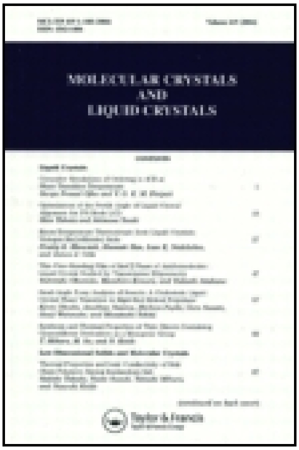

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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D. J. Gibbons [a]

[a] Physics Department, Leicester University, England

To cite this article: D. J. Gibbons (1970): Electronic Structure of the S_8 Molecule and Its Ions and the Transport Properties in the Crystalline Solid and the Liquid, Molecular Crystals and Liquid Crystals, 10:1-2, 137-149

To link to this article: http://dx.doi.org/10.1080/15421407008083491

Molecular Crystals and Liquid Crystals. 1970. Vol. 10, pp. 137–149

Printed in Great Britain

Electronic Structure of the S_8 Molecule and Its Ions and the Transport Properties in the Crystalline Solid and the Liquid

D. J. GIBBONS

Physics Department
Leicester University‡
England

Received January 5, 1970

Abstract—Recent work by a number of different authors on mobility of electrons and holes in both crystalline and molten sulphur has shown that this material possesses interesting and unusual transport properties. In this paper an attempt is made to interpret these properties in the light of the electronic structure of S_8, S_8^- and S_8^+. A number of relevant intramolecular and intermolecular overlaps are calculated to show that the electron band is sufficiently narrow for a Franck-Condon molecular distortion to accompany the motion of the carrier. Reasons are presented indicating that this distortion is the same that takes place when S_8 is ionized in solution when either the positive or negative ion is formed. It is shown that the most likely rearrangement involves a flattening of the molecule and a change of at least some of the sp^3-orbitals to sp^2-hybrids.

1. Introduction

Experimental studies in recent years on the electron and hole mobilities in sulphur have led to a fairly clear-cut picture of carrier transport in solvent-grown crystals,[1–5] vapour-phase grown crystals,[5] natural crystals[6] and in the liquid state.[9] A careful study of the optical properties or orthorhombic crystals[10] has also added considerably to our knowledge of this interesting example of an elemental molecular solid. All these measurements are substantially in agreement with each other.

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‡ Now at the Central Research Laboratories of E.M.I. Ltd., Hayes, Middlesex.

The experimental evidence shows that the fundamental hole mobility in the solid is consistent with transport within a narrow band; the room-temperature lattice mobility is about 10 cm^2 V^{-1} s^{-1} and this mobility decreases with increasing temperature, suggesting scattering by lattice vibrations. Evidence also emerges, particularly at lower temperatures, of the presence of shallow traps with which the hole interacts during transit across the crystal to give rise to an activated mobility. The electron transport in the solid, on the other hand, is an activated process over the entire temperature range from − 100 °C to + 119 °C and its room-temperature value is only 6×10^{-4} cm^2 V^{-1} s^{-1}; this transport is interpreted in terms of an intermolecular hopping mechanism.[2,3,11]

Measurements on sulphur beyond the melting-point show that both holes and electrons "hop" and that between 110 °C and 160 °C the magnitudes of their mobilities are similar, viz. 10^{-4} cm^2 V^{-1} s^{-1} at 120 °C. A significant fact which became prominent in this investigation was that the hopping activation energy for both signs of carrier was the same as that for electrons in the solid.

