

Anomalous Dispersion and Absorption of Electric Waves in Solutions of Amino-Acids and Dipeptides

The dielectric constants and absorption coefficients of aqueous solutions of several amino-acids and dipeptides, listed in Table I, have been measured for electric waves of $\lambda = 25.5$ cm ($\nu = 1.18 \times 10^9$ cycles). The method used was a modification of Drude's second method. The waves were generated as described earlier.¹ The table shows the results obtained: $\Delta\epsilon'/c$ is the so-called dielectric increment per mole and $\Delta\epsilon''/c$ is the absorption coefficient increment per mole; ϵ' and ϵ'' being the real and the imaginary parts of the dielectric constant $\epsilon = \epsilon' - i\epsilon''$. The increments $\Delta\epsilon_0/c$ of the static dielectric constant per mole were taken from the literature.^{2,3} The table shows also the relaxation times τ calculated from our data for the dielectric increment by the use of Debye's theory formulae with the Wyman's formula $\tau = a + bp$ in place of the Clausius-Mossotti relation (p —volume polarization; a and b —Wyman's constants). The relaxation times τ_0 calculated for spherical molecules from molecular volumes are given for comparison in the last column.

Attention may be drawn to the following points: (a) the anomalous dispersion and absorption were increasing with increasing molecular size; (b) the dielectric increment was independent of concentration within the limits of error; (c) the absorption coefficient increment tended to increase with the concentration; this could be quantitatively accounted for as being due to the change in relaxation time with the change in viscosity to which ϵ'' is very sensitive when frequency corresponds to the edge of the dispersive region.

As is well known the observed static dielectric increments of simple straight-chain dipolar ions in a polar solvent have been accounted for statistically on the assumption of free rotation about the various single bonds of the chain, irrespective of whether polarization in a static field is accomplished by deformation or by orientation of the entire molecule.^{4,5} At high frequencies, however, the dielectric properties of the solution should depend upon the mechanism of polarization, each mode of deformation or orientation having its own relaxation time. The behavior of the higher peptides of glycine strongly suggests polarization by deformation of a flexible chain, since no anomalous dispersion has been observed at frequencies corresponding to the rotation of the molecules as a whole.³ The present data for the simple dipeptides, on the other hand, suggest orientation of these molecules, and are further consistent with the assumption of an asymmetry factor of about 2. The amino-acids, with the

very doubtful exception of glycine, also give evidence of relaxation times not greatly different from those corresponding to molecular rotation. A fuller discussion of the experiments will be published elsewhere.

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³ Greenstein and Wyman, J. Am. Chem. Soc. **58**, 463 (1936).

⁴ W. Kuhn, Zeits. f. physik. Chemie **A175**, 1 (1935).

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Radioactive Element 93

Last year a nonrecoiling 2.3-day period was discovered¹ in uranium activated with neutrons, and an attempt² was made to identify it chemically, leading to the conclusion that it is a rare earth. Impressed by the difficulties raised by this identification, the authors independently decided that the subject was worth further investigation. In Berkeley it was found that: (1) If a layer of $(\text{NH}_4)_2\text{U}_2\text{O}_7$ with about 0.1 mm air equivalent stopping power, placed in contact with a collodion film of 2 mm air equivalent, is activated by neutrons from the cyclotron, the 2.3-day period appears strongly in the uranium layer, and not at all in the collodion, which shows a decay curve parallel to, and 1/7 as strong as, that of a paper "fission catcher" behind it. One day after bombardment the uranium layer has five times the activity of the fission catcher. This shows that the 2.3-day period has a range of <0.1 mm air and an intensity larger than all the long period fission products together. (2) When a thin layer of uranium is bombarded with and without cadmium around it, the fission product intensity is changed by a large factor, while the 2.3-day period and the 23-minute uranium period are only slightly changed, and their ratio remains constant. Also absorption of resonance neutrons by uranium changes these two periods in the same ratio, suggesting a genetic relation between them, and the consequent identification of the longer period with element 93. In Washington it was found that the 2.3-day period probably does not behave consistently as a rare earth, since attempts to concentrate it chemically with the rare earths from activated uranium failed, although it is known to have an intensity large compared with that of the rare earth fission products.

At this stage of the investigation one of the authors (P.H.A.) came to Berkeley on a visit, and a combined attack was made. With pure 2.3-day substance from thin uranium layers, the chemical properties were investigated, and a very characteristic difference from the rare earths was soon found; namely, the substance does not precipitate with HF in the presence of an oxidizing agent (bromate in strong acid). In the presence of a reducing agent (SO_2) it precipitates quantitatively with HF. Cerium was used as a carrier. This property explains the erratic nature of previous chemical experiments in which the oxidizing power of the solution was not controlled. Further chemical

TABLE I. Dielectric constants, absorption coefficients, and relaxation times.

