

SHORT COMMUNICATIONS

GEOMETRIES OF GUANINE IN FREE STATE AND IN THIN FILM: NON-PLANAR TO PLANAR MODIFICATION*

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NUCLEIC acid bases have been studied by x-ray crystallography and their geometries are found to be planar¹. However, certain purines have also been found to be non-planar^{2,3}. Quantum chemical geometry optimization calculations yield results for the bases which differ significantly from those obtained by the above method⁴. Of these, the case of guanine is the most prominent. This molecule has been predicted by theory to be appreciably non-planar⁴. It is difficult to resolve such ambiguities since effects of crystal environment on molecular geometry are in general not known. This aspect of guanine has been examined in the present work by a comparative study of vibronic features and intensity distribution in the electronic absorption spectrum of guanine with those of the other bases and benzene. The vibronic structure of benzene is well known, hence it can serve as a standard⁵. Spectra were recorded in on a Hitachi 320 UV/vis spectrophotometer. The solutions used were very dilute giving about 1% absorbance. Thin film of guanine was prepared by putting a dilute solution of the compound in alcohol in a cuvette and then allowing the solvent to evaporate.

Only the spectra of benzene in vapour phase and in aqueous environment and those of guanine in a dilute aqueous solution and in thin film are presented in figure 1. All the spectra have 11 vibronic features, each of which is designated from A to K, have the same structure. The vapour phase spectrum of benzene shows some differences on the lower wavelength side of the region H. It is appropriate to compare the spectrum of benzene

taken in aqueous environment with those of guanine in figure 1. The region C is the most structureless and may be recognized as the transparent region from the infrared absorption point of view. The (0,0) band should lie about 2000 cm^{-1} away on the lower wavelength side of this region. Thus the (0,0) band should be expected in the region F. This is true for benzene and should also be true for the other bases including guanine. As the same vibronic features are present in the spectra of both the molecules, it is clear that a single system constitutes the spectrum lying between 295 and 232 nm which has been studied in this work in each case. If there were two absorption systems in guanine as suggested earlier⁶, the vibronic features would have been quite different in the 260 nm region where the two systems have been suggested to join each other⁶, in comparison to the case of benzene where a single system is known to extend over the whole region.

