Physics

V. M. Krasnoperov, A. N. Murin, N. K. Cherezov, I. A. Yutlandov

1969

SovietRxiv

Abstract

Full Text

Physics

V. M. Krasnoperov, A. N. Murin, N. K. Cherezov, I. A. Yutlandov

Proof of the Existence of Charge States of Krypton in Rubidium Halide Matrices by the Mössbauer Method

(Presented by Academician B. M. Pontecorvo, October 22, 1968)

We studied the emission spectra of nuclear recoil-free gamma resonance of the isotope Kr^{83*}, formed as a result of electron capture in Rb^{83*} ($T_{1/2} = 83$ days). The sources used were rubidium fluoride, chloride, and bromide. Rb^{83} was isolated from the products of deep spallation of strontium (enriched with the isotope Sr^{84}) by protons with an energy of 150 MeV, accelerated on the synchrocyclotron of the Laboratory of Nuclear Problems of the Joint Institute for Nuclear Research. The mass of the isotopic carrier—natural rubidium—was from 0.5 to 1.0 mg. As absorber, krypton β-hydroquinone clathrate with a known absorption-line width was used (^{1}). The detector was a proportional counter with an argon–methane filling, which completely resolved the γ-quanta of the 9.3 keV Mössbauer transition from the intense KX-radiation ($E = 12.6$ keV). Resonance absorption was recorded on a nuclear-gamma-resonance spectrometer with the absorber moving according to a harmonic law and using a 400-channel SA-40B analyzer operating in the time mode. The instrumental error in determining the velocity did not exceed 1%. The velocity spectra of nuclear gamma resonance were processed by the method of least squares on a "Minsk-22" computer, assuming a Lorentzian form of the experimental absorption line.

Characteristic of the sources $\mathrm{Rb}^{83}\mathrm{HF}_2$, $\mathrm{Rb}^{83}\mathrm{Cl}$, and $\mathrm{Rb}^{83}\mathrm{Br}$ studied by us at a temperature of 78°K was the presence of resonance absorption with a maximum near zero velocity. Taking into account the dispersion character of the interaction of krypton atoms with the hydroquinone matrix, we assigned to this state in the lattices of rubidium halides the form of neutral Kr^0 (^{2}). In the case of $\mathrm{Rb}^{83}\mathrm{HF}_2$, a clear deviation of the line shape from a single Lorentzian is noticeable. In the velocity interval ±20 mm/sec we found in the spectrum of this source five more weak lines, which, together with the peak superimposed on the "central" one, are undoubtedly components of the quadrupole splitting of the levels of Kr^{83}. Indeed (see, for example, (^{3})), in this case the positions of individual lines are determined by the formula

$$v_{m^*\to m} = \frac{e^2qQ}{4}\left(\frac{c}{E_\gamma}\right)\left[RC(m^*, I^*) - C(m, I)\right] + s,$$

where

$$C(m, I) = \frac{3m^2 - I(I+1)}{I(2I-1)}, \qquad R = Q({}^7/_2)/Q({}^9/_2), \qquad I^* ={}^7 /_2, \qquad I ={}^9 /_2,$$

m^* and m are the projections of the nuclear spin on the Z axis in the excited and ground states, and s is the chemical shift. The asymmetry parameter

$$\eta = (V_{xx} - V_{yy})/V_{zz}$$

was assumed by us to be equal to zero. Presentation of the experimental results in coordinates $[v_{\text{exp}}(m^* \to m)]$ versus $[RC^* - C]$ gave a straight line whose slope was

$$A = \frac{e^2qQ}{4}\left(\frac{c}{E_\gamma}\right),$$

and which intersected the ordinate axis at the point $v = s$. The value $R = 1.98$, adopted in this calculation, ···

Table 1

Chemical shifts and splittings of krypton in rubidium halide matrices

Mössbauer pair	Isomer shift s, relative to Kr^0 at source temperature, mm/s	Quadrupole splitting A, mm/s	Parameters of the “central” peak s, mm/s; Γ mm/s; ε_{exp}, %
Rb(Kr)HF$_2$ (78° K) – clathrate (78° K), 90 mg/cm^2 Kr^{83}	$+9.70 \pm 0.08$	-11.08 ± 0.11	$+0.13 \pm 0.072.25 \pm 0.212.57 \pm 0.15$
Rb(Kr)Cl (310° K) – clathrate (78° K), 20 mg/cm^2 Kr^{83}	$+1.15 \pm 0.15$	$+1.10 \pm 0.25$	$-0.20 \pm 0.110.50^{(4)}0.12 \pm 0.06$

Mössbauer pair	Isomer shift s, relative to Kr^0 at source temperature, mm/s	Quadrupole splitting A, mm/s	Parameters of the "central" peak s, mm/s; Γ mm/s; ε_{exp}, %
Rb(Kr)Br (193° K) – clathrate (78° K), 20 mg/cm^2 Kr^{83}	$+0.65 \pm 0.06$	$+0.94 \pm 0.11$	$-0.14 \pm 0.070.90^{(4)}0.65 \pm 0.13$

calculated by us from the data of work (4). This value of R differs somewhat from the value 1.70 indicated by the authors*.