In the light of these results, the electron band in the solid would be expected to be very much narrower than the hole band. In addition, the experimental results suggest that the excess electrons interact strongly with molecular vibrations, and that holes also do this in the liquid. By fitting experimental mobility results to the theories of hopping transport developed by Yamashita and Kurosawa[15] and Holstein,[16] it has been shown that the excess electron is localized on a molecule for many periods of molecular vibration. The above transport theories involve the electron-lattice interaction parameter, γ, defined by

$$\gamma = \frac{E_b}{\hbar\omega_0} \qquad (1)$$

The electron is assumed to interact predominantly with vibrational modes of frequency ω_0, and E_b is the polaron binding energy. By careful curve fitting, it was shown[3] that four of the most prominent fundamental I.R. absorption peaks lie between the limiting values of γ in the range $\gamma = 17$ to $\gamma = 27$. The average value of E_b corresponding to these modes is 0.48 eV.

Two main questions arise out of these interpretations of mobility:

(1) What is the fundamental reason for the marked differences between the electron and hole bandwidths in the solid?

(2) Can we account for the strong vibrational interaction and the large polaron binding energy for electrons in the solid and for both electrons and holes in the liquid?

2. Electronic States of the Neutral S_8 Molecule

As a first step towards an understanding of these results, it is necessary to enquire into the electronic structure of the isolated S_8 molecule. In a molecular solid or liquid, one would expect a fairly close correspondence between this and the band structure of the condensed state. The S_8 positive and negative molecular ions are discussed in section 4.

The neutral sulphur molecule is in the form of an eight-numbered puckered ring.[17] It is a normal practice to describe the bonding in terms of sp^3 hybrids.[19] Two hybrids per atom are occupied by lone pairs and the remaining two are engaged in forming single covalent bonds with neighbouring sulphur atoms in the ring.

The orientation of the MOs which accommodate the unshared pairs and those which are bonding is shown in Fig. 1(b) and (c).

The orientation of the atomic orbitals with respect to four adjacent atoms in the S_8 ring was calculated to be as shown in Fig. 2.

Atomic orbital overlap integrals between all orbitals centred on two adjacent atoms in the ring were calculated for single Slater neutral sulphur 3s and 3p wavefunctions with an orbital exponent of 1.817 A.U. determined from Slater's rules.

Using the notation of Fig. 2 the overlap matrix was calculated to have the following numerical values:

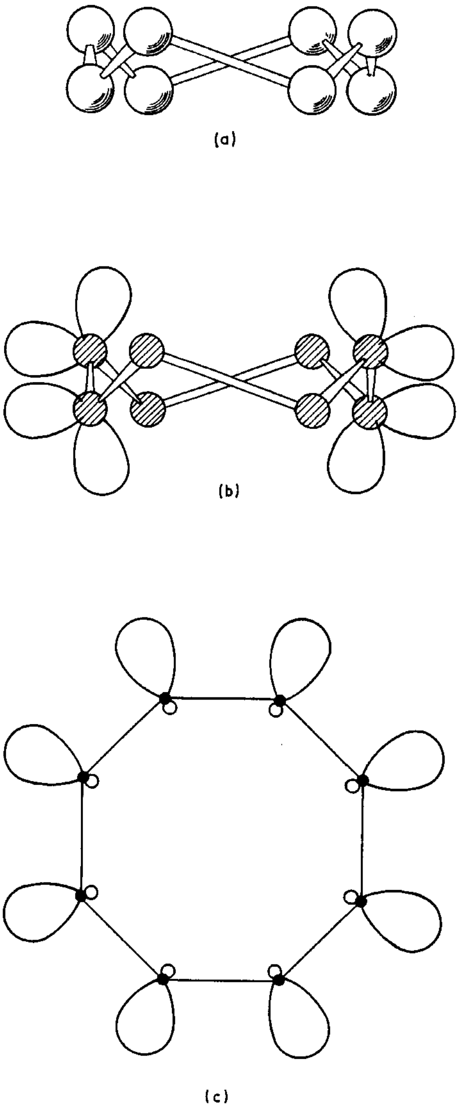

Figure 1. The shape and structure of the neutral S_8 molecule. (*a*) The S_8 puckered ring, (*b*) side view in the median plane showing orientation of lone-pair orbitals, (*c*) perpendicular to the median plane.

