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Density of states in the gap of a disordered material using E.S.R./optical correlations

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ABSTRACT

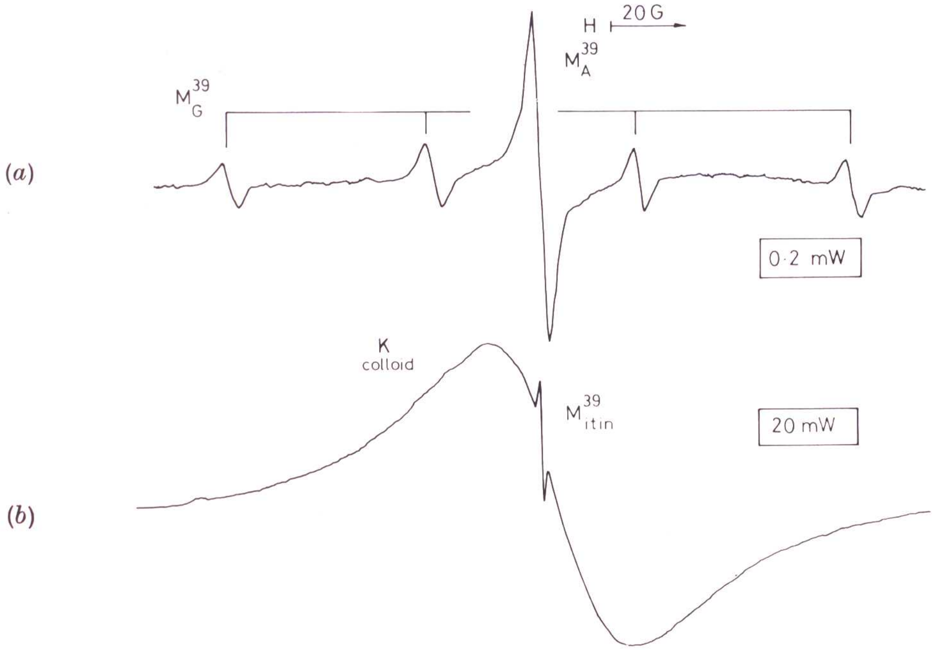
Electron-spin-resonance studies of rapidly frozen solutions of alkali metals in anhydrous hexamethylphosphoramide (HMPA) indicate the presence of several, distinct localized electron states. Optical studies of similar species in a variety of fluid solutions reveal a simple correlation between the optical transition energy and the degree of occupation of the alkali-metal *ns* orbital. From this information we evaluate a distribution function for the various (localized) paramagnetic states present in the low-temperature disordered system. The localized states assume only a few, discrete eigenstates within the host (HMPA) bandgap. We speculate on the possible origin of these states; particular emphasis is placed upon the influence of lone-pair electrons and steric effects in determining the molecular configurations of the host matrix around the alkali atom during the quenching process. We point out the striking similarities between the eigenfunctions/eigenstates of matrix-bound states and the excited electronic states of alkali atoms in the gas phase. It is suggested that the existence of a variety of (matrix-induced) local potential fields around the alkali atom in the condensed system essentially reproduces the overall behaviour of the valence (*ns*) electron of the isolated (gas phase) alkali atom in its excited electronic configurations.

§ 1. INTRODUCTION

Hexamethylphosphoramide, $((CH_3)_2N)_3PO$: HMPA, is a typical organic insulator with a wide bandgap (>6 eV) separating a filled valence band from an empty conduction band. When solutions of alkali metals ($\sim 0{\cdot}1$ mole per litre) in HMPA are cooled rapidly to 77 K, crystallization is inhibited and homogeneous blue (vitreous) solids are produced (Catterall and Edwards 1975 a, b). The alkali metal is trapped in a variety of states, but greater than 99% of the metal forms deep diamagnetic (electron spin-paired) states, best described as solvated alkali cations (M^{+}_{solv}) and anions (M^{-}_{solv}) (Catterall and Edwards 1975 b, Brooks and Dewald 1968, Dye 1973). We are not primarily concerned with these states in this communication. A small fraction ($<1\%$) of the metal, however, forms donor states of overall atomic stoichiometry M^{0}_{solv} ($\equiv M^{+}_{\text{solv}} + e^{-}_{\text{solv}}$), but with varying degrees of occupation of the alkali-metal *ns* wavefunction. We have previously identified seven localized states and one itinerant (completely delocalized) electron state *coexisting* in these materials (Catterall and Edwards 1975 a, b, 1976 a, b, c, 1977).