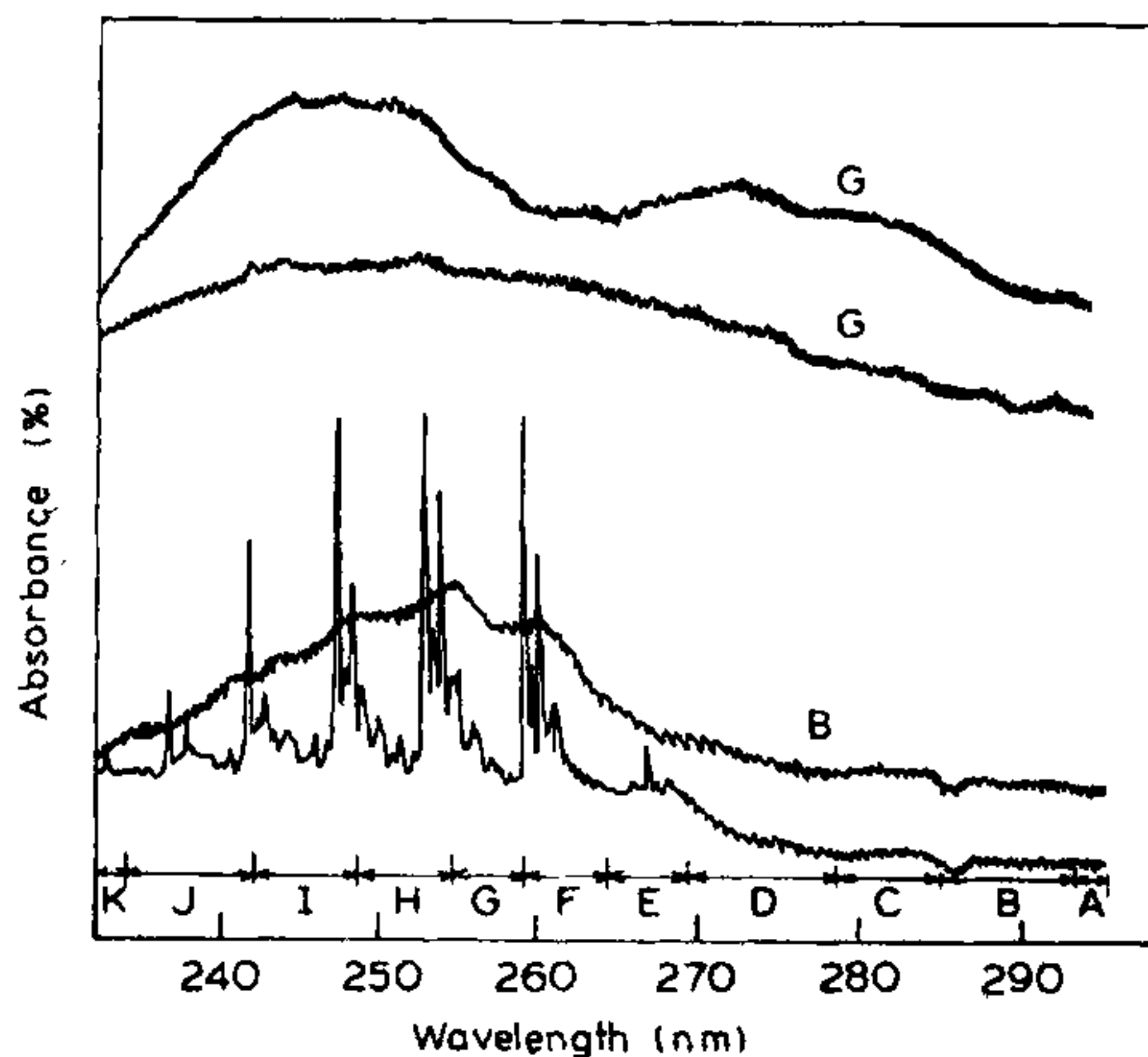


Figure 1. Vibronic features of electronic absorption spectra. The uppermost spectrum is that of guanine (G) in dilute aqueous solution while that just below it is the spectrum of a thin film of the same compound. The spectrum shown with dashes in the lower part is that of benzene (B) in aqueous environment while the other one superimposed over it is of the same molecule in vapour phase.

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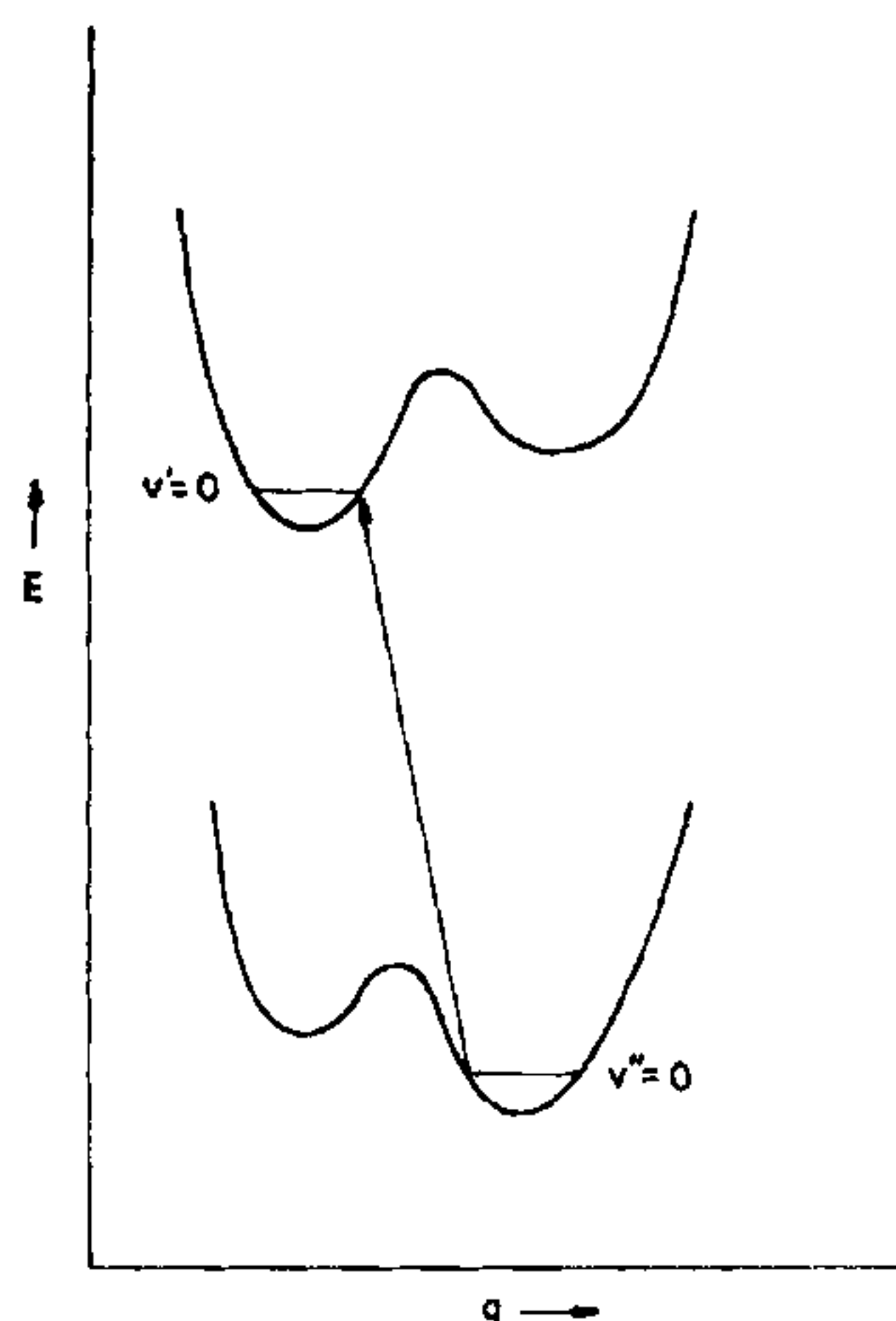


