small pool of unlabeled HCO_3^- (which cannot be dilutable with labeled HCO_3^- from the external medium) must be proposed as the source of oxygen. Lacking any supporting evidence, such a scheme must be considered improbable at the present time.

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11. Maize (*Zea mays*) chloroplasts were isolated by the procedure described in (*6*). The source and manner of isolating chloroplasts, however, is not of great importance here. More critical is the HCO_3^- depletion procedure. To deplete chloroplasts of HCO_3^-, they were suspended at a concentration of 50 μg of chlorophyll per milliliter in a solution containing 0.175*M* NaCl, 0.1*M* sodium formate, and 0.05*M* sodium phosphate buffer, *p*H 5.0 [higher *p*H for chloroplasts from C_3 plants; see (*5*)]. The solution was made CO_2-free by boiling before it was used. The chloroplast suspension was flushed with a continuous stream of pure N_2 or Ar gas for 10 minutes in the dark at room temperature. Portions were then drawn off with a syringe and placed in cooled screw-capped test tubes previously flushed with N_2. After centrifugation, the supernatant was poured off and the tubes were placed in ice. The HCO_3^--depleted chloroplasts were later suspended in CO_2-free reaction mixture and assays were conducted.
12. The mass spectrometer inlet system used in these experiments was similar to one described earlier [G. Hoch and B. Kok, *Arch. Biochem. Biophys.* **101**, 160 (1963)]. It utilized a semipermeable membrane (MEM 213, General Electric) which allowed dissolved gases (but not the liquid phase) to enter the mass spectrometer from the (~1 ml) reaction vessel. The response time of the system, end-to-end, was about 3 seconds. The quadrupole mass spectrometer (Extranuclear Laboratories) was programmed by using a peak selection–stepper system developed by O. Ollinger.
13. A stock solution of $HC^{18}O_3^-$ was made by dissolving ordinary $NaHC^{16}O_3$ in water (obtained from Monsanto Research Corporation) containing 97.2 percent ^{18}O. Several days were allowed for isotopic equilibration.
14. A more rapid rate of photoinactivation, reflected by a decreasing rate of O_2 evolution in the light, is usually observed once chloroplasts are HCO_3^--depleted. The reason for this is not clear [see (*7*)].
15. Partially supported by NSF grants GB36751, GT33537, and NSFC-704 and ERDA contract E (11-1) 3326. Preliminary experiments were done at the University of Illinois, Urbana, with the cooperation of G. Haight and Govindjee. While the methods employed proved limiting, the results appeared similar to some of those presented here. We are grateful for the valuable experience gained through their support. We thank B. Kok for permission to use the facilities at the Martin Marietta Laboratories in Baltimore and for helpful discussion. Carnegie Institution of Washington, Department of Plant Biology, Publication No. 555.
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Vibrational States of the Biopolymer Polyglycine II: Theory and Experiment

Abstract. *The density of vibrational states, and hence the heat capacity, has been calculated for the parallel-chain hexagonal lattice of 3_1 helical polyglycine. The agreement with experimental results in the temperature range from 1 to 20 K, including an anomaly near 8 K, is the best obtained thus far for homopolypeptides.*

Simple polypeptides, homopolypeptides in particular, have long been considered as model systems for the study of proteins (*1*). Solid-state and polymer physics have now advanced to the stage where one can treat the vibrations of polymers by using techniques that have been well established for simple molecules and for oligomers, based on springlike interactions between the atoms of the polymer. However, the computational difficulties become progressively much more severe as one considers polymers more complicated than polyethylene. We have calculated here the density of vibrational states and thence the specific heat for the simplest homopolypeptide, polyglycine II (PG II), and also measured the low-temperature specific heat from 1 to 20 K. The specific heat for PG II measurements are by far the lowest in temperature yet reported.

The specific heat provides a test of how the vibrational modes are distributed over different frequencies (that is, the density of states). The theory and experiment are in fair agreement, particularly with respect to the unexpected specific heat behavior near 8 K; PG II is thus the most complicated polymer for which a first-principles vibrational (lattice dynamical) calculation is in good agreement with experiment. Even though this study bears the same relation to biological systems as many structural studies on proteins (for example, in neither case are the studies carried out on the molecule under true intracellular aqueous conditions), the approach is valuable, particularly for the low-energy skeletal modes.