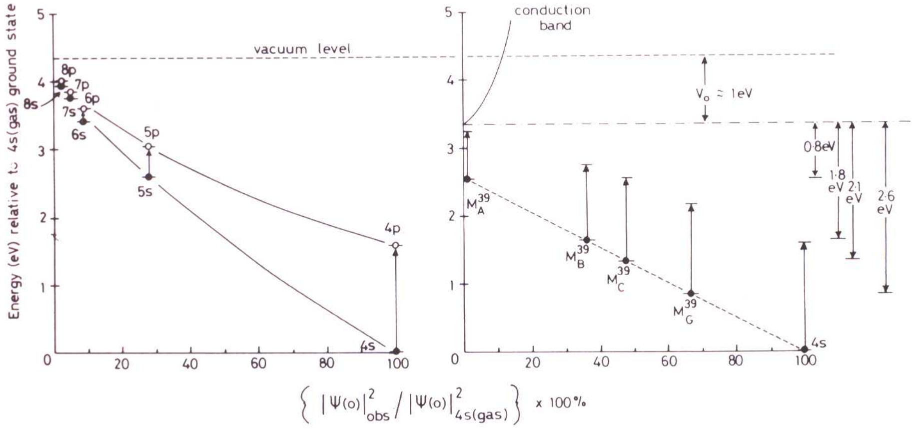
Each state gives rise to a characteristic electron-spin-resonance (E.S.R.) spectrum (fig. 1). The spectra of the localized states comprise hyperfine multiplets of lines of Gaussian shape (evident *only* at low incident microwave power levels, *ca.* 0·2 mW, see fig. 1 (*a*)) whilst the itinerant electron state gives rise to a narrow singlet resonance of Lorentzian shape (evident *only* at high microwave power levels, *ca.* 20 mW, fig. 1 (*b*)). The intrinsic differences between electron spin-lattice relaxation times for the localized- and itinerant-electron regimes are entirely responsible for their experimental distinction at low and high microwave power levels (Edwards and Catterall 1979). These properties, together with microwave saturation effects, are used to characterize the various paramagnetic entities, and fig. 2 shows identified resonances from the various localized electron states in a frozen rubidium-HMPA solution.

Fig. 1



Electron-spin-resonance spectra (77 K) of a rapidly frozen solution of potassium in hexamethylphosphoramide. Spectra were recorded at (*a*) low and (*b*) high microwave power levels. The isotropic quartet and narrow Gaussian absorption observed at 0·2 mW originate from *localized* electron states having electron spin-lattice relaxation times (T_{1e}) of the order of 10^{-2} s. The broad Lorentzian line at high power levels (*b*) arises from colloidal potassium metal particles ($T_{1e} \sim 10^{-9}$ s). The narrow resonance ($M^{39}{}_{itin}$) evident at 20 mW (again of Lorentzian form) originates from spin transitions of *itinerant* electrons in a metallic impurity band within the host (HMPA) bandgap ($T_{1e} \sim 10^{-8}$ s).

