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On the Separation of Nuclear Isomers

EUGENE P. COOPER* Department of Physics, University of California, Berkeley, California (Received November 10, 1941)

The fact that nuclear isomers can be separated chemically cannot be explained on the basis of the recoils involved. However, with K capture, or with internal conversion accompanying the isomeric transition, there is a mechanism for the separation. The positive charge built up by the Auger effect during the electronic readjustment is enough to cause molecular dissociation. To illustrate this, the probabilities for Auger effect and for x-rays for all shells of the Br atom were calculated and compared, and they show that the excess charge in this case becomes as high as 4.7e. The effect on homopolar binding is examined by using a hydrogen molecule model. It is found that excess charges considerably less than 4.7e should cause dissociation in the Br case.

1. INTRODUCTION

OR the study of artificial radioactivities it is a fortunate experimental fact that two nuclear isomers can be separated chemically.¹ However, since no transmutation of elements is involved in the isomeric transition, the mechanism of the separation is not at once clear. Evidently molecular dissociation must accompany the transition; that is, the emission of a gamma-ray must in some way rupture chemical bonds. It has been suggested of course that the recoil given the nucleus by the gamma-ray supplies such a mechanism. The momentum imparted to the nucleus is $h\nu/c$, where $h\nu$ is the energy of the gammaray, c the velocity of light. Thus the kinetic energy of recoil is $2.5 \times 10^5 (m/M) (h\nu/mc^2)^2$, where M is the mass of the nucleus, m the mass of the electron. For $M \sim 100$ and rather high energy gamma-rays, i.e., $h\nu \sim mc^2$, this gives a few volts

(the order of magnitude of chemical binding energies) for the recoil. However, it is just characteristic of nuclear isomerism that the gamma-rays usually have low energies ~ 100 kev. A typical and thoroughly investigated activity is that of Br^{80,1-4} whose daughter isomer emits a beta-ray with half-life of 18 min. The bromine is usually in soluble organic form, and the 18-min. activity may be separated from the 4.5 hr. with simple reagents, for example with water. The energy of the gamma-ray in the isomeric transition is less than 50 kev ($\sim mc^2/10$) and m/M $\sim 7 \times 10^{-6}$. The nuclear recoil, ~ 0.02 ev, is very small compared to chemical binding and cannot be responsible for an appreciable separation.

The amount of chemical separation is usually large. For Br it is at least 85 percent. Now, since the long lifetimes of gamma-rays in nuclear isomerism are, in many cases, probably due to

^{*} Now at the University of North Carolina, Chapel Hill, North Carolina.

¹ E. Segrè, R. S. Halford, and G. T. Seaborg, Phys. Rev. **55**, 322 (1939).

² F. Fairbrother, Nature 145, 307 (1940).

⁸ D. DeVault and W. F. Libby, Phys. Rev. 58, 688 (1940). ⁴ J. E. Willard, J. Am. Chem. Soc. 62, 256 (1940).



hypothetical molecule.

angular momentum changes of several units, most of the gamma-rays are then internally converted, which suggests that the internal conversion is connected with the separation as has. in fact, been experimentally established, particularly in experiments in which Zn and Te isomers were subjected to similar chemical conditions. No separation was attained for the Zn isomers where the gamma-rays are unconverted, but with the large internal conversion of the Te gamma-rays was associated a large separation.5, 6 In any case the conversion is accompanied by another and, for low energy gamma-rays, more energetic recoil. The electron on leaving, say, the K shell gives the atom the momentum $(2mh\nu)^{\frac{1}{2}}$ or energy $(h\nu)m/M$. This differs from the direct recoil by a factor $mc^2/2h\nu$. For Br this factor is ~ 5 and the recoil is thus ~ 0.01 ev, still small compared to chemical bonds. This example illustrates the necessity of abandoning the idea of recoil as a general primary explanation of the separation. (In Te¹²⁷ the conversion recoil is ~ 0.1 ev. There are, however, cases in which it is of the order of chemical binding, viz., Sc44 and In¹¹³.)

We have found that internal conversion, independent of the recoil it allows, is responsible for a very efficient mechanism leading to dissociation. What is of importance here is the hole, left in an inner shell, that induces serious subsequent electronic and molecular readjustments. Even for low energy conversions the time for complete ejection of the electron is short com-

pared with that for any electronic transitions to the hole. Thus the atom becomes a positive ion of charge +e and its chemical properties are temporarily altered. The outer electrons, responsible for molecular binding, move in a new field to which the wave functions are readjusted in times short compared to molecular periods. Thus the unchanged configuration of atoms in the molecule no longer necessarily represents minimum potential energy and, since the atoms will move along their new potential curves, dissociation may occur as in other examples of the Franck-Condon principle.

