NAPHTHALENE PHOSPHORESCENCE IN RARE GAS MATRICES*

By A. M. Turek and J. Najbar

Institute of Chemistry of the Jagellonian University, Cracow**

(Received November 19, 1979)

The naphthalene phosphorescence spectra in Ar, Kr and Xe show a multiplet structure with two groups of the subspectra separated by 172,246 and 254 cm^{-1}, respectively. Various insertion modes of the naphthalene molecule in the rare gases were analysed by constructing the intermolecular potential energy functions for naphthalene in the substitutional sites obtained by displacement of six or seven rare gas atoms. The multiplet structures of the naphthalene phosphorescence spectra in these matrices were preliminary assigned. Assuming a twofold increase in the polarizability of the naphthalene molecule in the triplet state relative to the ground state and by adjusting the parameters of the repulsive part of the carbon atom — rare gas atom potentials, reasonable agreement between the calculated and observed spectral shifts and the site splittings for argon and krypton were obtained.

1. Introduction

The resolution of the electronic spectra of the organic molecules dissolved in molecular crystals, rare gases and Shpolsky type matrices at low temperatures are dependent on the geometrical fit in various insertion modes and couplings between the matrix and the solute apart from the intramolecular factors [1–9]. The specific influence of the matrix on the luminescence and absorption spectra of the aromatic molecules involves several effects such as: shifts in transition energies [10], changes in the frequencies of internal vibrational modes [5], modifications of librations and internal rotations, the crystal field induced geometry changes and perturbations in the intensity distributions in the electronic spectra of the matrix isolated molecules [7–9].

The influences of the matrix may be described by taking into account the potential energy functions for the solute molecule in the substitutional sites [11]. The structures of the electronic spectra and diffuseness of these spectra may be correlated with the distortions and the displacements of the potential energy functions during electronic transition [2].

For the ground electronic states the intermolecular potential energy functions are

* The work was partially supported by the Polish Academy of Sciences.

** Address: Instytut Chemii UJ, Karasia 3, 30-060 Kraków, Poland.

used extensively in various crystallographic problems and in the vibrational spectroscopy of the solids. The approach developed by Kitaigorodsky [12, 13] is usually used for constructing the potential energy functions for the molecular crystals of organic molecules. The matrix isolated molecules may have different orientations in the substitutional sites. Recently, Merle et al. [11] calculated the intermolecular potential functions for the ground state of pyrene, triphenylene and coronene in the *n*-heptane matrix. They were able to interpret different orientations of the solute molecules in the matrices, responsible for the multiplet structure of their phosphorescence and MIDP spectra of the triplet state [9, 11, 14–16].

In this paper the naphthalene molecules in various substitutional sites in rare gas matrices are considered. The intermolecular potential energy functions were constructed for naphthalene molecules in matrices for the ground and excited electronic states, taking into account atom-atom interactions. This approach seems to be justified for the lowest excited states, especially for the lowest triplet state of organic molecules [17]. The results of calculations for the potential functions suggest a possible interpretation for the multiplet structure of the naphthalene phosphorescence spectra in Ar, Kr and Xe. The shifts in the electronic energy levels of the solute molecule appear to be dependent on the exact geometry of the substitutional site and are very sensitive to short range repulsive intermolecular interactions.

2. Experimental

The vacuum UV equipment was described by Pantos et al. [18, 19]. Zone refined naphthalene was used. The mixture used consisted of saturated naphthalene vapour and rare gases (Air Products research grade) was deposited on a liquid-He cooled LiF disc. Excitation light from a Xe—Hg high pressure lamp was dispersed by a McPherson 225 monochromator. The emission was observed at 90° to the exciting beam through a Hilger and Watt 0.3 m analysing monochromator and an EMI 6256QB cooled photomultiplier. The naphthalene phosphorescence was excited with a strong line of 2537 Å from a high pressure Xe—Hg lamp. The spectra were plotted on a Bryans 2700 chart recorder. After deposition of the mixtures of the rare gas and naphthalene on the LiF window the phosphorescence spectra were recorded without any annealing. The deposition temperature was lower than 10 K and the deposition rate was about 1 atomic layer per second.

3. The phosphorescence spectra of naphthalene in Ar, Kr and Xe

The phosphorescence spectra of naphthalene in Ar, Kr and Xe matrices are shown in Fig. 1 a, b and c. The resolution of the naphthalene phosphorescence spectra in rare gas matrices is much inferior to the benzene phosphorescence in the same matrices [7, 8]. In Fig. 1 the assignment of the naphthalene phosphorescence spectrum in Ar is shown. The phosphorescence spectra shown in Fig. 1 have complicated multiplet structures and large splittings between two groups of the subspectra. The subspectra are indicated as α (high energy subspectrum) and β (low energy subspectrum). The shapes of the the $0-0$ bands show that they consist of closely lying transitions. The band positions of $0-0$