Fig. 5



(*a*) (*b*)

Eigenenergies and eigenfunctions of gaseous and matrix-bound states of the potassium atom : In (*a*) the energies and *ns* orbital occupation factors of the ground (4*s*) and excited (5*s*–8*s*) states of the gas-phase potassium atom are indicated. The limiting situations are : (i) the 4*s* ground state ($\Phi = 100\%$) located at 4·339 eV) relative to the vacuum (ionization) level ; and (ii) the ionization limit for the free atom, $\Phi \rightarrow 0$ as $n \rightarrow \infty$. In (*b*) we show the corresponding situation for (localized) donor states in rapidly quenched potassium HMPA solutions using eigenfunctions obtained from our E.S.R. studies (see the table). In this case the limiting situations are : (i) the 4*s* isolated atom (as in (*a*) with $\Phi = 100\%$) ; (ii) the series-ionization limit in the condensed medium (see text).

locates the respective electron states relative to the (ionization-limit) vacuum level (located 4·339 eV above the potassium 4*s* level, i.e. the ionization potential of the 4*s* state). We can therefore set *approximate* values to the corresponding eigenenergies for the localized donor states, $M^{39}{}_A$–$M^{39}{}_G$ of potassium in the bandgap of HMPA†. For this purpose, the energy V_0 of an electron in the lowest quasi-free level (conduction band) relative to the vacuum level has been estimated as approximately -1 eV (Edwards 1974, Edwards and Catterall 1977). This estimate is based on the Wigner–Seitz model for the quasi-free electron state in polar fluids (Springett, Cohen and Jortner 1968) where V_0 represents the combination of the short-range (repulsive) energy contribution and the long-range (attractive) polarization energy.

Since the atomic character of the itinerant electron states is extremely small ($<0{\cdot}1\%$, see the table), we can reasonably locate $M^{39}{}_{\mathrm{itin}}$ as being very close to the host conduction-band edge—that is, consistent with our description of the state in terms of a narrow impurity band split off from the host

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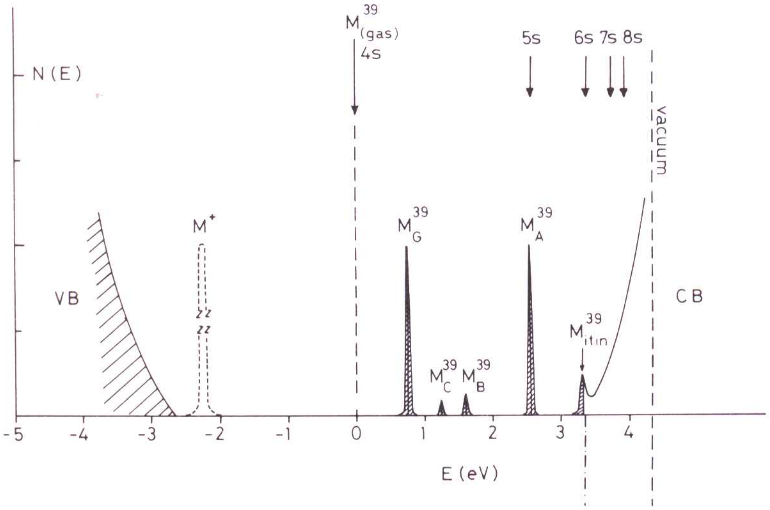
† Unrestricted Hartree–Fock SCF calculations on the model system $Li(NH_3)_4$ essentially reproduce the approximate trends suggested by our analysis of optical and magnetic data (R. Catterall, unpublished results). The ground-state energy of the spin orbital containing the unpaired electron increases as the electron (spin) is delocalized onto the surrounding medium.

conduction band (Catterall and Edwards 1975 a, b). We locate the M^+_{solv} state close to the valence-band edge since the bonding to the host solvent in this case must be very strong (Guttermann 1968, Allegria, Fontanez and Stevenson 1976).

The strong dependence of the E.S.R. linewidth on the nuclear spin quantum number (figs. 1 and 2) can be quantitatively interpreted (Catterall and Edwards 1975 a) in terms of a very small statistical range of coupling constants around the average value (see the table) for each of the localized electron states. Such an analysis yields (directly) the distribution function for the various paramagnetic entities (Catterall and Edwards 1975 a). In this manner we arrive at a representative picture (fig. 6) of the electronic density of states for rapidly quenched potassium-HMPA solutions.