Polyglycine, or poly(–COCHRNH–) with R = H, is dimorphic in the solid state, existing as a β sheet structure (PG I) or as 3_1 helices (PG II). In these calculations the helices were assumed to be arranged in a parallel array with their axes on a hexagonal lattice. Theoretical (*2*) and experimental (*3*) results indicate that the helices are arranged antiparallel as well as parallel. However, to lessen the computational difficulties the model was restricted to the parallel arrangement only. The main differences between this calculation and earlier normal mode calculations (*4–8*) is that in this model all atoms are considered explicitly and the interchain interactions are included. The valence force field developed (*4*) for the polyamides and PG I was used for the intrachain interactions, and only the hydrogen bonding interactions were included in the interchain force field. The lattice dynamical secular equation was approximated with the use of a perturbation technique in which the secular equation was initially transformed with the eigenvectors of the isolated chain calculation (that is, no interchain interactions) and then truncated to the 21 lowest-frequency modes. This method yielded the approximate frequencies below 350 cm^{-1} and at selected wave vectors was shown to yield frequencies in excellent agreement with those found by diagonalization of the full secular determinant. The smaller secular equation leads to a substantial savings in computational time since a large number of wave vectors must be sampled to adequately describe the density of states. The vibrational frequencies above 350 cm^{-1} were assumed to be dependent only on the wave vector components in the chain axis direction. The resultant density of states is shown in Fig. 1. The higher frequencies (greater than 300 cm^{-1}) have little influence on low-temperature specific heat.

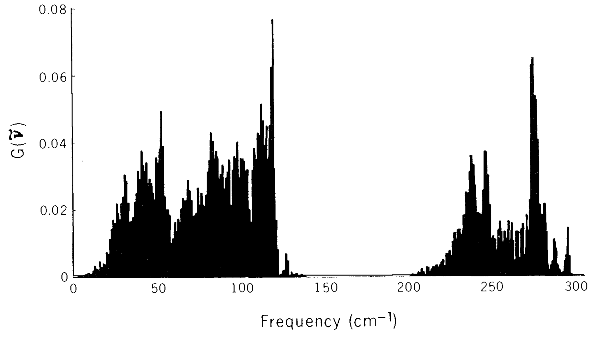

Fig. 1. Density of vibrational states $G(\bar{\nu})$ versus frequency for PG II. The number of total states is normalized to the number of vibrations in one chemical repeat unit, that is, 21.

The experimental input to the lattice

dynamical calculations consisted of the structure, atomic masses, and force field constants of PG II and did not involve low-temperature specific heat measurements at all. The results of the calculations are shown as the smooth curves in Fig. 2, a and b.

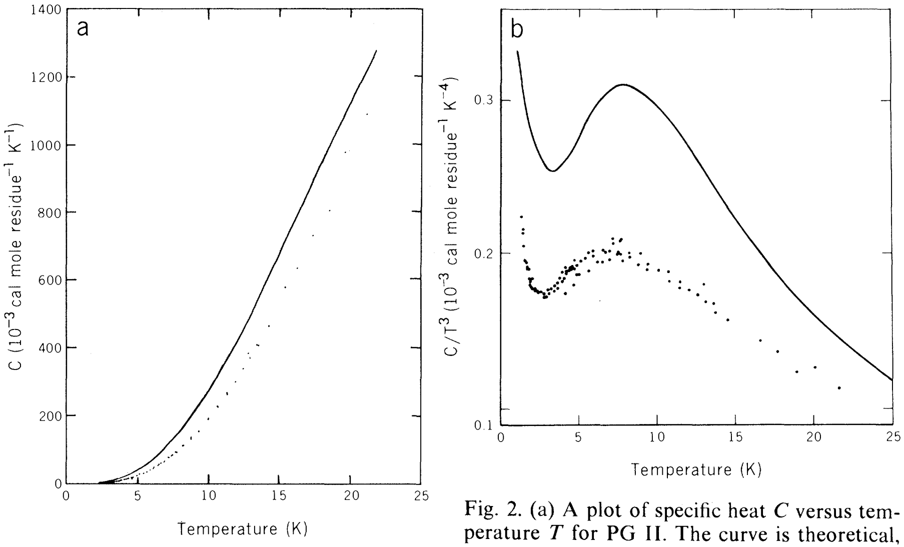

Fig. 2. (a) A plot of specific heat C versus temperature T for PG II. The curve is theoretical, the points are experimental (1 cal = 4.184 joules). (b) A plot of C divided by T^3 versus T for PG II. The curve is theoretical, the points are experimental.