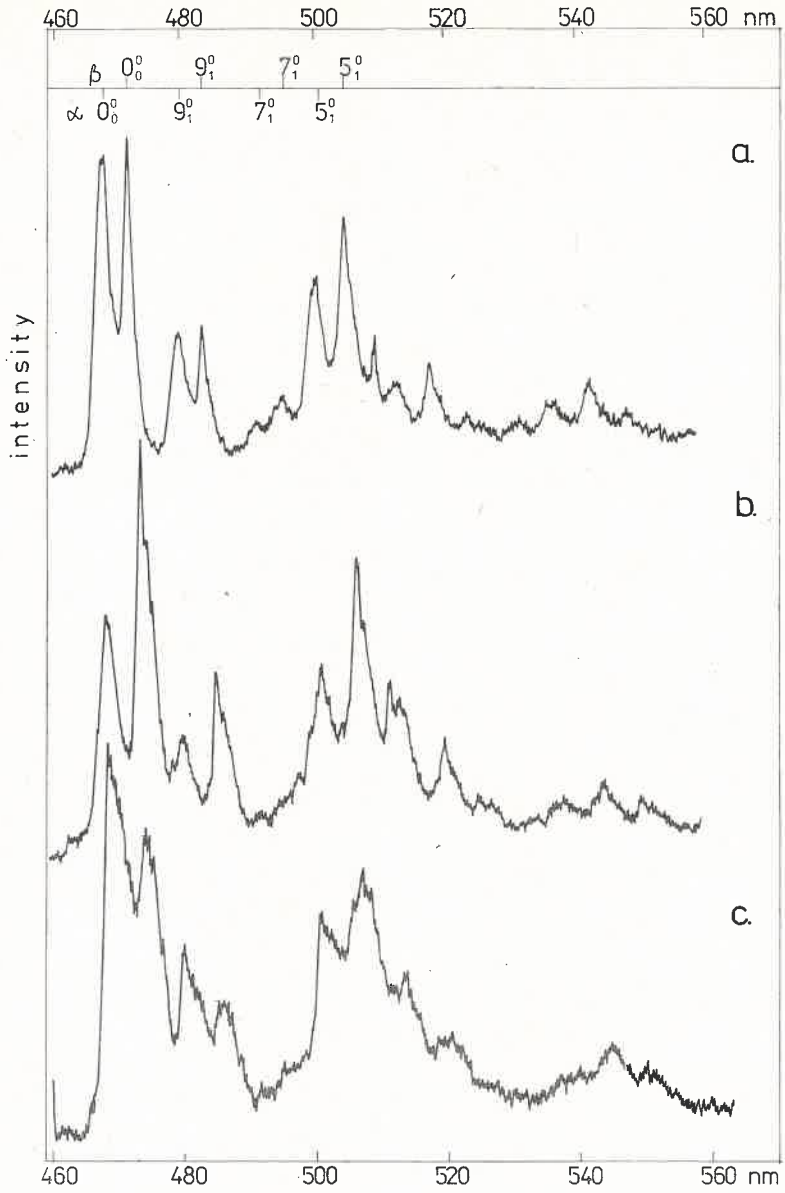

Fig. 1. The phosphorescence spectra of naphthalene in argon (*a*), krypton (*b*) and xenon (*c*) matrices

transitions which could be identified in the spectra are given in Table I. The analysis was done according to Gattermann et al. [20] assignment of the naphthalene phosphorescence in the vapour phase. The fundamental frequencies identified in the Ar phosphorescence spectrum are: 9 (512 cm^{-1}), 7 (1020 cm^{-1}) and 5 (1383 cm^{-1}) in both subspectra α and β. The splittings of the $T_1 \rightarrow S_0$ transitions are 172, 246 and 254 cm^{-1} for Ar, Kr and Xe, respectively (Table I).

TABLE I

The 0–0 transition energies

Matrix	0–0 bands positions		Difference
	Subspectrum α [cm^{-1}]	Subspectrum β [cm^{-1}]	
Ar	21 321	21 149	172
Kr	21 370	21 124	246
Xe	21 336	21 082	254

4. *The system*

In the presence of impurities of ~1% the noble gases crystallize at 4.2 K with an h.c.p. structure [6–8]. The naphthalene molecules isolated in the h.c.p. or c.c.p. phases, due to geometric restrictions take place in the hexagonal planes replacing 6 or 7 rare gas