Fig. 6

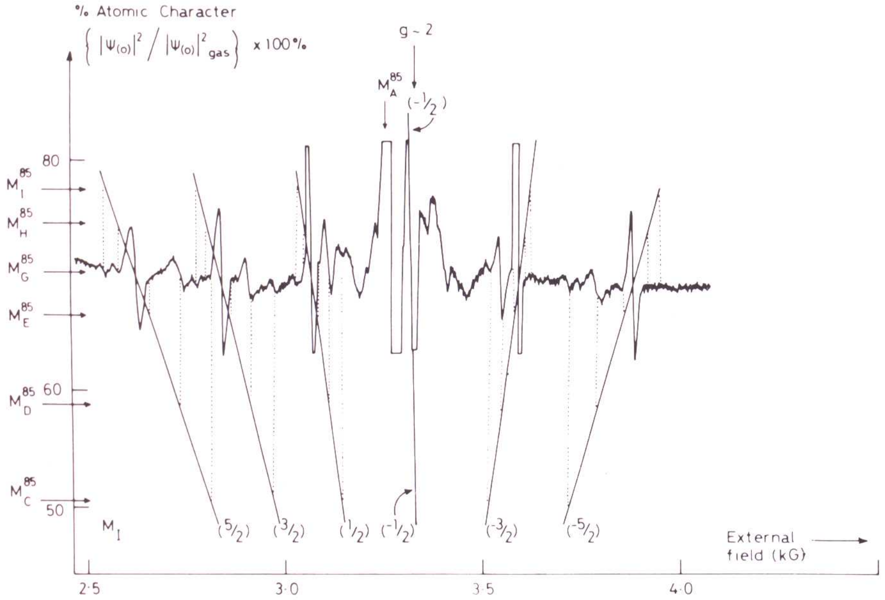


A representative picture of the electronic density of states for rapidly quenched potassium-HMPA solutions (77 K). Energies are defined relative to the ground and excited states of the gas-phase potassium atom (arrows indicate the appropriate positions of the ground (4*s*) and excited states 5*s*–8*s*).

§ 3. ORIGIN OF LOCALIZED STATES IN THE GAP

Our observations (encompassed in fig. 6) of a series of characteristic excess-electron states requires further comment. The discrete nature of these states, coupled with the reproducibility of results (Catterall and Edwards 1976 c) and the absence of any significant anisotropy in the E.S.R. spectra (fig. 1), rules out the possibility of *random* freezing-in of defect centres, etc. Rather, we believe they are a manifestation of an intrinsic property of the disordered (host) material which allows donors to assume only a few, discrete eigenstates within the bandgap. The range of states observed (fig. 6) represent fractionally distinct trapping sites associated with various local environments around the donor (alkali) atom.

Fig. 2



Electron-spin-resonance spectrum (77 K) of a rapidly frozen solution of rubidium in hexamethylphosphoramide. The full lines show the predicted variation of resonant-field position with the per cent occupancy of the rubidium 5*s* orbital. M_I is the nuclear spin quantum number of the rubidium-85 nucleus. The full lines are all fixed at the experimental line positions of the six allowed electron spin transitions of the species $M^{85}{}_G$ (rubidium-85 isotope 69·43% atomic character). Resonances from the variety of localized electron states ($M^{85}{}_A$–$M^{85}{}_I$) are indicated, as well as the per cent occupation of the rubidium 5*s* orbital for each of the centres.