In the case of the sources $Rb^{83}Cl$ and $Rb^{83}Br$, it was found that the temperature dependence of the intensity and shape of the "central" peak has an anomalous character. We assumed that this is caused by the superposition on the "central" peak of lines of a weakly split multiplet, whose relative position changes with temperature, and were able, in our opinion, to choose the most favorable temperature conditions for observing charge states in these sources. The data obtained are given in Table 1, and the spectrum of rubidium bromide in Fig. 1. The processing of the $Rb^{83}Cl$ and $Rb^{83}Br$ spectra was based on approximating the poorly resolved quadrupole splitting corresponding to a krypton state different from Kr^0 by three and two Lorentzian peaks, respectively, whose parameters were calculated on a computer. In the computer processing, in addition to the χ^2 criterion, theoretical ratios of the intensities of the quadrupole-splitting components and the magnitude of the temperature shift of the "central" peak were also taken into account; this shift was taken by us, according to (5), as equal to

$$\frac{\partial s}{\partial T} \simeq \frac{-0.05 \text{ mm/s}}{70^\circ}$$

relative to Kr^0 at 78° K.

Fig. 1. Velocity spectrum of $Rb^{83}Br$ (193° K) –clathrate (78° K). Absorber thickness 0.3 mg/cm^2 Kr^{83}. The shaded area corresponds to chemically bound krypton. $\chi^2 = 38.54$.

The shift values found make it possible to suppose that part of the krypton atoms formed in rubidium halide matrices from Rb^{83}, at least during the mean lifetime of the excited state (~ 0.2 μs), has a density of $4s$-electrons at the nucleus different from that characteristic of Kr^0. Taking into account the identical sign of these chemical shifts with

---

* We believe that in work (4), an error was made in calculating R, A, and s.

Fig. 2. Dependence of σ on the electronegativity of F, Cl, Br on the Pauling scale. σ is the number of p-electrons per bond with one halogen atom.

Figure 1: Fig. 2. Dependence of σ on the electronegativity of F, Cl, Br on the Pauling scale. σ is the number of p-electrons per bond with one halogen atom.

with the shift of KrF_2 relative to Kr^0 (^{4}), we assume that in our case the shift is likewise caused by a decrease in the shielding action of the $4p$-electrons on the density distribution of the $4s$-electrons. Taking the data of that work, where the shift of 1.61 mm/sec is attributed to the loss by a krypton atom of 0.94 electron, and assuming a linear dependence of $|\Psi_s(0)|^2$ on the number of $4p$-electrons, we obtain, for krypton in the matrices

$$\mathrm{Rb(Kr)HF_2}, \qquad \mathrm{Rb(Kr)Cl}, \qquad \mathrm{Rb(Kr)Br}$$

electronic configurations of the outer shell of the form

$$4s^2 4p^{0.34}, \qquad 4s^2 4p^{5.33}, \qquad 4s^2 4p^{5.62},$$

respectively. Although the Kr—F bond apparently has considerable ionic character, we nevertheless regard the electronic configuration in this system, close to $4s^2$, as purely hypothetical. Assuming that the coordination number of krypton in Rb(Kr)Cl and Rb(Kr)Br remains equal to 6 and that the observed splitting is caused by a small distortion of the octahedral environment, we calculated the value σ, equal to the number of p-electrons participating in the bond with one halogen atom (for fluorine the value 0.47 was adopted). The dependence of σ on the electronegativity of the corresponding halogens on the Pauling scale (^{6}) is shown in Fig. 2.

Fig. 2. Dependence of σ on the electronegativity of F, Cl, Br on the Pauling scale. σ is the number of p-electrons per bond with one halogen atom.

The value of σ, obtained by rectilinear extrapolation and corresponding to iodine, whose electronegativity is 2.5, is negative, which makes it possible to suggest that analogous bonding of krypton with this halogen is impossible.

The authors express their sincere gratitude to B. G. Lur' e for his constant interest in the work and to Yu. S. Grushko for the computational programs provided.

Leningrad State University
named after A. A. Zhdanov

Joint Institute for Nuclear Research

Received
4 X 1968

CITED LITERATURE

[1] V. M. Krasnoperov, B. G. Lur’ e et al., *Atomic Energy*, **23**, no. 1, 60 (1967).
[2] M. Pasternak, T. Sonnino, *Phys. Rev.*, **164**, 384 (1967).
[3] J. S. Griffith, *The Theory of Transition Metal Ions*, London, 1961, p. 11.
[4] S. Ruby, H. Selig, *Phys. Rev.*, **147**, 348 (1966).
[5] M. Pasternak, A. Sinopoulos et al., *Phys. Lett.*, **22**, no. 1, 52 (1966).
[6] L. Pauling, *Nature of the Chemical Bond*, 3rd ed., N. Y., 1960, p. 93.