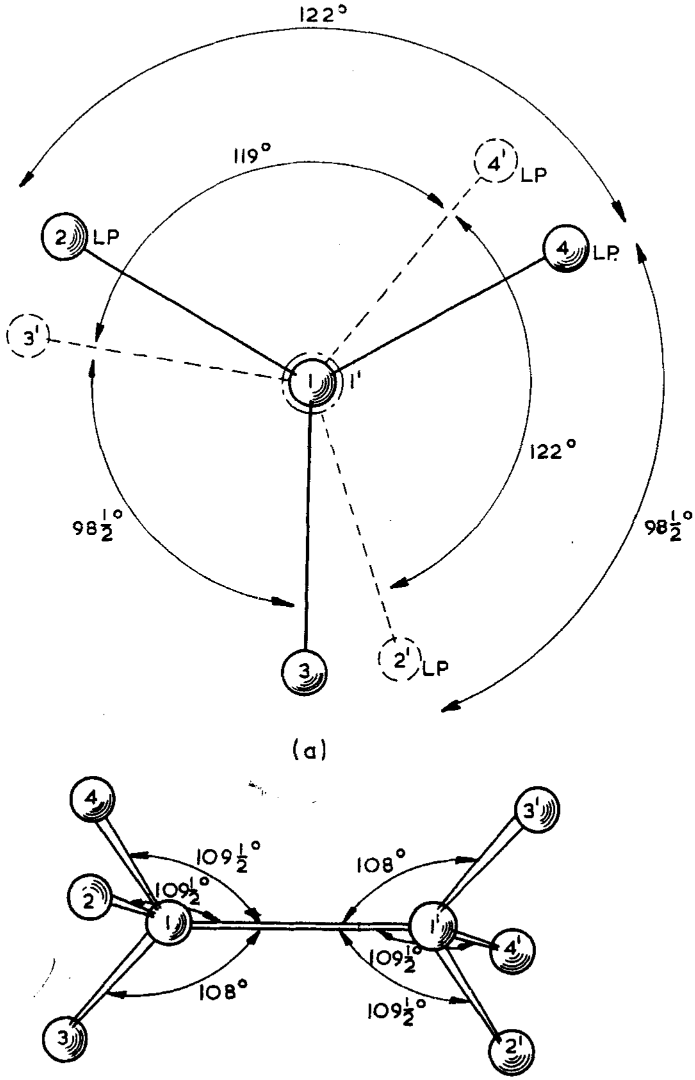

Figure 2. Relative orientation of the principal axes of the sp^3-hybrid atomic orbitals centred on two adjacent sulphur atoms in the neutral S_8 ring. (*a*) View looking along the direction of one S—S bond, (*b*) view perpendicular to a bond. Orbitals denoted by 1, 1′, 3 and 3′ are all bonding.

$$\langle\psi|\psi'\rangle = \begin{pmatrix} 11' & 12' & 13' & 14' \\ 21' & 22' & 23' & 24' \\ 31' & 32' & 33' & 34' \\ 41' & 42' & 43' & 44' \end{pmatrix}$$

$$= \begin{pmatrix} .572 & .073 & .066 & .073 \\ .073 & -.059 & +.009 & -.064 \\ .066 & .087 & -.009 & -.064 \\ .073 & -.007 & -.064 & +.084 \end{pmatrix}$$

Examination of this intramolecular overlap matrix shows that the overlap between bonding hybrids is nearly an order of magnitude larger than that between any other pair. The magnitudes of these overlaps suggest that, to a first approximation, interactions between the bonding orbitals and the lone pair orbitals can be neglected.

Figure 3 shows what happens if a molecule is built-up by bringing together eight isolated atoms. The energy level scheme of the molecule is shown qualitatively in the same figure, together with the notation adopted. It can be easily shown that the 48 outer shell electrons in the molecule exactly fill the σ, π and π^* orbitals and leave the σ^* system unoccupied.