We find (see the table†) that the localized states, labelled $M^X{}_I$ to $M^X{}_A$ on a system of nomenclature outlined elsewhere (Catterall and Edwards 1976 a), have markedly different electronic wavefunctions. These range from perturbed ‘ atomic ’ functions, possessing considerable parentage in the electronic states of the isolated (gas phase) alkali atom, to weakly-localized variants in which there is a predominant leakage of electron (spin) density away from the cation-core ($M^+{}_{solv}$) onto the surrounding medium. Accompanying this partial delocalization of the wavefunction into the bulk medium is a corresponding decrease in the alkali-atom parentage. In addition the itinerant electron state ($M^{39}{}_{itin}$, fig. 1), having very little parentage in the atomic states (see the table), arises from the formation of a narrow impurity band split off from the host (HMPA) conduction band (Catterall and Edwards 1975 b, 1977).

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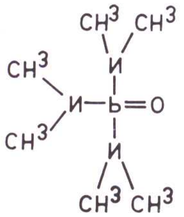
† Paramagnetic states are classified in terms of their percentage occupancy of the appropriate alkali-atom *ns*-orbital ; labelling alphabetically from the lowest atomic character state ($M^X{}_A$, *ca.* 1%) to the highest ($M^X{}_I$, ca. 80%). Superscripts denote the mass number of the particular isotope.

Ovshinsky (1976) has pointed out that the absence of long-range order in a disordered material, coupled with the intra- and inter-molecular dipole interactions associated with electron lone-pairs, can result in a few discrete localized states lying within what would otherwise be the bandgap of a completely ordered (crystalline) material. We believe that the alkali metal-HMPA glasses are best regarded in this light. A representation of the structure of HMPA is given in fig. 7. The molecule is pyramidal with a symmetrical distribution of positive charge over the (N_3P) grouping. A high electron density on the exposed oxygen atom gives rise to a large dipole moment (5·54 Debyes) and an unusually high basicity (electron-donating ability). In fact, HMPA is one of the most powerful *cation*-solvators known, and the importance of the oxygen lone-pair in the chemistry of HMPA has been recognized for some time (Normant 1967, Guttermann 1968). The temperature dependence of the low-frequency dielectric constant (K_{st}) of HMPA has been reported by Dubois and Viellard (1965). At 25°C, K_{st} has a value (29·64) similar to that of liquid ammonia (Burow 1966). On cooling to 6°C, K_{st} increases to 33·16 ; this behaviour is typical of polar liquids where a decrease in temperature usually ensures less thermal agitation of molecular dipoles and a concomitant increase in the dipole-response to an applied electric field. This increase is usually indicative of free rotation of molecules in the liquid state (Kittel 1963). However, close to the freezing point of HMPA (~ 4°C), K_{st} *decreases* rapidly to a value (~ 19) more typical of the alkylated amines (Cronenwett 1973). This trend represents a departure from the usual behaviour of polar-liquids approaching, or crossing, the freezing point. A decrease in K_{st} far below the melting point is generally interpreted (Kittel 1963) in terms of the freezing-in of certain *specific* configurations of the matrix. That this effect is observed in HMPA so close to the freezing point appears to us to be indicative of specific (oxygen) lone-pair interactions coupled with the bulky nature of the molecule.

Fig. 7



A representation of the structure of hexamethylphosphoramide.

Here, we believe, is an indication of the origin of the localized states in the gap. The specific configurations of the matrix are simply a manifestation of the various interactions between lone-pair electrons and their local environment (including the donor atom). These interactions lead to different molecular configurations (and polarization fields) around the alkali (donor) atom during the quenching process. A high polarization field surrounding

Per cent atomic character for localized (M_A to M_I)- and itinerant (M_{itin})-electron donor states in alkali metal-HMPA glasses.