To measure specific heat, one applies a quantity of heat ΔQ to a thermally isolated sample and measures the resulting temperature rise ΔT; the specific heat is then $C = \Delta Q/\Delta T$. The heat energy excites the various modes of vibration. As the temperature is raised higher-energy modes are excited, and so one can think of specific heat measurements made at different temperatures as, in some sense, sweeping through the curve of density of states versus energy. (The specific heats at constant pressure and constant volume are equal at low temperatures.) At these low temperatures the thermal diffusivity of polymers is very low; as a result the thermal relaxation times of the sample can be unacceptably long, and this leads to inaccuracies. We obtained reasonable relaxation times by mixing the sample with copper powder and compressing it at 10^8 pascals (1 pascal = 1 newton/m^2), which also resulted in a sample of convenient compactness (*9*). The specific heat apparatus has a mechanical heat switch and a germanium resistance thermometer (*10*), and has been checked against exceedingly high-purity copper (*11*).

Polyglycine (Sigma Chemical Company, St. Louis) was dissolved in saturated LiBr solution; PG II precipitated when this solution was poured into excess water (*5*). The precipitated PG II was repeatedly washed and centrifuged until the LiBr in the wash water was in the parts-per-million range, and then dried.

The experimental results are shown in Fig. 2, a and b. In Fig. 2b the results are plotted as C/T^3 since, at a low enough temperature, C will be proportional to T^3 [that is, the Debye model (*12*)]. (The differences between our experiment and theory are unlikely to be due to any of the usual systematic ills that arise in low-temperature specific heat measurements.)

Although increases in C/T^3 and low-temperature maxima have already been observed in some polymeric and other materials below 1 K and explanations attempted (*13*, *14*), the maximum in the experimental results of Fig. 2b at about 8 K is a new feature for homopolypeptides. We were particularly delighted, therefore, when Fanconi's theoretical calculations became available several months later and reproduced the main features of the maximum in Fig. 2b. We stress that the input to the theoretical calculations and the calculations themselves are completely independent of any low-temperature information.

Because C comes from the density of states, which in turn is provided by the lattice dynamical model (*6*, *7*), it is not a straightforward process to deconvolute the calculations and find the origin or origins of the maximum in Fig. 2b. The computer calculations are sufficiently costly in time and money that a simple variation-of-parameters approach is not feasible. However, the maximum seems to be related to the soft hydrogen-bonded interchain interactions. Two earlier theoretical calculations for homopolypeptides, one based on an isolated helical chain model (*8*) and another for PG I based on a simple model of the chemical repeating unit in a two-dimensional array (*6*), do not predict the anomalous behavior seen in Fig. 2b. A comparison of the density of states of these two models with Fig. 1 shows that the contribution of the hydrogen bonds to low-frequency modes is less in PG II than in either the α-helix or the β-structure (PG I). Normal modes of vibration in which the hydrogen bonds are fully extended occur for the α-helix and β-structure but not for the parallel-chain PG II structure.

The excellent agreement that is found (*7*) between the calculated spectroscopically active mode frequencies and the experimental infrared and Raman frequencies is one test of the validity of the parameters of the calculation. The maximum in Fig. 2b corresponds to a frequency (about 5 cm^{-1}) that is too low to be observed by either infrared or Raman spectroscopy, even if one assumes that the relevant modes are spectroscopically active.

The rise in C/T^3 seen for PG II below 1 K has been observed experimentally in amorphous materials (*14*) and in other polymers (*13*), but the reasons are unclear. Although the calculations presented here do show a corresponding trend, at these lowest temperatures the computational inaccuracies become large. However, the agreement between experiment and theory presented here for PG II is particularly satisfying when one notes that the theoretical (*8*, *15*) and experimental results for poly-L-alanine in both the α- and β-conformations differ by orders of magnitude (*12*).

The results of this work should be of value to those working on theories of proteins, and on aspects of the mode of action of enzymes.

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16 June 1975

Charging for Radioactive Emissions

Abstract. *Radioactive emissions from nuclear power plants can be controlled by using a pollution charge. This is a more effective and simpler procedure than the present method of shutting down plants and leads to a more desirable balance between alternative sources of energy.*

Emissions of radioactive materials in normal operation of nuclear power stations must, according to Nuclear Regulatory Commission (NRC) rules, be kept as low as practicable following the guidelines of the International Committee on Radiological Protection (ICRP). The exact meaning of these words was left to a public hearing lasting 3 years, started by the Atomic Energy Commission and only recently adjudicated by NRC (*1*). This hearing was concerned with the design criteria for power stations using light-water-cooled nuclear reactors (*2*). In the final adjudication, the NCR reaffirmed stringent rules for the design of these plants to reduce radioactive effluents. One basic principle is that a cost-benefit analysis be performed on further reducing the integrated radiation exposure (measured in man-rem, the product of population and radiation dose) to the general public below the stipulated design guides. The NRC proposes a future hearing, but suggests that meanwhile a cost equivalent to $1000 per man-rem be selected as a figure below which it would be deemed worthwhile to install equipment to reduce the dose. This figure of $1000 is very conservative, but we will take it for the purpose of subsequent argument.