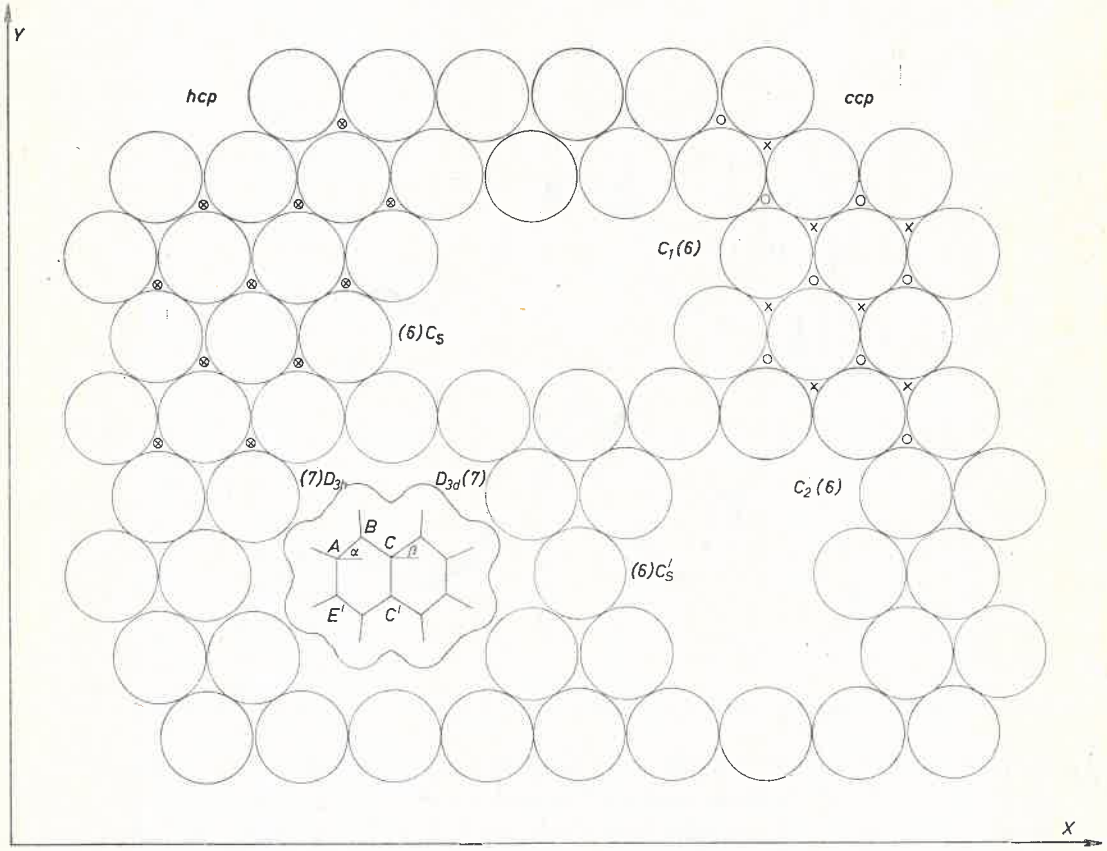

Fig. 2. The model for the substitutional sites created by the displacement of six ($(6)C_s$, $C_1(6)$ and $(6)C_s'$, $C_2(6)$) and seven ($(7)D_{3h}$, $D_{3d}(7)$) atoms in the hexagonal plane, (×, ○ — indicate the centres of the atoms in adjacent top and bottom atomic layers for h.c.p. and c.c.p. structures)

atoms. The traps obtained in this way (Fig. 2) are the smallest ones to accomodate naphthalene molecules with negative interaction energies.

In the system considered here, the naphthalene crystallographic data of Cruishank [21] were used. The values of bond lengths were: $AB = 1.363$ Å, $BC = 1.421$ Å, $CC' = 1.418$ Å and $AE' = 1.415$ Å. For these data we fitted the pertained values of angles: $\alpha = 31°10'$, $\beta = 29°43'$ and also modified the angles centered on carbon atoms to the "C_2 symmetry" relative to the C—H bond (Fig. 2).

5. The interaction energy parameters

The interaction energy calculations based on the assumption of pair additivity of the intermolecular atomic interactions [12, 13, 22–33]. The Lennard-Jones atom-atom interaction potential has been incorporated throughout this work.

$$V(R) = -4\varepsilon\left[\left(\frac{\sigma}{R}\right)^6 - \left(\frac{\sigma}{R}\right)^{12}\right]. \tag{1}$$

The choice of this potential should be justified by its reliability in the description of the interactions between rare gas atoms [32]. We assumed this type of potential for all atom–atom interactions. The parameters for C and H atoms were recalculated from Williams

TABLE II

The van der Waals radii and parameters of the interaction potential

	r_0 [Å]	σ [Å]	ε (kcal/mole)	U [eV]	α [Å^3]	$\sigma_{X_i—C}$ [Å]	$\varepsilon_{X_i—C}$ [kcal/mole]
H	1.170	2.796	0.04016				
C	1.800	3.794	0.04287	27.3	1.028		
Ar	1.878	3.405	0.23780	34.2	1.630	3.5889	0.2079
Kr	1.996	3.600	0.33960	31.4	2.480	3.7407	0.2516
Xe	2.168	4.070	0.44740	29.0	4.010	4.0421	0.2836

[30, 31] for the exp-6 potential used in the hydrocarbon systems. The values of these parameters are similar to those given by Kitaigorodsky [12, 13, 22] for the hydrocarbons, Table II. Values of parameters ε_{ij} and σ_{ij} for two types of atom interactions have been calculated using the Lorentz and Berthelot rules, respectively

$$\varepsilon_{ij} = \frac{\varepsilon_i + \varepsilon_j}{2}, \tag{2}$$

$$\sigma_{ij} = \sqrt{\sigma_i \sigma_j} \tag{3}$$

i = C or H, j = Ar, Kr or Xe.

For the ground electronic state the attractive part of the Lennard-Jones potential in our system can be expressed by the London formula [29]

$$E_L = -\frac{3\bar{\alpha}_i\bar{\alpha}_j}{2R^6}\frac{U_iU_j}{U_i+U_j}, \tag{4}$$

where U_i, U_j are the effective ionisation potentials, $\bar{\alpha}_i$, $\bar{\alpha}_j$ are the atomic polarizabilities, and i = C or H, j = Ar, Kr or Xe.

