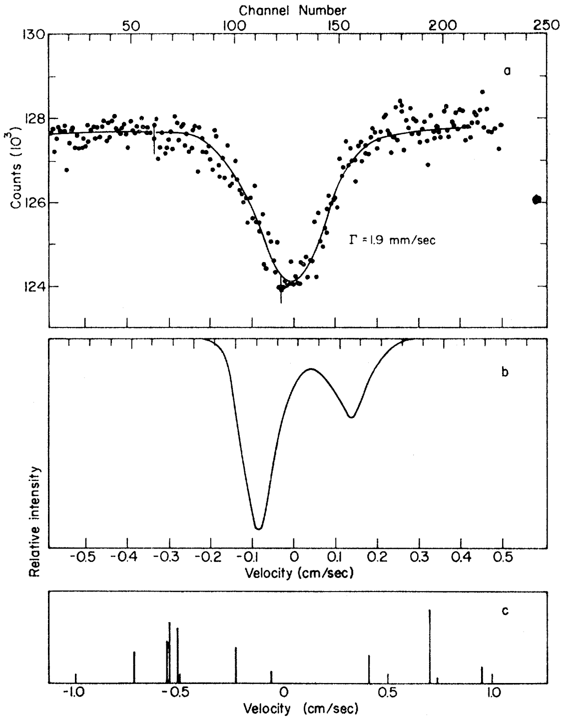


FIG. 7. (a) The Mössbauer spectrum of a $KBrO_3$ source against β hydroquinone clathrate absorber. (b) The computed spectrum assuming a static $e^2qQ$ of 38.4 Mc/sec. (c) Line position and intensity for $KBrO_3$ assuming that the hypothetical $KrO_3$ had the same e.f.g. as $KBrO_3$.

---

[14] S. Margulies and J. R. Ehrman, Nucl. Instr. Methods **12**, 131 (1961).

TABLE II. The calculated values of $(B^p)^2$ summed over all nearest and next-nearest neighbors of Kr in the various alkali-bromide lattices. The numbers in parentheses are the values calculated for the iodine ion in Ref. 14.

| Source | $(B^p)^2$ |
|---|---|
| LiBr | 0.048 (0.093) |
| NaBr | 0.034 (0.066) |
| KBr | 0.020 (0.054) |
| CsBr | 0.042 (0.066) |

“$KrO_3$” species does not exist, at least within the $Kr^{83m}$ lifetime (1.9 h). The broad line observed cannot be attributed to any static quadrupole splitting, since, in such a case, because of the $\frac{7}{2}\rightarrow\frac{9}{2}$ transition, one would observe an asymmetric shape as shown in Fig. 7(b). This spectrum has been constructed using $\Gamma_a=3\Gamma_{\mathrm{nat}}$ absorber linewidth. The fact that no isomer shift is observed also proves that the Kr electronic shell is unaffected by the oxygen neighbors. In the case of the $(I^{129}O_3)^-$ decay to $Xe^{129}O_3$, a quadrupole splitting has been observed[9] indicating the existence of the $XeO_3$ molecule. We should mention that this case differs from ours, since the $I^{129}$ decays straight to the Mössbauer level of $Xe^{129}$ ($T_{1/2}=9.6\times10^{-10}$ sec), while in the $Br^{83}$ case the decay to the Mössbauer level is through the metastable state ($T_{1/2}=1.9$ h). It is of course possible that within this time the Kr ion, formerly in a high-valence state, disappears and is transformed into a neutral atom.

### The Bromide Decay

The zero isomer shift of all the bromide sources shows that, as a result of the $Br^-$ nuclear transformation, the Kr atom attains the same atomic configuration as when it is situated in the solid krypton. However, by virtue of the binding potential imposed at the krypton atom by its neighbors, the alkalis and the bromide ions, one could expect changes in $|\psi_s(0)|^2$. Flygare and Hafemeister,[15] on dealing with the various mechanisms responsible for the isomer shift of the iodine in alkali-iodide crystals, proposed that, besides deformation of the $\psi_s$ function due to overlapping, the $s$-electron density at the nucleus is altered because the outer-shell $p$ electrons are depleted by excitation due to induced-dipole interaction. In our case, we may expect that the first factor, overlap deformation of the Kr outer closed shell, does not exist. However, the second factor which arises as a result of interaction between the induced dipole in the Kr and the induced dipole in the bromine and the alkalis is not negligible, at least in comparison with the iodine cases.