In the solid, neighbour interactions between nearby molecules broaden the molecular energy levels into energy bands. The band picture is shown qualitatively in Fig. 3. This suggested scheme[11] is strongly supported by interpretation of the vacuum ultraviolet spectrum of S_8.[10]

The equal mobilities and hopping activation energy for electrons and holes in the liquid could not be explained in terms of the band scheme shown in Fig. 3 however. The description of the bonding given above for neutral S_8 is not very satisfactory for its ions, and it is therefore not surprising that an alternative band scheme for S_8^+ and S_8^- is needed.

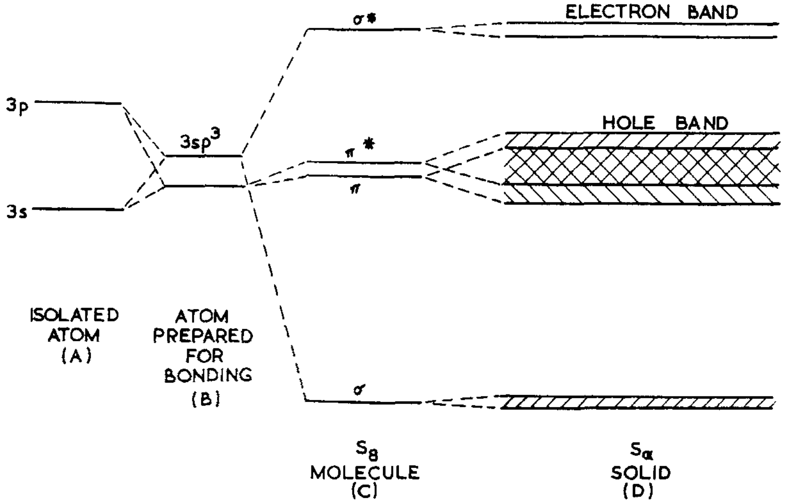

Figure 3. Diagram showing how the energy band scheme in either the solid or liquid would be derived from the energies of the isolated atoms. No Franck-Condon shifts are shown here.

3. Bandwidths in Orthorhombic Sulphur

It is possible to obtain an approximate width of the electron band in the orthorhombic solid in terms of the experimentally measured mobility of holes. Since this transport can be described in terms of normal band motion, we can use the condition derived by Fröhlich and Sewell[21] that

$$\frac{m^*_h}{m} \geqslant \frac{30}{\mu} \cdot \frac{300}{T} \cdot \tag{2}$$

This leads to an effective hole mass, $m^*_h \geqslant 3m$ for $\mu_h = 10$ cm^2 V^{-1} s^{-1} at 300 °K. We can now estimate the bandwidth, W_h, by using as a first approximation the Bloch tight binding scheme applied to the case of a simple cubic lattice. Substituting for m^* we obtain

$$W_h \geqslant \frac{2h^2}{ma} \tag{3}$$

The approximate width of the electron band can now be ob-

tained by a comparison between the intermolecular integrals, because, using the tight binding scheme as before $W_h/W_e \sim J_h/J_e \sim S_h/S_e$, where W is the carrier bandwidth, J is the intermolecular exchange integral and S is the intermolecular overlap.
With an average spacing of molecules of 5.95 Å, this leads to an estimate for the maximum width of the hole band of 0.4 eV. This may be compared with a value of about 0.8 eV suggested by interpreting the optical data in Ref. 10.

Intermolecular orbital overlaps were calculated but in view of the small magnitudes of overlaps between atomic orbitals not centred on adjacent atoms in the ring, molecular orbitals were constructed by taking a linear combination of only two atomic wavefunctions in the case of electrons and only four in the case of holes.

The hole band in the absence of any Franck-Condon shift, will be formed from the highest antibonding lone-pair states, π^*, and the electron band from the antibonding σ^* states.