The parameters $\bar{\alpha}_i$, $\bar{\alpha}_j$, U_H and U_j were taken from Pitzer [29] except for the carbon atom parameters. The values, $\bar{\alpha}_C$, and U_C were evaluated by iteration using (1) and (4) and U_j and $\bar{\alpha}_j$ values given in columns 4 and 5 in Table II. Estimations for these parameters are based on the additivity of the isotropic atomic polarizabilities [10]. The theoretical justification for the possibility to express the experimental polarizabilities of molecules as a sum of bond polarizabilities or atomic polarizabilities was discussed by Claverie [17]. The atomic polarizabilities are less transferable from one molecule to another, but they are simple in application. In the present application we used this procedure for the mean polarizability in order to simplify the computations.

For the excited states the attractive part of the Lennard-Jones potential was also taken in form of [4] with changed atomic polarizabilities. We assumed that for excited states of aromatic hydrocarbons only carbon atoms contribute to the total polarizability change. Under this assumption we used the experimental changes in the total polarizability of anthracene molecule in the ^1L_a excited state for the estimation of carbon atomic polarizability in the excited states, ($\bar{\alpha}_{aC}$ = 2.075 Å^3). Estimated in this way the carbon atom polarizability changes gave reasonable values of the molecular polarizabilities for the ^1L_a and ^1L_b excited states of naphthalene, anthracene, tetracene, which are close to the available experimental values [10, 34]. We applied this parameter for the lowest triplet state of the naphthalene molecule. Parameters for the repulsive part of the interaction potential in (1) for the carbon... Ar, Kr or Xe interaction, for the naphthalene molecule in the T_1 excited state were adjusted to reproduce a matrix shift of 0−0 transition in the naphthalene phosphorescence spectrum (relative to the vapour phosphorescence spectra). The corresponding shifts of low energy transitions in our recorded spectra are: 0.71 kcal for Ar, 0.78 kcal for Kr and 0.90 kcal for Xe.

6. The calculation

The intermolecular energy potential function was calculated as a function of the coordinates R, θ and a_i, where R is the translational displacement in the X or Y direction of the molecule centre and θ is the angle of rotation of the molecule around the axis normal to the molecular plane. a_i are cell parameters for the matrix of Ar, Kr and Xe. For all the systems investigated the interaction energy was plotted as the function of the angle θ between the long axis of the molecule and the axis X of the trap at a given translational position.

Calculations were done for two types of phases, namely the h.c.p. and c.c.p. structures for each matrix. The anisotropy of interaction mainly results from H ... X interactions (X = Ar, Kr or Xe), the anisotropy of C ... X interactions is of less importance.

When the naphthalene molecule is rotated in the geometrical centre of the seven-rare-gas-atom trap (h.c.p., c.c.p.) the interaction energy is an oscillating function of the θ angle with two types of energy wells appearing with a period of 60° at $\theta = 30° + n\,60°$ and $\theta = 0° + n\,60°$, respectively. In the case of argon the first well is deeper with an energy

barrier of 0.61 kcal (Fig. 3). In krypton these wells are practically equal and in xenon the second well becomes deeper while the first one almost disappears.

The behaviour of the interaction energy function changes when the naphthalene molecule is translated from the centre of the trap. We considered translations along the X and Y directions to evaluate the shape of the energy hypersurfaces and the positions

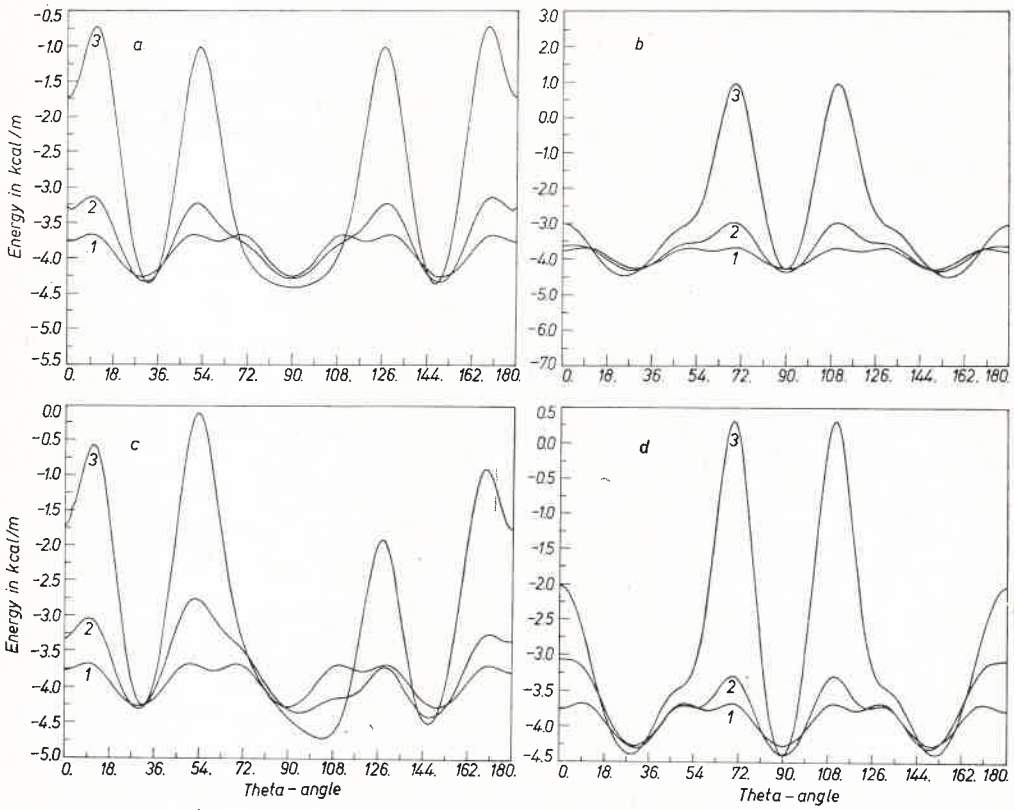

Fig. 3. Angular dependence of the total interaction energy function of naphthalene with the argon lattice in the centre (1) and after translation of the naphthalene molecule in the X and Y directions by 0.5 Å (2) and 0.75 Å (3): (a) c.c.p. structure, translation in the X direction, (b) c.c.p. structure, translation in the Y direction, (c) h.c.p. structure, translation in the X direction, (d) h.c.p. structure, translation in the Y direction

