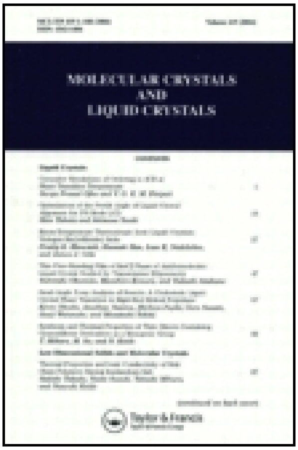

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Benzene-Rare Gas Matrices: Evidence from Electron Photoemission Spectra for Wannier Impurity States

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Benzene–Rare Gas Matrices: Evidence from Electron Photoemission Spectra for Wannier Impurity States

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Recent experiments on rare gas solids doped with benzene⁽¹⁾ and naphthalene⁽²⁾ have supported the suggestion⁽³⁾ that large radius impurity states of molecules in rare gas matrices should be observable. The energy of the impurity Wannier state (E_n) is related to the band gap I_s, the photoemission threshold F and the ionization potential of the free molecule I_G by the following expressions

$$E_n = I_s - G/n^2 \tag{1}$$

$$I_s = (I_G + P_+) + V_0 = F + V_0 \tag{2}$$

where G equals $m^*e^4/2\chi^2\hbar^2$, P_+ is the polarization energy of the medium by the positive impurity hole, V_0 is the energy of the quasi-free excess electron in the medium.

Katz *et al.*⁽¹⁾ assigned absorption bands in a benzene-xenon matrix at 60 350 cm^{-1} and in a benzene-krptyon matrix at 62 230 cm^{-1} to transitions to the $n = 2$ impurity Wannier state. But since Wannier states of higher n were not identified, and no independent measurement of the band gap had been made, this important assignment has remained tentative.

We report here the measurement of the threshold (F) for electron photoemission in benzene-rare gas matrices and use this value to re-examine the assignment of large radius impurity states in these matrices.

The thresholds for electron photoemission were measured as 8.08 ± 0.10 eV (benzene in Xenon) and 8.25 ± 0.10 eV (benzene in krypton).† In Fig. 1 log (relative quantum yield) is plotted against the photon energy. The threshold is determined using the analytic method of Marchetti and Kearns.(5) From the known(6) value of the ree molecule ionization potential (9.25 eV), the values of P_+ are − 1.17 ± 0.10 eV (benzene-xenon) and − 1.00 ± 0.10 eV (benzene-krypton). Such values compare with P_+ for naphthalene-rare gas solids (Xe − 0.91 ± 0.10 eV, Kr − 0.7 ± 0.10 eV)(2,7)‡ and the pure

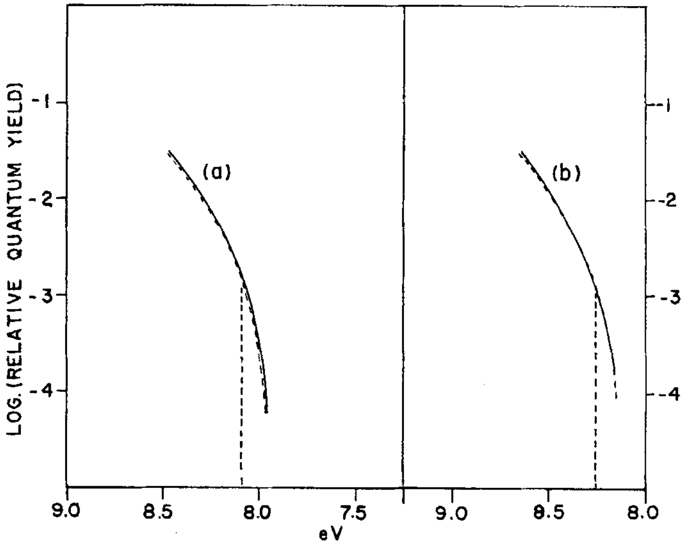

Figure 1. Variation of the relative quantum yield of photoelectrons as a function of photon energy (in eV) for benzene doped xenon (Curve *a*) and benzene doped krypton (Curve *b*) at 20 °K. The broken curves are those calculated by Marchetti and Kearns(5) for a solid with a polarization energy of − 1 eV. The vertical broken lines represent the threshold for electron photoemission.

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† Matrices of molar ratio 1 : 200 were prepared by codeposition at 40 °K. Electron photoemission currents were measured at 20 °K. Light sources were continuous and employed a microwave discharge through krypton and xenon.

‡ Our previous data(2) for naphthalene-rare gas solids gave values of F—the photoemission threshold—of 7.07 ± 0.05 eV (Xe matrix) and 7.25 ± 0.05 eV (Kr matrix). However, the recent analytic technique of Marchetti and Kearns(5) provides a more accurate assessment of F from the photoemission yield curves. Using this technique, the values of F are 7.28 ± 0.10 eV (Xe matrix) and 7.45 ± 0.10 eV (Kr matrix). From this data the values of P + are − 0.86 ± 0.10 eV (Xe) and 0.69 ± 0.10 eV (Kr) and of V_0 are 0.35 ± 0.15 eV (Xe) and 0.25 ± 0.15 eV (Kr) at 20 °K.

solids (Xe 1.32 eV; Kr 1.10 eV).(8) P_+ for the benzene doped solid is intermediate in value between that for the pure solid and that for the naphthalene doped solid as expected from the size alteration of the ion.