Species / Isotope	Localized states									M_{itin}†
	M_I	M_H	M_G	M_F	M_E	M_D	M_C	M_B	M_A	
Li^6	—	—	—	—	—	—	—	—	~1	~0·5
Li^7	—	—	—	—	—	—	—	—	1·0	~0·5
Na^{23}	—	—	62·78	—	—	47·49	—	—	—	~0·5‡
K^{39}	—	—	66·64	—	—	—	47·34	36·62	0·97	~0·5
Rb^{85}	76·80	74·23	69·43	—	64·57	58·94	49·60	—	0·41	~0·2§
Rb^{87}	—	—	69·63	—	—	57·92	—	—	—	—
Cs^{133}	79·9	73·8	73·08	72·6	67·7	60·2	—	—	0·23	~0·1

† For the itinerant electron states, the unpaired *s*-electron density $\langle|\psi(0)|^2\rangle_F$ represents the *s*-electron probability amplitude at the alkali nucleus *averaged over all states at the Fermi level*. This is related to the spin density of the appropriate localized centre (M_A) via $\xi = \{\langle|\psi(0)|^2\rangle_F / |\psi(0)|^2_{M_A}\}$ where ξ is the 'penetration-factor' (Knight 1956). For the alkali metals, ξ typically takes the values 0·44 (Li) and 0·55 (Na). For our purposes, we set $\xi = 0{\cdot}50$.

‡ Value obtained for a frozen solution of Na/K (alloy) in HMPA.

§ The observed spin-resonance signals from the states M^{85}_A to M^{85}_I are shown in fig. 2.

In this communication we report a correlation between the optical and magnetic properties of these localized states which enables us to evaluate approximate eigenenergies for the various paramagnetic entities lying in the host (HMPA) bandgap. We further speculate on the origin of these localized states in the gap.

§ 2. CHARACTERIZATION OF DONOR STATES ; THE PASSAGE FROM EIGENFUNCTIONS TO EIGENENERGIES

We have characterized the donor states in this system using E.S.R. to estimate a value for $|\psi(0)|^2_M$, the square of the modulus of the unpaired electron density at the metal nucleus. That is, the contribution of the (alkali) atomic *s* state to the overall eigenfunction of the donor state. By reference to the value $|\psi(0)|^2_{gas}$ for isolated (gas phase) alkali atoms (Kusch and Hughes 1959) we are then in a position to specify, in quantitative terms, the parentage or identity of paramagnetic states lying in the bandgap (Cohen 1971, Webber, Rice and Jortner 1965). A detailed account of the procedures involved is given elsewhere (Catterall and Edwards 1976 c). Observed values of $|\psi(0)|^2_M$ range from near zero to approximately 80% of the value observed for the gas-phase alkali atoms (see the table).

The optical absorption spectra of similar species in various fluid solutions have recently been measured (Seddon, Fletcher and Catterall 1977, Catterall, Slater, Seddon and Fletcher 1976). These transient (short-lived) species are formed by reaction of solvated alkali cations (M^+_{solv}) with solvated electrons (e^-_{solv}) produced by a 0·3 μs pulse of 2·25 MeV electrons.

$$e^-_{solv} + M^+_{solv} \rightarrow (M^0_{solv}).$$

the alkali metal would lead to a considerable reduction in the cation–electron Coulomb interaction and a corresponding large leakage of unpaired spin (electron) density onto the surrounding medium (Kohn 1957). Smaller potential fields would give rise to weaker perturbations on the gas-phase states of the alkali atom and a large spin density at the alkali-metal nucleus. Accompanying this is an immediate recognition of the extent of the parentage of the donor states ($M^{39}{}_A$–$M^{39}{}_G$ in fig. 6) in the states of the (gas-phase) isolated alkali atom (Webber *et al.* 1965).

Thus, the alkali *ns* electron wavefunction serves as a direct probe for the local potential fields associated with the various inter- and intra-molecular lone-pair interactions. At room temperature, various configurations fluctuate rapidly and E.S.R. spectra represent only a time-average of characteristic resonances from each state (Catterall and Edwards 1975 a, Catterall 1970). However, by the technique of rapid-quenching, thermal fluctuations are minimized and the various configurations are frozen in position sufficiently long to be detected in our E.S.R. experiment.

It is of interest to compare the results of freezing HMPA solution with those reported previously for potassium–ammonia solutions (Catterall 1970). In that case the solvent also possesses lone-pairs but, in the absence of pronounced steric effects from large molecular units, there is a much stronger tendency for the system to crystallize upon cooling. Even when crystallization is inhibited by the addition of structure breaking alkali halides, only a single E.S.R. line is observed (Catterall 1970).