of the energy minima. A full search of the minima for the interaction energy involved translations with a 0.25 Å step and 1° step for rotation about the axis normal to the trap plane. Because we were interested in the anisotropy of interaction and not in the total energy, only the first coordination shell of rare gas atoms (36 atoms) was taken into account. In short range domain we omitted contributions from distances lower than 2 Å.

The interaction energy function for argon matrix with a seven-atom trap is shown in Fig. 3 (a, b, c, d). Here it is shown that when the molecule of naphthalene in h.c.p. Ar matrix is translated along the X direction, the wells at $\theta = 30° + n\,60°$ decrease their energies. For translation in this direction only a minimum at $\theta = 90°$ corresponds to the

true bottom of the potential energy valley. The minima at $\theta = 30°$ and 150° in Fig. 3 are connected with two other potential energy valleys corresponding to translations in directions 120° and 240° relative to X direction. We can derive some information concerning the properties of the potential function from Fig. 3b, where the potential energies as functions of θ are drawn for displacements in the Y direction. For the c.c.p. matrix the minima in Fig. 3b correlate directly with the minima in Fig. 3a. Fig. 3a and Fig. 3b show that after the displacement of the naphthalene molecule from the trap centre, the fusion of minima at $\theta = 30° + n\,60°$ and $\theta = 0° + n\,60°$ occurs except for the translational minimum in the X direction at $\theta = 0°$. In Fig. 3c, d the intermolecular potential energy for the naphthalene molecule in the h.c.p. Ar matrix is shown as a function of the θ and X or Y displacement. These functions in the h.c.p. matrices are similar to those in c.c.p. matrices. The main difference in the interaction energies of the naphthalene molecule in the c.c.p. and h.c.p. phases are rotation and splittings of the energy valleys of the potential function for the naphthalene molecule translated in the X direction for the h.c.p. phase compared to the potential function for the c.c.p. structure. Due to this rotation there is a breakdown of the symmetry of the potential function for the naphthalene molecule translated in the X direction (Fig. 3c) and a difference in potential functions (translations in the $+Y$ and $-Y$ directions).

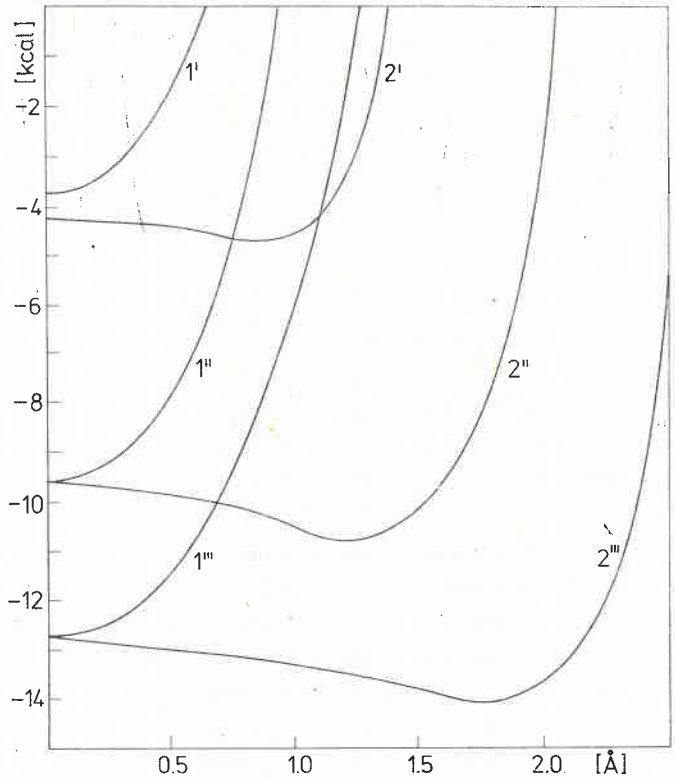

Fig. 4. Translational dependence of the total interaction energy function of naphthalene for $\theta = 0°$ (1) and $\theta = 90°$ (2) with argon ($1'$, $2'$), krypton ($1''$, $2''$) and xenon ($1'''$, $2'''$) matrices, for the c.c.p. structure

Thus when the naphthalene molecule is placed in the symmetrical site created by the displacement of seven rare gas atoms it can occupy a small minimum in the centre of the trap or one of three equivalent broad minima with low energy (c.c.p.) or six such minima (h.c.p. phase).