In order to aid in identifying the overlaps calculated in the present paper, the environment about one molecule has been simplified in Fig. 4 where the open circles denote the centres of neighbouring molecules. Below the diagram is a table in which the largest overlaps between electron molecular orbitals and between hole states have been calculated using accurate crystallographic data for the unit cell.[17] It can be seen that the overlap between electron states is smaller by a factor of at least 40 than that between hole states. With a value of $S_h/S_e = 40$, the maximum electron bandwidth comes to 10^{-2} eV.

These crude arguments clearly claim no great accuracy, but they do indicate that the electron bandwidth in the solid is considerably narrower than the hole bandwidth and furthermore that the electron bandwidth may well be small compared with kT.

4. The Molecular Ions

Before we can estimate the bonding in S_8^+ and S_8^- it is necessary to calculate the extent to which the odd hole or electron is localized

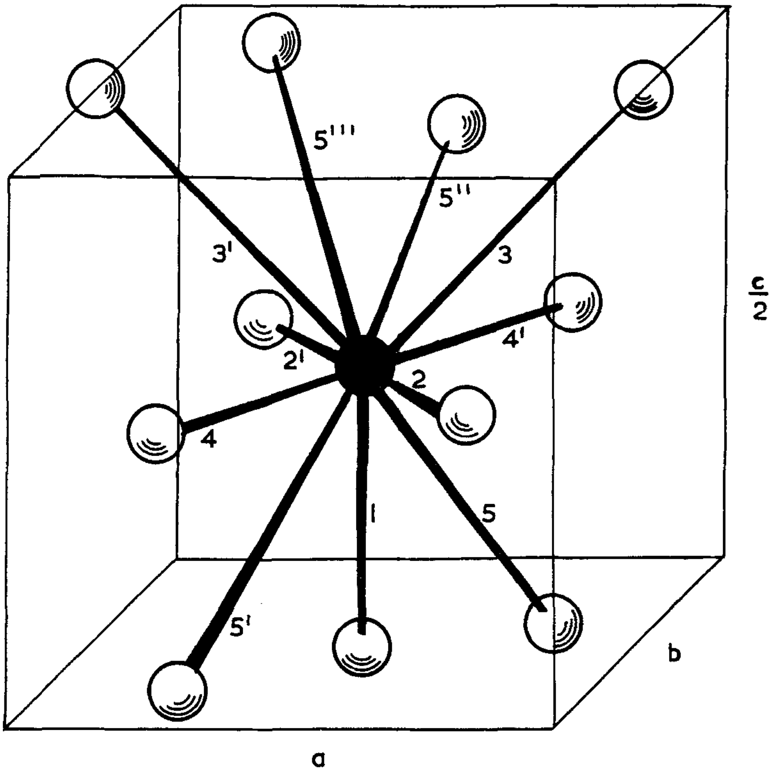

Figure 4. Simplified diagram of the environment about one molecule in orthorhombic sulphur to aid in identifying the overlaps calculated. The table below gives the calculated intermolecular overlaps using accurate crystallographic data.

OVERLAP	ELECTRONS	HOLES
1		2×10^{-3}
2	10^{-3}	3×10^{-3}
3	5.6×10^{-3}	3.5×10^{-3}
4		2×10^{-3}
5		3×10^{-3}

between two adjacent sulphur atoms in the molecule. In the absence of any Franck-Condon shift, transitions round the ring are governed by overlaps between purely electronic wavefunctions corresponding to the initial and final states. Using the Slater wavefunctions, these overlaps were calculated to be 1.2×10^{-3}

and 4×10^{-3} respectively. These overlaps are sufficiently small for the carrier to be localized between two sulphur atoms in the ions for several periods of molecular vibration. Thus, in a discussion of S_8^+ and S_8^- it is valid to make a comparison with radicals having a similar single bond between only two atoms. In the present case, the two molecules for which data are available and in which the bonding is strictly comparable are $N_2H_4^+$ and Cl_2^- respectively.