The probability of exciting the outer $np$ electrons in the Kr atom to the $(n+1)s$ empty state is given by[15,16]

$$(B_{\mathrm{Kr:Br}}{}^{p})^2=3\alpha_{\mathrm{Kr}}\alpha_{\mathrm{Br}}\epsilon_{\mathrm{Kr}}\epsilon_{\mathrm{Br}}[2r_{\mathrm{Kr:Br}}{}^{6}(\epsilon_{\mathrm{Kr}}+\epsilon_{\mathrm{Br}})^2]^{-1},\tag{4}$$

where the $\alpha$'s and $\epsilon$'s are respectively the polarizabilities and excitation-energy values. (For Kr $\alpha=2.46\times10^{-24}$ cm$^3$,[17] $\epsilon=17\times10^{-12}$ erg [18]; for Br and the alkalis, see Ref. 15.) The results are shown in Table II, where the values in parenthesis are for the alkali iodides as calculated in Ref. 15.

As can be seen, the values for Kr differ by less than a factor of 3 from those calculated for the iodides. As our experimental results show, the influence of these changes on the $p$-electron population in Kr, and therefore on $|\psi_s(0)|^2$, is not detectable, despite the fact that the $\Delta R/R$ of $Kr^{83}$ is 8 times larger than that of $I^{129}$.

One can estimate the contribution of the electrostatic perturbation on the i.s. by using the results for the alkali iodides measured by Hafemeister *et al.*[19] Taking, for instance, the difference between the i.s. of $KI^{129}$ and $LiI^{129}$, we calculate the expected difference between the i.s. of $KBr(Kr^{83})$ and $LiBr(Kr^{83})$, assuming that the isomer shifts observed in the iodides are solely due to electrostatic perturbation. In that case we may write the following:

$$\begin{aligned}\Delta\delta(I^{129})&=\delta(\mathrm{KI})-\delta(\mathrm{LiI})\\&=a(I^{129})\Delta R/R(I^{129})[(B^p)^2(\mathrm{Li})-(B^p)^2(\mathrm{K})]b\\&=1.2\times10^{-8}\ \mathrm{eV},\\\Delta\delta(Kr^{83})&=\delta(\mathrm{KrBr})-\delta(\mathrm{LiBr})\\&=a(Kr^{83})\Delta R/R(Kr^{83})[(B^p)^2(\mathrm{Li})-(B^p)^2(\mathrm{K})]b',\end{aligned}\tag{5}$$

where the values of $\Delta\delta(I^{129})$ were taken from Ref. 19,

$$\Delta R/R(I^{129})=0.5\times10^{-4},{}^{15}$$

$$\Delta R/R(Kr^{83})=4\times10^{-4},{}^{2}$$

$$a(I^{129})=1.9\times10^{-29}\ \mathrm{eV\ cm}^3,$$

$$a(Kr^{83})=0.6\times10^{-23}\ \mathrm{eV\ cm}^3,$$

the $(B^p)^2$ values were taken from Table II, and $b$ and $b'$ correspond to the absolute values of the $s$ density of the iodine and krypton [see Eq. (14) in Ref. 15], which we assume to be equal in the first approximation. From expression (5) we find that the expected $\Delta\delta(\mathrm{Kr})$ is $2\times10^{-8}$ eV, which is one order of magnitude greater than our maximum error of $0.3\times10^{-8}$ eV. We then conclude that the electrostatic per-

---

[15] W. H. Flygare and D. W. Hafemeister, J. Chem. Phys. **43**, 784 (1965).

[16] H. Margenau, Rev. Mod. Phys. **11**, 1 (1939).

[17] See Ref. 8, p. 151.

[18] *Atomic Energy Levels*, edited by C. E. Moore, Natl. Bur. Std. (U.S.) Circ. No. 467 (U.S. Government Printing Office, Washington, D.C., 1952), Vol. 2.

[19] D. W. Hafemeister, G. de Pasquali, and H. de Waard, Phys. Rev. **135**, B1089 (1964).

TABLE III. Calculated values of $e^2qQ$ and $q_{\max}$.

| Source | Kr clathrates | LiBr | NaBr | KBr | CsBr | $NH_4Br$ | $KBrO_3$ | $h_p$ | 3 Å |
|---|---|---|---|---|---|---|---|---|---|
| $\Gamma_s/\Gamma_{\rm nat}$ | 3.4 | 6.5 | 9.6 | 7.5 | 8.6 | 8.7 | 16 | ⋯ | ⋯ |
| $e^2qQ$ (Mc/sec) | 8.14 | 15.6 | 23.6 | 18.8 | 20.6 | 20.9 | 38.4 | 630 | 34 |
| $q_{\max}$ ($\text{cm}^{-3}\times 10^{24}$) | $11.1\times 10^{-3}$ | $18\times 10^{-3}$ | $27\times 10^{-3}$ | $21\times 10^{-3}$ | $18\times 10^{-3}$ | $18\times 10^{-3}$ | $43\times 10^{-3}$ | 66 | $33\times 10^{-3}$ |

turbation invoked to explain the isomer shift is negligible.