The changes in the intermolecular potential energies of the naphthalene molecule along the potential valley (in the X direction) for the c.c.p. structure of Ar, Kr and Xe are shown in Fig. 4. In this figure, curves $1'$, $1''$, $1'''$ correspond to the intermolecular energies for the translations of the naphthalene molecule at $\theta = 0°$, in the X direction, for Ar, Kr and Xe matrices, respectively. For this particular translation the minima occur at the centre of the trap and are common for both h.c.p. and c.c.p. structures. Curves $2'$, $2''$ and $2'''$ correspond to intermolecular potentials as functions of translations of the naphthalene molecule in the X direction at $\theta = 90°$ for the site in the c.c.p. structure.

TABLE III

Values for the energy minima for naphthalene in Ar, Kr and Xe matrices

h.c.p.	Trap symmetry	Minim. value (kcal/mole) in ground state	Minim. value (kcal/mole) in excited state	c.c.p.	Trap symmetry	Minim. value (kcal/mole) in ground state	Minim. value (kcal/mole) in excited state
Ar	(6)C_s'	−2.99	−4.25	Ar	C_2(6)	−2.99	−4.25
	(6)C_s	−3.93	−5.33		C_1(6)	−3.93	−5.33
	(6)D_{3h}	21.11	20.63		C_{3v}(6)	19.14	20.64
	(7)D_{3h}	−5.06	−5.62		D_{3d}(7)	−4.61	−4.90
Kr	(6)C_s'	−12.27	−13.80	Kr	C_2(6)	−12.27	−13.80
	(6)C_s	−12.13	−13.71		C_1(6)	−12.13	−13.71
	(6)D_{3h}	−3.85	−5.60		C_{3v}(6)	−6.44	−9.60
	(7)D_{3h}	−11.91	−12.62		D_{3d}(7)	−10.76	−12.62
Xe	(6)C_s'	−14.40	−16.13	Xe	C_2(6)	−14.40	−16.13
	(6)C_s	−13.93	−15.77		C_1(6)	−13.93	−15.77
	(6)D_{3h}	−10.27	−12.60		C_{3v}(6)	−12.88	−15.93
	(7)D_{3h}	−13.77	−15.75		D_{3d}(7)	−14.13	−14.94

The energy values for the minima of the intermolecular potential function for naphthalene in Ar, Kr and Xe in both possible crystallographic structures are given in Table III. The minima for the intermolecular potential for naphthalene in the h.c.p. phase occur at $X = 0.72$ Å, $Y = 0.19$ Å for Ar, $X = 1.25$ Å, $Y = 0.0$ Å for Kr, $X = 0.0$ Å, $Y = 1.5$ Å for Xe and at equivalent positions which can be obtained by the symmetry operations of the system.

We also investigated the sites obtained by displacement of five or six atoms of rare gas in the matrix. Five atom holes were found to be small and isolation of the naphtha-

lene molecules in such sites gave high positive energy values of the interaction energy. From the sites obtained by displacement of six atoms the sites of (6)D_{3h} (h.c.p.) and C_{3v}(6) (c.c.p.) symmetry have improper geometry and gave energy values similar to five atom holes. We considered six-atom traps with low interaction energies having (6)C_s' (h.c.p.), C_2(6) (c.c.p.) and (6)C_s (h.c.p.), C_1(6) (c.c.p.) symmetries (Fig. 2). For these traps we obtained results which show that there is no difference between the c.c.p. and h.c.p. phases. In both kinds of traps we found only one minimum of the interaction energy. If we put one more rare gas atom in the right side of seven-atom trap (Fig. 2) we obtain the (6)C_s' or C_2(6) trap. In this trap the minimum of interaction energy function always occurs at $\theta = 90°$ with the additional translation of the molecule centre along the X direction. The values of these translations in the $-X$ direction referring to the seven-atom traps are: 1.27 Å in Ar matrix, 1.45 Å in Kr and 1.63 Å in Xe. The position of the naphthalene molecule in this trap indicates a close correlation with the results obtained for seven-rare-gas-atom trap. The minimum values for the interaction energy function at these positions of naphthalene molecule are: −2.99 kcal for Ar, −12.27 kcal for Kr, −14.40 for Xe. For the (6)C_s or C_1(6) traps (Fig. 2), the interaction energy functions have their minimum values at $\theta = 80°$ in all matrices and with the molecule centre placed in the trap centre. Values for the interaction energy function minima are: −3.93 kcal in Ar, −12.13 kcal in Kr and −13.93 kcal in Xe.

For the T_1 excited state of the naphthalene molecule the interaction energy was calculated in the same way. We fitted the parameters connected with the repulsive part of carbon-rare gas atom interactions to reproduce the matrix shifts of the low energy phosphorescence (β-subspectrum) relative to the gas phase. Using these parameters we could calculate the excited state energy values for all matrices in different traps. The energetical distribution of the insertion site modes is shown in Fig. 5, for the ground and the excited T_1 state. When we tried to fit the parameters to the seven-atom traps, with the naphthalene molecule in the site centre, for subspectrum α in the phosphorescence spectrum, we obtained values which do not change the ordering of the insertion site energies in Fig. 5a, but give much lower values for the transition energies in the simulated spectra (Fig. 5b). The minima of the intermolecular potential for these traps are approximately at the same coordinates in the ground and excited states.