Finally, we wish to point out the general similarities between the eigenfunctions and eigenenergies of these ‘ matrix-bound ’ states and the excited electronic states of the alkali atoms in the gas phase (fig. 4). The existence of an accessible range of local potential fields, arising from the presence of a lone-pair material (HMPA), essentially reproduces the overall behaviour of the valence electron of the isolated alkali atom in its electronically excited configurations (for potassium, 5*s*, 6*s*, etc.). The similarities between the excited state configurations of a crystalline material and the electronic states existing in solution were first noted by Wannier (1937).

It has not escaped our notice that the electronic transition energy for a state of zero-per cent atomic character lies remarkably close to that observed for solvated electrons in all the media included in fig. 4.

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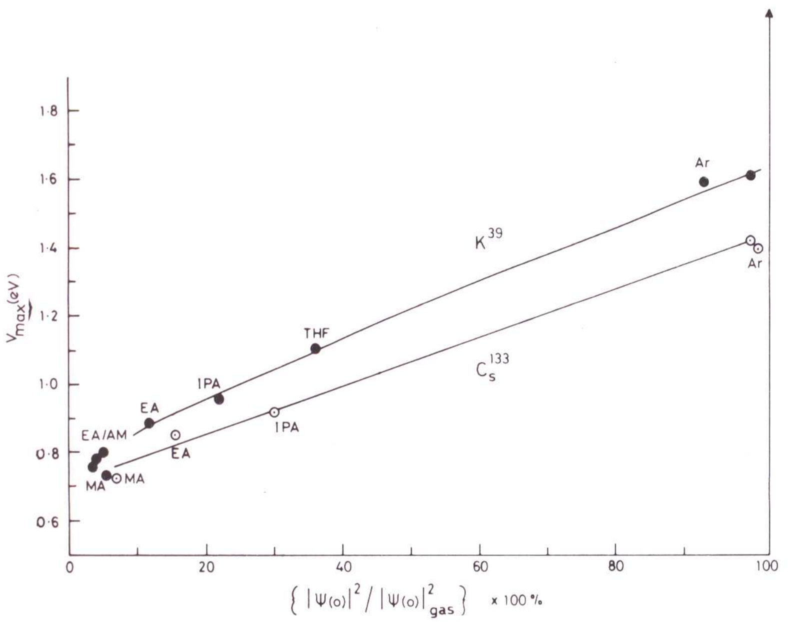
These optical bands exhibit a distinct blue shift from that of e^-_{solv} observed in the same solvent, and the magnitude of the shift shows a correlation with the per cent atomic character for the species M^0_{solv} as obtained from E.S.R. studies (Seddon *et al.* 1977). In fact, we find a *simple* correlation between the per cent atomic character, Φ, of these localized states (expressed as $\{|\psi(0)|^2_M \div |\psi(0)|^2_{\mathrm{gas}}\} \times 100\%$) and the energy ($\nu_{\mathrm{max}}$) of the absorption band; this is shown in fig. 3. This correlation holds for both potassium and caesium systems (the two metals for which extensive results are available) over the entire range from weakly localized states, with $<1\%$ parentage in the gaseous donor atom, to atomic-like states isolated in the rare-gas matrices, argon, krypton and xenon (Weyhmann and Pipkin 1965, Kupferman and Pipkin 1968).

Fig. 3



Correlation of optical- and electron-spin-resonance data for potassium and caesium monomeric states (M^0_{solv}) in a variety of host matrices. Matrix indentification: MA, methylamine (CH_3NH_2); EA, ethylamine ($C_2H_5NH_2$); AM, ammonia (NH_3); IPA, isopropylamine ($(CH_3)_2CHNH_2$); THF, tetrahydrofuran (C_4H_8O); Ar, argon.