### Line Broadening

A common and characteristic result of all the $Kr^{83}$ sources is the broad emission line (see Table I).

We proceed to discuss the possible reason for the observed broadening. First, we reject the explanation of broadening as due to different valence-state configurations. Such an effect, if it existed, should produce continuously different values of i.s. But the production of a symmetric unshifted absorption depth would require a very specific *p*- and *s*-electron-depletion mechanism. Broadening due to diffusion is improbable because of the working temperature ($\simeq$90°K), and because the Kr and $Br^-$ radius are similar, while the Kr radius is even larger than the $Br^{+5}$ radius.

We suggest the following mechanism: Following the total internal conversion decay of the 41-keV level of $Kr^{83m}$ (see decay scheme) an *L* or *K* electron ($K/L+M=0.32$) is emitted with a "macroscopic" interaction range. As a result of the internal conversion, a hole in the Kr atomic shell is produced which will finally be refilled from the nearest or next-nearest ions surrounding it. This electron-capture process will result in a rearrangement and displacement of the ligands. Assuming, for simplicity, that an octahedral symmetry exists previous to the metastable decay, the function of the defect will be to displace atoms in order to reduce the energy of the system. The distorted octahedral symmetry will create an electric field gradient (e.f.g.) at the nucleus, and therefore a quadrupole interaction. Further, since we observe a symmetric absorption depth, we conclude that at least two modes of distortion of the octahedra are present. One is an outward displacement of the axial ligands and a consequent inward movement of the planar ligands, and the second an axial shrinking and planar expansion. The two modes, which prior to the metastable decay were degenerate, will be equally favored energetically. This distortion mechanism, which can be related to the Jahn-Teller effect, will cause positive and negative e.f.g. with the same probability. Therefore a whole spectrum of electric field gradients will be presented according to the distortion mode and magnitude. The maximum e.f.g. ($q_{\max}$) is related to the experimental linewidth $\Delta E$ and is given to a first approximation by

$$q_{\max}=\sum_i \xi_i[(3z_i^2-r_i^2)/r_i^5]\propto(\Delta r/r)\langle 1/r^3\rangle, \qquad (6)$$

where $\xi_i$ is the charge fraction at each point *i* and $\Delta r$ is the largest displacement deviation of the ligands from the nondistorted octahedron. From expression (7), one can see that, depending on the sign of $\Delta r$, *q* will be either negative or positive.

In principle, a dynamic effect could explain the broadening if several transitions would occur between the two octahedral modes within the nuclear lifetime ($T_{1/2}=0.15$ $\mu$sec). For this case we should require a very specific "inversion frequency" which would be (a) temperature-dependent and (b) alkali-dependent. With the Kr-hydroquinone source, we observed no broadening variation—in addition to that due to the change in $T_s$—in the temperature range of 300–80°K. On the basis of this model we may explain the broadening magnitude order (Kr–Clt, bromide and bromate) as shown in Table I. The Br atom in the bromate ion originally sits on the top of an oxygen tripyramid with atomic distances of 2.2 A.[20] In the crystal it forms a very distorted octahedral of six oxygens. As a result of the decay and the "long rest" in the metastable level, the Kr atom, which has expanded from 0.80 to 1.98 Å radius, will be in the center of the octahedron closely attached to the six oxygens. The previous effect described will be in this case "amplified" because of the closer distances. In the clathrate case, because of the larger distances of the Kr atom to the hydroquinone cage walls, the effect will be smaller. We have calculated the values of the $q_{\max}$ as given by Eq. (6) for the sources we used and they are given in Table III. This was done by applying the following expression:

$$\Delta E=(c/E_\gamma)\tfrac{1}{4}[e^2q_{\max}Q(1-\gamma)](K^*R-K), \qquad (7)$$

where $\Delta E$ is observed at half-maximum linewidth corrected for the absorber thickness, *Q* is the ground-state (g.s.) quadrupole moment of $Kr^{83}$ ($Q=0.27b$),[21] $K^*$ and *K* are related to the 11 transitions for the $I^*=\frac{7}{2}$

---

[20] R. W. G. Wyekoff *Crystal Structure* (Interscience Publishers Inc., New York, 1964), Vol. 2, p. 386.

[21] G. H. Fuller and V. W. Cohen, in *Nuclear Data Sheets*, compiled by K. Way *et al.* (U.S. Government Printing Office, National Academy of Sciences—National Research Council Washington 25, D.C., 1965), Appendix I.