The values of the interaction energy minima in different traps for the ground and the excited T_1 state of the naphthalene molecule are given in Table III (and shown in Fig. 5). In this figure the calculated positions of the 0−0 transitions for the naphthalene phosphorescence are also given. The parameters for the repulsive part of the carbon-rare gas atom potential were adjusted assuming the correspondence between β subspectrum and (6)C_s or C_1(6) sites. Thus the calculated spectra suggest that the sites of the (6)C_s' or C_2(6) symmetry obtained by displacement of six rare gas atoms also contribute to the β subspectrum. Hence, according to the calculations presented, the high energy subspectrum should be connected with larger substitutional sites, possibly with a symmetrical site created by the displacement of seven rare gas atoms. For the Ar matrix this situation occurs both in the c.c.p. and h.c.p. phases, but for the Kr matrix only the h.c.p. structure gives this ordering of the 0−0 transitions.

The interaction energy of the naphthalene molecule with the matrix is a sum of C ... X interactions, where the main contribution gives out-of-plane rare gas atoms, and H ... X interactions in the plane of the naphthalene molecule. The change in the carbon polarizability influences the C ... X interactions. On the other hand the H ... X interactions are very sensitive to changes in the geometry of the site. The calculated splittings compare qualitatively with the observed splittings for the naphthalene phosphorescence in Ar and

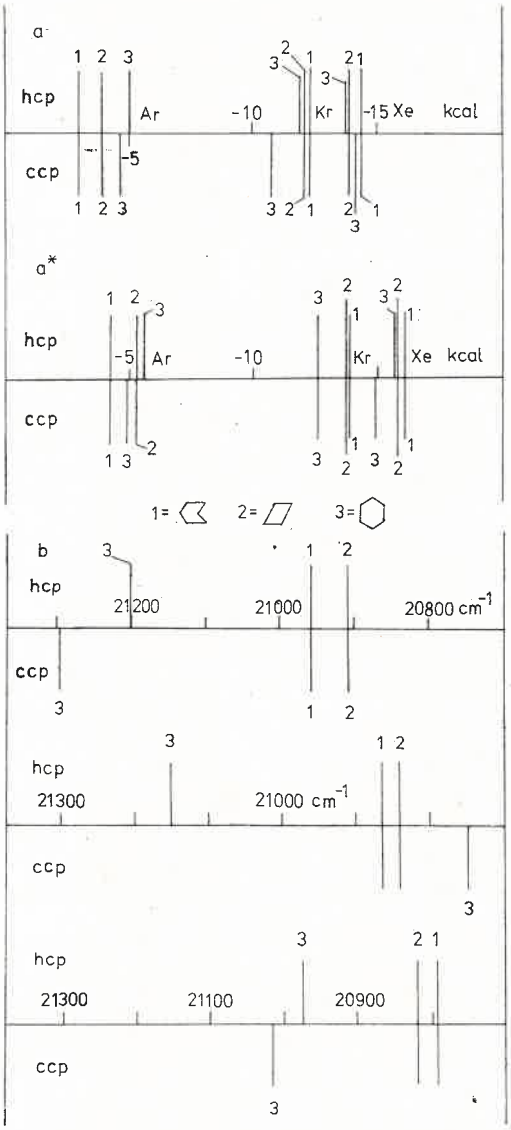

Fig. 5. The values of the energy minima for naphthalene in argon, krypton and xenon matrices for the ground (a) and excited states (a*), and the simulated site structures of the naphthalene phosphorescence spectra for Ar, Kr and Xe matrices

Kr matrices. For Xe the results are less satisfactory indicating that for this matrix the symmetrical sites obtained by the displacement of seven rare gas atoms are not good models for the system.

In calculations we essentially should allow for the change in the geometry of the naphthalene molecule between the ground and the lowest triplet state. The geometry change for S_1 state of naphthalene mainly involves an expansion of the naphthalene molecule along the short molecular axis. The geometry changes for the T_1 state of the naphthalene molecule are not known. However, a comparison of the displacements of the atoms for different totally symmetric modes of naphthalene forming the progressions in the fluorescence and phosphorescence spectra suggests that for the T_1 state of naphthalene the geometry change probably involves an expansion in the direction of long molecular axis. Thus, considering the geometry of the sites taken into account here, the neglection of the geometry change for the triplet state in calculations should not introduce much errors in our results.

7. Conclusions

In this paper we considered the simplest modes of isolation of the naphthalene molecule in a rare gas matrix taking into account two possible crystallographic structures for the solid rare gases. The smallest substitutional sites which can accomodate the naphthalene molecule without deformations correspond to the displacement of six atoms. We considered the naphthalene molecule in two such sites. The difference in the stabilization energies for the ground and the excited state of the naphthalene for both sites in the h.c.p. and c.c.p. phases is similar and we suggest that they both contribute to one group of the low energy subspectra of the naphthalene phosphorescence. The rare gas matrices obtained by condensation at low temperatures (10 K) are polycrystalline and contain many defects [35]. There are many possibilities of introducing the defects into structures obtained by displacement of six rare gas atoms. To simulate the corresponding structure we considered only one symmetrical substitutional site obtained by the displacement of seven rare gas atoms from the hexagonal plane for the h.c.p. and c.c.p. phases. In this site the naphthalene molecule can freely accomodate with the main equilibrium positions out of the trap centre. The calculated for this site stabilization energies of the ground and the excited state of naphthalene (using the parameters based on the six-atom hole) suggest that naphthalene in the seven-atom hole contributes to the broad high energy group of the phosphorescence subspectra in rare gas matrices. The sites considered have different properties in the h.c.p. and c.c.p. phases of the noble gases. Our model of the seven atom trap is a great simplification of the matrix isolation of the naphthalene molecule. Probably we should ascribe the high energy transitions in the naphthalene molecule to different sites created by the displacement of the seven rare gas atoms from crystallographic plane.