In the Cl_2^- ion it is shown that the unshared electron occupies a pure p-orbital and that the sp^3 bonding hybrids of the neutral molecule change to sp^2 hybrids upon ionization.[12,20] Spectroscopic data provides evidence to show that this change is accompanied by considerable internuclear expansion.[14] As far as the bonding in the isolated S_8^+ ion is concerned, the following model has been suggested.[18] The unpaired electron would occupy a *p*-orbital of a single sulphur whose density axis is perpendicular to a plane containing this atom and its nearest neighbours. Thus there would be a π-bond, with three electrons between two sulphurs; these would be coplanar with two more, the π-bond being constructed from pure *p*-orbitals. This unit has something in common with a radical which was recently studied by e.s.r. techniques, namely $N_2H_4^+$. This radical appears to be planar with a three-electron π-bond.[7] Obviously, at least part of the S_8 molecule would have to flatten when either sign of molecular ion is formed. If only part of the molecule flattens then the odd hole or electron would be self-trapped between two sulphurs in the ring, whereas, if all the orbitals change to non-equivalent sp^2-hybrids then the unpaired electron would be mobile round the ring in a π-system similar to that in the benzene molecular ions.

Such a drastic orbital rearrangement is only possible in the fairly isolated molecule. It could only take place in the solid or liquid if the carrier were localized on one molecule for a time comparable with the period of molecular vibration. From the experiments, the probability that an electron makes a site jump is 10^{+9} sec^{-1} at room temperature,[2,3] so that such a rearrangement is possible. However, the much wider hole bandwidth in the solid implies that the localization of the hole is unsufficiently long for any appreciable rearrangement to take place. But, in the liquid, with smaller average overlap for holes, this model would apply and it may also occur in the solid if lattice defects locally reduce the normal overlap[8]. Thus the thermal activation energy of 0.19 eV observed for these shallow hole traps[1] would consist entirely of vibrational interaction energy.

5. Discussion

The models developed in the preceding sections give a satisfactory explanation of the observed transport and optical properties of sulphur, both in the crystalline and the liquid state. In particular the analysis clarifies the reasons why two fundamentally different transport mechanisms, intermolecular hopping for electrons and polaron band conduction for holes, occur in crystalline S. The electron band is sufficiently narrow both in the solid and in the liquid for strong vibrational interaction to take place; the same occurs for holes in the liquid. By taking into account the almost equal mobilities of both electrons and holes in the liquid and the comparison in Section 4 of the S_8 ions with the behaviour of Cl_2^- and $N_2H_4^+$ has led to the conclusion that the localization of the excess carrier should result in a flattening of part (or all) of the puckered S_8 ring. From the far infrared vibrational spectrum of S_8 and the assignments of Ref. 13, the mode corresponding to a flattening of the molecule is designated as A_1; in this weakly dispersed mode, the atoms vibrate alternately up and down with respect to the median plane. The energy of the A_1 fundamental is 0.0265 eV and it was shown in Ref. 3 that if this is the only mode involved, a fit can be made to the experimental mobility results most satisfactorily if $\gamma = 18$. This being the case, since $E_b = \gamma\hbar\omega_0$, the polaron binding energy turns out to be 0.48 eV, as previously quoted.[3,9] It is believed that this is the first time that true hopping conduction in a molecular insulator has been supported strongly by all the available experimental evidence.

The presently available data are not sufficient to decide unequivocably whether the whole molecule or only part of it flattens.

Acknowledgements

This work was started when the author was on the staff at Leicester University and more recently completed at the Research Laboratories of E.M.I. Ltd. Encouragement and discussion throughout with Professor W. E. Spear has been much appreciated. Permission to publish given by the Directors of Electric and Musical Industries Ltd. is also gratefully acknowledged.

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