Now, since it is very unlikely that the atom return to its ground state solely by the emission of x-rays, the excess charge does not remain +ebut increases due to the Auger effect. With each Auger process the increase is +e and another Franck-Condon process occurs. The molecular states will tend to become more and more repulsive since the excess charge will tend to distribute equally over the molecule. If, as a result, the molecule becomes unstable by several volts there will be ample time for dissociation before the excited atom returns to the ground state by electron capture.

It is clear that, for a quantitative discussion, two questions are involved: (1) How much charge builds up by the competition of Auger effect with x-ray emission, and (2) how do the Franck-Condon curves shift with the charge. We have investigated (1) for the special case of the bromine atom with a hole initially in the Kshell by calculating, from the individual x-ray and Auger transitions, the probabilities of the many possible series of states, and from these made estimates of the average charges and average times for their accumulation as shown in Table I. For (2) actual molecules like C₂H₅Br

TABLE I. Average charges and times for their accumulation.

Condition of Br atom	Average excess charge	Average time between conditions		
Hole in K shell	+1.0e	400.1 /		
K shell filled	+1.5	$480 n/mc^2\alpha^2$		
L shell filled	+2.4	800		
M shell filled	+4.7	6500		

⁵ J. W. Kennedy, G. T. Seaborg, and E. Segrè, Phys. Rev. 56, 1095 (1939). ⁶ G. T. Seaborg, G. Friedlaender, and J. W. Kennedy, J. Am. Chem. Soc. 62, 1309 (1940).

were not considered directly, because of mathematical complexities, but, since homopolar bonds are usually involved, the hydrogen molecule was, for simplicity, taken as a model, and an Auger process idealized by increasing the charge on one proton and leaving the molecule unaltered by any other causes. Energy calculations (Heitler-London) even with this model are rough, but reasonable estimates show that, even for molecules in question, excess charges less than are actually built up by Auger effect must cause dissociation. In Fig. 1 are shown Franck-Condon curves for this hypothetical molecule for various charges Z on one proton, the other having Z=1. In spite of the rough nature of the calculations we believe they indicate that the mechanism we have considered is responsible for the chemical separation. (See Part 3 for the meaning of $\nu = 1$.) However, it should be remarked that there is also an even more potent mechanism which would operate, were the molecule to remain undissociated in spite of the excess positive charge. This is the actual loss by Auger effect of some of the bonding electrons themselves. An examination of Table I shows that such loss will most certainly occur, but not until times of approximately $10^3 - 10^4 h/mc^2 \alpha^2$ after ample positive charge has been built up for dissociation by the Franck-Condon principle, and in such times two atoms in a molecule unstable by a few volts will separate by several atomic radii.

Molecular dissociation may also accompany radioactive transitions involving K capture. (Of course it would usually occur anyway because of the atomic transmutation, but not until the completion of processes of the type we are considering, i.e., the outer (valence) shell would not be characteristic of the new element until the completion of electronic readjustments in the inner shells, the probability for these readjustments being greater than for those in the valence shell.) Here the bonding wave functions are little perturbed by the transition since it corresponds merely to the transfer of a charge in the atomic interior. But the charge built up by the subsequent Auger processes, although always one unit less than it would be for the corresponding internal conversion, should again be sufficient to cause dissociation. Recently individual atoms in

TABLE II. Probable transitions	(units of $mc^2\alpha^2/h$).
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Transition to K shell		to L shell		to M shell	
2s - 1s	2.8×10 ⁻³	3s - 2s	4×10 ⁻³	4s-3s	5×10 ⁻⁴
$2p-\infty$		$3p-\infty$		$4s - \infty$	
2p - 1s	6.5×10 ⁻³	3p - 2s	7×10-3	4p - 3s	.8×10 ⁻³
$2p - \infty$		$3p-\infty$		$4p-\infty$	
2p-1s	2.0.10-3	3s-2p	3.5×10 ⁻³	4p-3d	6×10-4
$3p-\infty$	2.0 × 10 *	$3p-\infty$		$4p-\infty$	0 \ 10
3p - 1s	2.0 × 10-8	3p-2p	7.8×10 ⁻³		
$3p-\infty$	3.9×10 °	$3p-\infty$			
3p-1s	1 8 × 10-3	3 <i>p</i> -2 <i>p</i>	4.0×10 ⁻³	·	(for Te)
$3d - \infty$	1.0 \ 10	$3d - \infty$		to iv shell	
		3d-2p	4 2 > / 10-3	5p-4s	2×10-
		$3d - \infty$	4.2×10 °	$5p-\infty$	2×10 ·

K capture have been observed.⁷ Cd¹⁰⁷ which decays to Ag¹⁰⁷ was electroplated on a filament and Ag atoms were collected in a Geiger counter. It was hoped that such an experiment would be direct evidence for neutrino recoil. However the calculations made in this paper show an effect so definite that we believe similar calculations for the perturbations on the periodic potential in a metal surface by the K capture would show them to be enough to overcome the work function and eject individual atoms. Further theoretical work is needed here.