The luminescence measurements were done in Schuster Laboratory, Manchester University, UK. J.N. wishes to express his sincere thanks to Dr T.D.S. Hamilton for the kind support of the research and for helpful comments on the manuscript.

REFERENCES

[1] E. V. Shpolsky, *Sov. Phys. Usp.* **6**, 411 (1963).
[2] K. K. Rebane, *Impurity Spectra of Solids*, Transl. by J. S. Shier, Plenum. New York 1970.
[3] R. M. Hochstrasser, P. N. Prasad, in *Excited States*, Vol. 1, Ed. by E. C. Lim, Academic Press, New York, London 1974.
[4] M. A. El-Sayed, W. R. Moomaw, in *Excitons, Magnons and Phonons in Molecular Crystals*, Ed. by A. B. Zahlan, Cambridge Univ. Press, Cambridge, London, New York 1968, p. 103.
[5] S. Cradock, A. J. Hinchcliffe, *Matrix Isolation. A Technique for the Study of Reactive Inorganic Species*, Cambridge Univ. Press, Cambridge, London, New York, Melbourne 1975.
[6] H. E. Hallam, G. F. Scrimshaw, in *Vibrational Spectroscopy of Trapped Species*, Ed. by H. E. Hallam, John Wiley and Sons, London, New York, Sydney, Toronto 1974, p. 11.
[7] P. M. Johnson, L. Ziegler, *J. Chem. Phys.* **56**, 2169 (1972).
[8] Yei-Ping Hsu, P. M. Johnson, *J. Chem. Phys.* **59**, 136 (1973).
[9] W. M. Pitts, A. M. Merle, M. A. El-Sayed, *Chem. Phys.* **36**, 437 (1979).
[10] W. Liptay, in *Excited States*, Vol. 1, Ed. by E. C. Lim, Academic Press, New York, London 1974, p. 129.
[11] A. M. Merle, M. F. Nicol, M. A. El-Sayed, *Chem. Phys. Lett.* **59**, 386 (1978).
[12] A. I. Kitaigorodsky, *Molecular Crystals and Molecules*, Academic Press, New York, London 1973.
[13] A. I. Kitaigorodsky, *Rev. Chem. Soc.* **7**, 133 (1978).
[14] M. Lamotte, S. Risemberg, A. M. Merle, J. Joussot-Dubien, *J. Chem. Phys.* **69**, 3639 (1978).
[15] M. Lamotte, A. M. Merle, S. Risemberg, *J. Lumin.* **18/19**, 505 (1979).
[16] M. Lamotte, A. M. Merle, S. Risemberg, *J. Lumin.* **18/19**, 111 (1979).
[17] P. Claverie, in *Intermolecular Interactions: From Diatomics to Biopolymers*, Ed. by B. Pullman, A. Wiley Interscience Publications, Chichester, New York, Brisbane, Toronto 1978, p. 69.
[18] E. Pantos, T. D. S. Hamilton, *Chem. Phys. Lett.* **17**, 588 (1972).
[19] E. Pantos, T. D. S. Hamilton, I. H. Munro, *Proceedings of International Conference on the Excited States of Biological Molecules*, Lisbon, Portugal, April 1974.
[20] H. Gatterman, M. Stockburger, *J. Chem. Phys.* **63**, 4541 (1975).
[21] D. W. J. Cruishank, *Tetrahedron* **17**, 155 (1962).
[22] A. I. Kitaigorodsky, *Phys. Status Solidi* (b) **62**, 291 (1974).
[23] O. G. Peterson, D. N. Batchelder, R. O. Simmons, *Phys. Rev.* **150**, 703 (1966).
[24] D. L. Losee, R. O. Simmons, *Phys. Rev.* **172**, 944 (1968).
[25] D. R. Sears, H. P. Klug, *J. Chem. Phys.* **37**, 3002 (1962).
[26] A. Michels, Hub. Wijker, Hk. Wijker, *Physica* **15**, 627 (1949).
[27] J. A. Beattie, R. J. Barriault, J. S. Brierley, *J. Chem. Phys.* **20**, 1613 (1952).
[28] A. Michels, J. M. Levelt, W. de Graaf, *Physica* **29**, 659 (1958).
[29] K. S. Pitzer, *Adv. Chem. Phys.* **2**, 59 (1959).
[30] D. E. Williams, *J. Chem. Phys.* **45**, 3770 (1966).
[31] D. E. Williams, *J. Chem. Phys.* **47**, 4680 (1967).
[32] C. A. Croxton, *Liquid State Physics — A Statistical Mechanical Introduction*, Cambridge Univ. Press 1974.
[33] T. Kihara, *Intermolecular Forces*, John Wiley and Sons, Chichester, New York, Brisbane, Toronto 1978.
[34] R. Mathies, A. C. Albrecht, *J. Chem. Phys.* **60**, 2500 (1974).
[35] H. Abe, W. Schultze, *Chem. Phys.* **41**, 257 (1979).