SUBSTANCE	$\Delta\epsilon_0/c$	CONCENTRATION RANGE	$\Delta\epsilon'/c$	$\Delta\epsilon''/c$	$\tau \times 10^{10}$	$\tau_0 \times 10^{10}$
Glycine	22.8	0.2-2.0	21.3	14.3	2.60	6.61
α -Alanine	23.3	0.4-0.8	17.4	13.8	6.55	8.50
β -Alanine	34.8	0.4-0.8	25.7	19.1	6.72	8.50
Glycylglycine	71.1	0.2-0.4	28.7	41.2	14.94	10.82
Glycylalanine	72.3	0.2-0.4	20.2	39.5	20.28	12.71
Alanylglycine	71.5	0.2	18.9	40.3	21.28	12.71

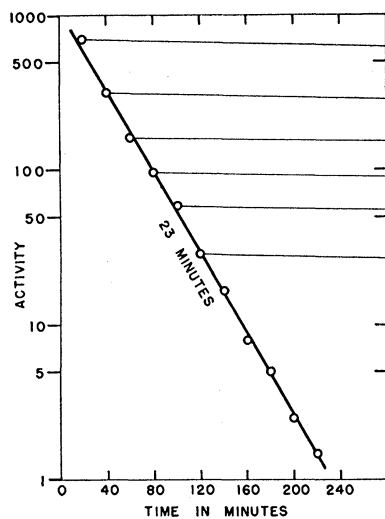


FIG. 1. Growth of 2.3-day 93^{239} from 23-minute U^{239} . The points indicate the activities of successive fluoride extractions, plotted at the times of extraction. Decay measurements were made a day later on the first six fractions, and the resulting slopes are shown on the plot.

experiments showed that in the reduced state with a thorium carrier it precipitates with iodate, and in the oxidized state with uranium as sodium uranyl acetate. It also precipitates with thorium on the addition of H_2O_2 . It precipitates in basic solution if carbonate is carefully excluded. These properties indicate that the two valence states are very similar to those of uranium (U^{++++} and UO_2^{++} or $U_2O_7^{--}$), the chief difference from that element being in the value of the oxidation potential between the two valences, such that the lower state is more stable in the new element. It is interesting to note that the new element has little if any resemblance to its homolog rhenium; for it does not precipitate with H_2S in acid solution, is not reduced to the metal by zinc in acid solution, and does not have an oxide volatile at red heat. This fact, together with the apparent similarity to uranium, suggests that there may be a second "rare earth" group of similar elements starting with uranium.

The final proof that the 2.3-day substance is the daughter of the 23-minute uranium is the demonstration of its growth from the latter. For this experiment activated uranium was purified twice by precipitation as sodium uranyl acetate, which was dissolved in HF and saturated with SO_2 . Then equal quantities of cerium were added at twenty-minute intervals and the precipitates filtered out. The first precipitate, made immediately after purification, carried all the fluoride-precipitable contaminations and was discarded; its weakness indicated a very good purification. The activities of the others are plotted in Fig. 1.

A preliminary study of the radiations from 93^{239} shows that it emits continuous negative beta-particles with an upper limit of 0.47 Mev, and a weak complex spectrum of low energy gamma-rays (<0.3 Mev) and probably x-rays. The question of the behavior of its daughter product 94^{239} immediately arises. Our first thought was that it should go to actinouranium by emitting an alpha-particle.

We sought for these by preparing a strong sample (11 millicuries) of purified 93 and placing it near a linear amplifier in a magnetic field to deflect the beta-particles. From this experiment we conclude that, if alpha-particles are emitted, their half-life must be of the order of a million years or more; the same experiment showed that if spontaneous fission occurs its half-life must be even greater. We wish to express our gratitude to the Rockefeller Foundation and the Research Corporation, whose financial support made this work possible.

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Masses of Stable Nuclei from Ne^{20} to Fe^{57}

The observation of the proton groups in (dp) and (αp) reactions recently made in this laboratory, together with a knowledge of beta-ray maximum energies makes it possible to give reasonably correct values for isotopic masses as far as Fe^{57} with a few exceptions. These values are given in Table I. The values from Ne^{22} to A^{38} are derived entirely from transmutation data, and mass-spectrograph values are given in parentheses for comparison where they are available. Above K^{39} the accuracy is less and reliance has to be placed on mass-spectrograph measurements of Ti^{48} , Fe^{56} ¹ and Cr^{52} ,²

Such mass values are useful in checking theories of nuclear structure and to facilitate a bird's-eye view of the trend of mass values a quantity called here the "mass deviation" is plotted against the mass number. This is simply the deviation from a whole number plotted on a sloping scale which enables the whole range of elements to be plotted in a small space. Precisely defined it is $M_A - A + 0.001(A - 20)$ where M_A is the mass of an element of

TABLE I. Isotopic masses.

Ne^{20}	19.99881 (Bainbridge)	A^{40}	39.97504 (Bainbridge)
Ne^{21}	21.00018 (20.99968)	Ca^{40}	39.9745
Ne^{22}	21.99864 (Bainbridge)	K^{41}	40.9739
Na^{23}	22.99680	Ca^{42}	41.9711
Mg^{24}	23.99189	Ca^{43}	42.9723
Mg^{25}	24.99277	Ca^{44}	
Mg^{26}	25.99062	Sc^{45}	44.9701
Al^{27}	26.98960	Ti^{46}	45.9678
Si^{28}	27.98639 (27.9866)	Ti^{47}	
Si^{29}	28.98685 (28.9866)	Ti^{48}	47.9651 (Dempster)
Si^{30}	29.98294	Ti^{49}	48.9664
P^{31}	30.98437 (30.9843)	Ti^{50}	49.9632 (Dempster)*
S^{32}	31.98306 (31.9823)	V^{51}	50.9587
S^{33}	32.98260	Cr^{52}	51.9575 (Aston)
S^{34}	33.97974	Cr^{53}	52.9572
Cl^{35}	34.98107	Cr^{54}	
Cl^{36}	35.97852	Fe^{54}	53.9601 (Dempster)*
Cl^{37}	36.97829 (36.9779)	Mn^{55}	54.9653
A^{38}	37.97544	Fe^{56}	55.9608 (Dempster)
K^{39}	38.97518	Fe^{57}	56.9609

* Considerably less accurate than the other values given.