An earlier attempt to show direct neutrino recoil was made by observing Cl³⁸ beta-rays in a cloud chamber.⁸ Small clusters of ions were always found at the beginning of the tracks. These were attributed to the ionization produced by the nuclear recoil from beta-ray and neutrino. However, quite aside from the fact that such drop-counting technique is very difficult and subject to large errors, the recoil velocities involved are so low that no appreciable ionization is to be expected from this source,⁹ and the

⁷ B. T. Wright, Ph.D. Thesis, University of California (1941).

⁸ H. R. Crane and J. Halpern, Phys. Rev. 56, 232 (1939).

⁹ It is true that the recoil Cl nucleus may have \sim 5 Mev kinetic energy, but this corresponds to a velocity which is only a small fraction of orbital electronic velocities. Most of the energy loss to a gas atom will contribute to the kinetic energy of the atom as a whole rather than to its individual electrons. Hence the efficiency of ionization

Initial state	Final state 1s	2 <i>s</i>	35
2 <i>p</i>	3.7×10^{-2}	1 2 10-3	
3p 4p	0.7×10^{-2}	0.5×10^{-3}	5.7×10 ⁻⁵
		2 <i>p</i>	3 <i>p</i>
35		3.6×10-4	
4s 3d		1.4×10^{-4} 8.5×10^{-4}	3.4×10 ⁻⁵

TABLE III. Transition probabilities for Br.

ionization actually observed may here again be largely attributed to Auger processes dissipating electronic excitation energy.

2. THE AUGER EFFECT

In order to show how Auger effect competes with x-ray emission in building up positive charge in the radioactive atom it is necessary to compare the individual transition probabilities for both processes. We have made no attempt to do this generally for all Z since for low Z the Auger effect is more important for individual transitions whereas for high Z more Auger transitions corresponding to a given x-ray are allowed, so that we should expect the competition not to change markedly with Z.

We have calculated individual Auger probabilities after the methods of Burhop¹⁰ and Pincherle,¹¹ using screened hydrogen-like wave functions (Slater's constants) for the bound states but, instead of exact Coulomb functions, a plane wave for the ejected electron. The transition probabilities agree, at least in order of magnitude, with those calculated with the Coulomb functions, which are, in any case, rough because of the absence of a true Coulomb field and the approximate nature of the bound wave functions. The expression for the transition probability reduces to:

$$\sum_{\nu=0}^{\infty} a_{\nu} \left| 2\pi \int_{0}^{\infty} \int_{0}^{\infty} R_{0}(r_{1}) R_{f}(r_{1}) R_{0}(r_{2}) \frac{J_{4}(\kappa r_{2})}{(r_{2})^{\frac{1}{2}}} r_{1}^{2} r_{2}^{2} \\ \times \left(\frac{r_{<}}{r_{>}} \right)^{\nu} dr_{1} dr_{2} \left| \frac{2}{n} \frac{mc^{2} \alpha^{2}}{h} \right|,$$

will not compare with that for high speed ions and the assumption, made by Crane and Halpern, of one ion pair for 30 volts kinetic energy is unternable, cf. N. Bohr, Phys. Rev. **59**, 270 (1941). ¹⁰ E. H. S. Burhop, Proc. Roy. Soc. **148**, 272 (1935). ¹¹ L. Pincherle, Nouvo Cimento **12**, 81 (1935).

where $R_0(r_1)$, $R_f(r_1)$ and $R_0(r_2)$ are the radial hydrogen-like functions for the initial and final state of electron 1 and the initial state of electron 2; κ is the momentum of the ejected electron in atomic units. The a_{ν} 's are numbers of order unity only a very few of which are nonvanishing. The r_1 integration is elementary and the final integration was done graphically. The most probable transitions are shown in Table II.

The probabilities for x-ray emission were found from the formula for electric dipole radiation. Experimental frequencies were used. The matrix element of the dipole moment, which takes the form $\int r^3 R_0(r) R_f(r) dr$ was again integrated graphically by using screened hydrogenlike functions for initial and final radial wave functions, $R_0(r)$ and $R_f(r)$. The transition probabilities for Br are shown in Table III.

A comparison of Tables II and III shows that in the outer shells Auger effect will occur exclusively. In Table IV the condition of the

TABLE IV.