On occasion, equipment is defective or unusual operation can occur. Then with continued operation radioactive emissions may temporarily increase above the technical specifications for the power station calculated according to the various rules, including the cost-benefit analysis below. The NRC notes that it would not be appropriate to shut a power station down merely because of a temporary increase of emissions, but the exact mechanism of control is not specified.

It is the purpose of this report to point out that this is a case where a pollution charge should be a very logical and efficient method of control. I do not wish to single out radioactivity as the only case for a pollution charge; pollution charges for sulfur emission control have also been suggested (*3*) for similar reasons. It is important to realize that, like the effects of sulfur emission, the effect of a temporary emission of radioactive material above the technical specification will not be catastrophic (and may even be zero if there is a threshold in the curve of health effect versus dose) so that instantaneous action such as shutdown of the power station is not warranted. Given our present lack of knowledge, it is desirable to be cautious and to encourage prompt correction. As we see in the example below, even assigning a large cost to a dose integrated over population (man-rem) will give a much smaller charge than the effects of some existing power reductions. The question for public policy is, Would it be better to run the nuclear power station with its higher than usual emission, or to forgo the benefits of the electric power generated and shut the station down? Many complex factors will enter into the decision, such as the length of time for which the shutdown will be necessary, the availability of other generating capacity, and so forth. By imposing a pollution charge, this complex question would be put firmly into the hands of the utility company in just the form they are uniquely qualified to deal with—namely, What is the cheapest way to generate electricity?

Therefore, I propose that whenever the emissions from a power station reach a point where action must, under present rules, be taken (I believe that this is when one-half the yearly emission allowed in the technical specification is reached in one quarter) a charge be made in lieu of all other actions, until the ICRP limit of 500 millirems a year is reached. This charge would be calculated on a yearly average to be based on $1000 per man-rem calculated or whatever other sum per man-rem the future NRC public hearing may decide on as appropriate. As noted above, $1000 is a very conservative figure, but a charge based on $1000 per man-rem will usually cost less than shutting a power station down. Using the figures from the recent National Academy of Sciences report on the biological effects of ionizing radiation (*4*), we find that 1 man-rem might (assuming no threshold below which radiation has no effect) cause 10^{-4} cancers; this corresponds therefore to a charge of $10 million per cancer, which is more than society usually spends on cancer-reducing actions (*5*). I would prefer to choose a charge of $100 per man-rem, but even with the higher charge, the examples below show that the pollution charge would be better than power restrictions.

A question might arise about how to calculate the dose effect of the excess emissions. This might arise, in particular, at an existing plant where the effects of such emissions have not been precisely calculated. In such a case the NRC could take an appropriately conservative view, which might then be contested by the power company (or by environmentalists). But all this argument could take place at our leisure, while the power station is still operating. It would clearly not be worth the trouble for a utility company to contest small NRC charges. After an initial flurry of activity, adjudication of charges will not happen too frequently because precedents will be set by the first few cases. At present the NRC asks for prompt reports and action on unusual emissions. The public health problem is calculated on the basis of a dose given all at once, and can only be less if spread out over a long time period. It is only the average over a year or so that counts. Since a utility company would want to reduce the charge it would be expected to take prompt action on its own, and no other immediate action should be necessary.

This might work in a particular case as follows. Under the present system, a 1000-Mwe reactor might be shut down and its contribution to the electrical grid replaced with power from another station that usually utilizes oil. This will be about 40,000 barrels a day. We should take the cost of the last barrels the country buys, presumably imported. This is half a million dollars, which adds this much to our balance of payments deficit. A power reduction to 80 percent of full power costs one-fifth of this—$100,000 a day. To this has to be added a pollution charge for the replacement fuel.

Such power reductions have been ordered at New England power stations, when high site boundary doses (dominated by iodine, with an assumed concentration through the grass-cow-milk-thyroid chain) due to unusual plant releases were calculated. Let us assume the dose goes up to 25