TABLE IV. Values of $\Theta_D$ as calculated from the absolute fraction of the sources at 80°K. The value of $\Theta_D$ for Kr-clathrate source was calculated from the recoilless fraction, not taking into account resonant self-absorption.

| Source | Kr clathrate | LiBr | NaBr | KBr | CsBr | $NH_4Br$ |
|---|---|---|---|---|---|---|
| Absolute $f$ | $0.52\pm0.04$ | $0.32\pm0.02$ | $0.43\pm0.02$ | $0.36\pm0.02$ | $0.42\pm0.02$ | $0.68\pm0.04$ |
| $\Theta_D$ (°K) | $74\pm3$ | $55\pm3$ | $65\pm3$ | $59\pm3$ | $64\pm3$ | $96\pm4$ |

to $I=\frac{9}{2}$ decay, $R$ is the ratio of the excited to ground quadrupole moments ($R=Q^*/Q=1.7$ [2]), and $\gamma$ is the Sternheimer antishielding factor ($\gamma=100$), which is somewhat larger than that of $Rb^+$ ($+71$) as calculated by Sternheimer and Foley.[22] For reference reasons we introduced the value of the e.f.g. due to one $p$ hole in the Kr valence shell ($4s^2\,4p^6$) and also that due to a unit charge (or hole) 3 Å away from the nucleus. For the Kr-clathrates we used the linewidth for $T_s=0$.

### Lattice Dynamics

For the absolute recoilless fraction for the bromides and clathrates we calculated the $\Theta_D$. The results are shown in Table IV. The trend of constancy in $\Theta_D$ for all the alkali bromides is consistent with that observed in the alkali iodides measured by the Mössbauer effect in $I^{129}$.[19] However, the magnitude of $\Theta_D$ is significantly lower than in the iodides ($\Theta_D=110$°K), and higher than found in solid $Kr^{83}$ [3] ($\Theta_D=37$°K). This may be explained by the different nature of forces holding the Kr and Br in their equilibrium positions. We note that the value of $\Theta_D$ obtained for the Kr clathrate calculated from the absolute $f$ (for $T_s=0$) is similar to the alkali results and higher than the value of the absorption frequency ($\bar{v}=37$ cm$^{-1}=57$°K), observed with the far-infrared (FIR) technique.[23] According to Burgiel *et al.*[23] the induced dipole observed via the FIR is due to the "rattling" of the Kr atom in the hydroquinone-clathrate cage. The large value derived for the $NH_4Br$ is remarkable. The force constant of the Kr impurity is proportional to the second derivative of the potential energy, therefore to the product of the polarizabilities of the Kr atom and its neighbors. The $NH_4^+$ polarizability$=1.66\times10^{-24}$ cm$^3$ [24] and its radius ($r=1.48$ Å) are very similar to those of the alkalis, and therefore could not be the reason for the enhancement of the recoilless fraction. Further, the recoilless fraction of $NH_4I^{129}$ which has the structure (CsCl) as $NH_4Br$ was found to be the same as that of the alkali halides and of $CuI^{129}$ crystals.[25] The explanation for such a phenomenum could be that upon $Br^-$ transformation to the neutral Kr atom, one of the $NH_4^+$ ion neighbors breaks up into $NH_3+H$. The combination of the hydrogen, $NH_3$, and the surroundings ions could then introduce an extra polarization on the Kr atom and therefore increase the force constants, which would enhance the recoilless fraction.

## 4. CONCLUSIONS

The main conclusions of this work are

1. A "$KrO_3$" species is not produced as a result of the $\beta^-$ decay of $Br^{83}O_3^-$ at 90°K.
2. It has been shown that all the $Kr^{83}$ *sources* including the Kr-hydroquinone reveal broad emission lines. This broadening is attributed to a noncubic environment resulting from the internal-conversion metastable decay of $Kr^{83m}$.
3. The absence of isomer shifts for all the sources shows that electrostatic perturbation due to the induced-dipole interaction between Kr and its neighbors does not affect the $s$-electron density at the nucleus. These results may suggest that the i.s. observed in the alkali iodides ($I^{129}$) are chiefly due to overlap deformations of the iodide wave functions.
4. The recoilless fraction values are essentially the same for all the alkali bromides. However, the $\Theta_D$ calculated from the Debye-Waller factors is significantly less than that of the alkali iodides as measured by the Mössbauer effect. The $f$ of $Kr^{83}$ in $NH_4Br$ crystals was found to be significantly larger than those of alkali bromides. The $\Theta_D$ of Kr-clathrates was found to be larger than that derived from far-infrared spectroscopy.

---

[22] R. M. Sternheimer and H. M. Foley, Phys. Rev. **92**, 1460 (1955).

[23] J. C. Burfiel, H. Meyer, and P. L. Richards, J. Chem. Phys. **43**, 4291 (1965).

[24] Y. K. Syrkin and M. E. Dyatkina, *Structure of Molecules and the Chemical Bond* (Dover Publications, Inc., New York, 1964), p. 199.

[25] S. Bukspan and M. Pasternak (private communication).