					2p and		3p and
Holes	2⊅	3p	4 <i>p</i>	2s and	Ž⊅ or	2⊅ and	3⊅ or
				2s or 2p	3d or 4s	3p or 3s	3d or 4s
Prob.	0.33	0.10	0.05	0.10	0.23	0.09	0.10

Br atom after the K shell has been filled is indicated. (Here we have used not only our own values for the more probable transitions as shown in Table II but also the values for the less probable transitions as given by Burhop and Pincherle.) By tracing the many possible series of events and finding the corresponding distributions after the L and M shells have been filled the averages in Table I were obtained.

3. THE HYDROGEN MOLECULE MODEL

To draw Franck-Condon curves one must calculate the total energy of the molecule at atomic separation R (diatomic molecule) and subtract off the energy at infinite separation. We have used the method of Heitler and London¹²

TABLE V.

z	$E\left(\begin{matrix}\lambda=0\\\nu=1\end{matrix}\right)$	λ	$E(\nu=1)$	$E\left(\nu=1+\frac{Z-1}{4}\right)$
1	-3.3 ev	0.16	-4.0 ev	-4.0 ev
2	+6.7	0.75	+3.2	+3.8
3	+16.6	1.2	+11.5	+13.7
4	+28.8	1.9	+19.4	+25.0

as modified by Slater and Pauling.¹³ Our hypothetical molecule has two protons with charges +Ze and +e. The distances of electron 1 from +Ze and +e are r_1 and R_1 , respectively. The corresponding distances of electron 2 are R_2 and r_2 . We define:

$$\begin{split} \Psi_1 &= (\nu^3/\pi a^3) \exp(-\nu r_1/a), \\ \Psi_2 &= (\nu^3/\pi a^3) \exp(-\nu R_2/a), \\ \varphi_1 &= (1/\pi a^3) \exp(-R_1/a), \\ \varphi_2 &= (1/\pi a^3) \exp(-r_2/a), \end{split}$$

where $a = h^2/4\pi^2 me^2$. For z = 1 a good zero-order wave function is:^{12, 13}

$$\Psi(R) = \Psi_1 \varphi_2 + \Psi_2 \varphi_1 + \lambda (\Psi_1 \Psi_2 + \varphi_1 \varphi_2) \quad \text{for } \nu = 1,$$

where λ is a constant depending on R and so chosen as to give minimum energy. We are interested in changes of Z of several units, but in atoms like Br the wave functions will contract with increasing Z far less than for the case of the hydrogen atom where $\Psi_1(\nu=1)$ is a correct atomic wave function. Therefore, to make our model correspond more closely to a molecule in question like, say, HBr where we are interested in different charges on the Br atom, we use atomic functions of the form Ψ_1 etc. but with $\nu-1$ only a fraction of Z-1. We have used for the fraction $\frac{1}{4}$ and zero. However, in the Hamiltonian we do not modify Z:

$$H = (-h^2/8\pi^2 m)(\Delta_1 + \Delta_2) + e^2(Z/R + 1/r_{12} - Z/r_1 - Z/R_2 - 1/R_1 - 1/r_2)$$

Also in the zero-order wave function we drop the term $\lambda \varphi_1 \varphi_2$ since it corresponds to the configuration in which both electrons are on the proton with lesser charge (except for Z=1where the term is included in the standard calculations¹³). With these modifications we have calculated the energy by: $\Psi(R) \cdot H\Psi(R)$ and subtracted off the energy of an atom in the state $\Psi_1(\nu)$ in the field of the charge Ze plus the energy of a normal hydrogen atom. All the integrals were evaluated in closed form except for

$$\int \frac{1}{r_{12}} \Psi_1 \varphi_1 \Psi_2 \varphi_2 dV_1 dV_2$$

for $\nu - 1$ not zero, but for this integral a good approximation was found. Each point on the curve (Fig. 1) is calculated for the minimum in λ . Table V shows values of E and λ for $R/a = \frac{3}{2}$ (the equilibrium separation of normal H_2) and also *E* for $\lambda = 0$ thus illustrating the effect of ionic terms in reducing the energy. Our hypothetical molecule, even for the case $\nu = 1 + (Z-1)/4$, is roughly the size of a normal hydrogen molecule. For larger molecules the displacement of the curves (Fig. 1) from the normal curve $(Z = \nu = 1)$ will be reduced by a factor roughly the ratio of the diameter of the molecule to that of the H_2 molecule. Even then the shift is still considerable for charges of at least two so that with the charges which are built up by Auger effect dissociation should certainly occur. Also, for conversion in the L shell, a high enough charge, \sim 3, will be built up.

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¹² W. Heitler and F. London, Zeits. f. Physik 44, 455 (1927).
¹³ J. H. VanVleck and A. Sherman, Rev. Mod. Phys. 7,

^{184 (1935).}