Just as the *matrix-bound* states of the potassium atom show clear correlations between ν_{max} and Φ, so do the excited electronic states of *gas-phase* potassium atoms. In fig. 4 we show the variation of Φ with the energy differences between the *ns–np* states ($n = 4$–8) of the gas-phase potassium atom (Moore 1949, Morton and Preston 1977).

As with the matrix-bound states a clear correlation exists, the major difference being that the series limit ($n \to \infty$, $\Phi \to 0$) for the gas-phase atom

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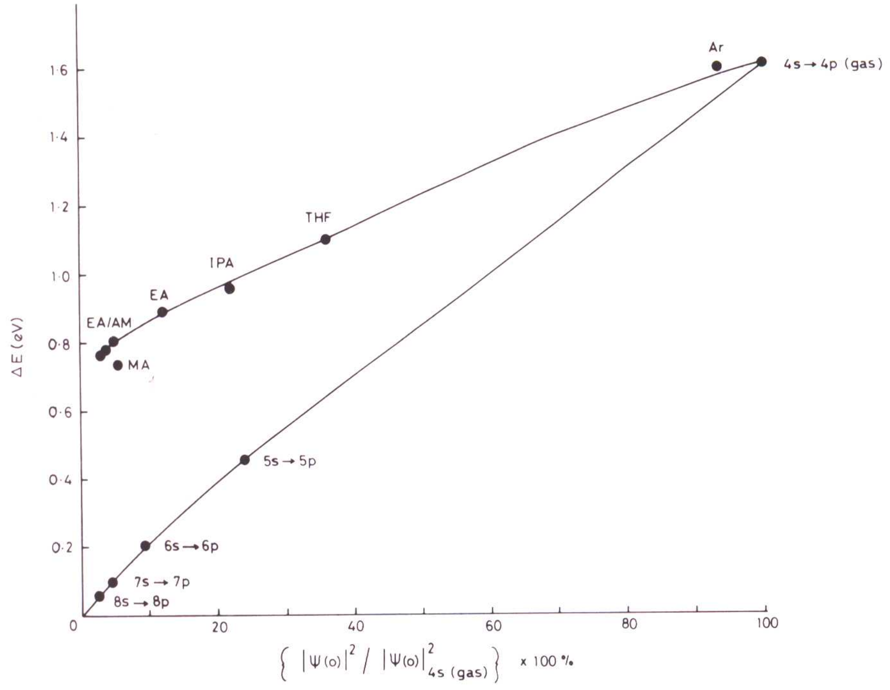
Fig. 4



Gaseous and matrix-bound states of the potassium atom. A plot of the optical transition energy versus the per cent occupancy of the appropriate ground-state *s* orbital. Upper curve: matrix-bound states (see fig. 3 for matrix identification). Lower curve: excited states of the potassium *gas-phase* atom. In the latter case we take ΔE as the energy separation between the appropriate *ns–np* levels (Moore 1949); the corresponding degree of occupation for the excited *ns* level is taken from the tabulation of Morton and Preston (1977).

merely defines the ionization limit for the isolated atom. For the matrix-bound states $\Phi \to 0$ implies the series ionization in the fluid (Wannier 1937) leading to the production (after dipole relaxation) of the solvated electron (Rentzepis, Jones and Jortner 1973). Indeed the limit $\Phi \to 0$ for the matrix-bound states does lead to an optical transition energy (approximately 0·6–0·8 eV) typical for the solvated electron in a dielectric medium (Kevan and Webster 1976). An extensive tabulation of magnetic data for the excited states of alkali atoms in the gas phase has been given by Morton and Preston (1977).

We now have a quantitative description of both the eigenfunctions and eigenenergies of the gas-phase potassium atom in its excited states. It is possible to construct† a representation of the form given in fig. 5 (*a*) that

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† A somewhat similar procedure for comparing gas-phase and matrix-bound states of rare gas atoms in host matrices has been proposed (Raz and Jortner 1973 and references therein).