Figure 2 Asymmetric double-well potential hypersurfaces of the ground and excited states of guanine. q is a geometrical variable mainly constituted by folding of the rings. The arrow shows a poor Frank-Condon factor of the (0,0) band region.

It is clear that the strong intensity dip observed in the solution spectrum of guanine around 260 nm does not account for two systems joining each other in this region. Instead, the dip appears to be due to the asymmetric double-well nature of the ground and excited state potential surfaces of the molecule and poor Frank-Condon factor of the (0,0) band region of the spectrum as illustrated in figure 2. This is confirmed by the fact that the strong dip in intensity observed in the solution spectrum of guanine does not appear in the spectrum of the film. The asymmetric double-well potentials are caused by non-planarity of free guanine, its rings being folded at the CC double bond and change in ring folding to the other side of the plane (of planar geometry) following excitation. This possibility is supported by earlier theoretical work on guanine and other bases as well as x-ray crystallographic work on certain purines²⁻⁴. It appears that the molecule becomes planar in the film in both the ground and excited states. This agrees with the results obtained by x-ray crystallography¹. Non-planarity and flexibility of guanine with respect to folding of the rings at the CC double bond has been recently suggested to be of crucial significance in making this base specially suitable for attack by

aromatic hydrocarbon carcinogens which act via intercalation in DNA⁴.

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HYDROGEN DIFFUSION IN LOW TEMPERATURE ANNEALED NICKEL

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THERMOELECTRIC studies of cathodically hydrogenated nickel wires which were previously annealed in vacuum at various temperatures have earlier been reported¹. In all the cases a complete filling-in of the d-band was observed. The present note describes the results for nickel wires annealed at lower temperatures with particular reference to the extent of d-band filling-in:

Sample preparation, annealing procedure, cathodic hydrogen diffusion and thermo emf measurements were as described earlier¹. However, it is appropriate to summarize the interpretation. Figure 1a shows the d-band shape i.e. $n(E)$ vs E curve. The unfilled part of the band lies beyond the Fermi-level. This part of the band gets filled by the electrons donated by the diffused H-atoms. Since the thermo emf is proportional to dn/dE , the curve for this latter function against E is plotted in figure 1b, only for the unfilled part. The process of H-outgassing is just the reverse of filling-in; it will, therefore, start from the higher energy side (T in figure 1a). The mirror image of figure 1b is drawn in