The value of G (and also of V_0) at 20 °K are expected to alter little from the pure solid to the doped solid.† Accepting the value of G for the benzene doped solids to be 1.04 ± 0.04 eV (Xe) and 1.73 ± 0.04 eV (Kr) the $n = 2$ impurity Wannier state should lie 0.26 eV below the xenon matrix conduction band and 0.43 eV below the krypton matrix conduction band. V_0 values of $-$ 0.6 ± 0.2 eV (Xe, Kr)(9) place the band gap (I_s) at 7.5 ± 0.3 eV (Xe) and 7.7 ± 0.3 eV (Kr), i.e. at $I_G + P_+ + V_0$. Therefore the $n = 2$ impurity Wannier states should lie at 7.2 ± 0.3 eV in a benzene doped xenon solid and 7.3 ± 0.3 eV (Kr) in a benzene doped krypton solid.

Figure 2 shows the absorption spectra of a benzene doped xenon solid (Curve *a*) and a benzene doped krypton solid (Curve *b*). Transition energies and suggested assignments are given in Table 1. The lines at 57 500 cm^{-1} (7.13 eV) (doped xenon) and 59 100 cm^{-1} (7.33 eV) (doped krypton) were assigned previously by Katz *et al.*(1) to the lowest molecular Rydberg state of benzene. However, our above estimates suggest that these lines may be assigned alternatively to the $n = 2$ Wannier impurity state. We note that the spectrum of the doped xenon solid does not show the line which was reported at 60 350 cm^{-1} by Katz *et al.* and assigned to the $n = 2$ impurity Wannier state. The only spectral feature we can identify at this energy is a C_1 emission line (60 350 cm^{-1}) arising from impurities in the rare gas light source.(10) A broad shoulder at 62 200 cm^{-1} (7.71 eV) in the benzene/krypton spectrum (see Fig. 1) may correspond to the line reported by Katz *et al.* at 62 230 cm^{-1} and assigned to the $n = 2$ impurity Wannier state. The absence of an analogous line in the benzene argon spectrum(1) and our inability to confirm the $n = 2$ line reported in the benzene spectrum suggests that this assignment requires further investigation.

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† For the naphthalene doped krypton matrix,(2) G is 1.72 ± 0.04 eV. For the krypton solid G is 1.73 eV (Baldini, G., *Phys. Rev.* **128**, 1562 (1962); **137**, 508 (1965)). For the naphthalene doped xenon matrix,(2) G is 1.04 ± 0.04 eV. For the xenon solid, G is 1.08 eV (Steinberger, L. T. and Schnepp, O., *Solid State Comm.* **5**, 417 (1967)).

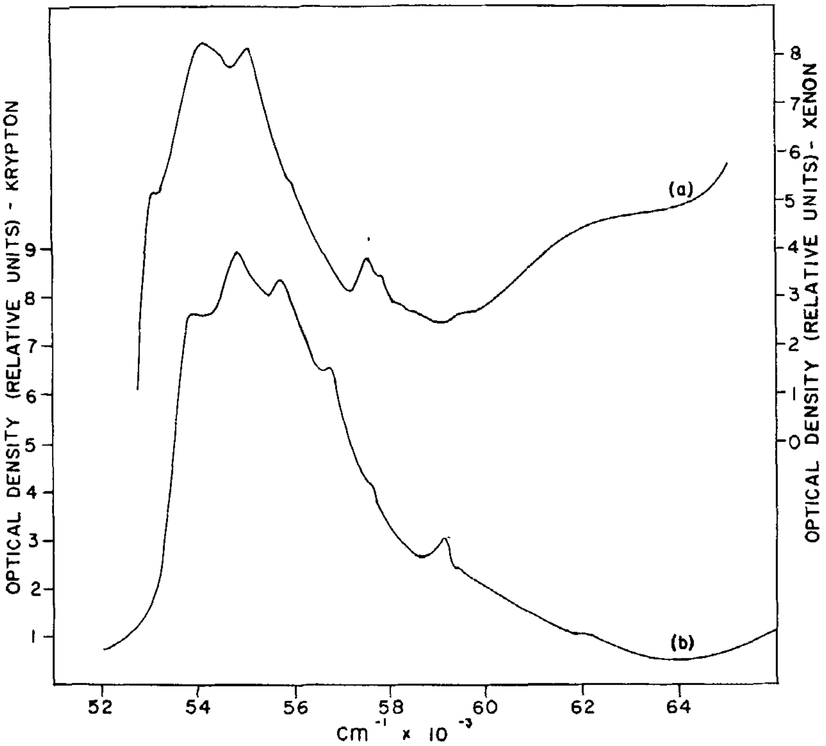

Figure 2. The absorption spectra of benzene doped xenon (Curve *a*) and krypton (Curve *b*) at 20 °K. Deposition temperature 40 ± 5 °K, molar ratio (benzene-rare gas) 1 : 200.

The lines at 57 500 cm^{-1} (Xe) and 59 100 cm^{-1} (Kr) which we suggest arise from the transition to an $n = 2$ impurity Wannier state have line profiles which are strongly temperature dependent. Figure 3 shows the line profile in the benzene-xenon spectrum at 48 ± 2 °K (Curve *a*) and at 20 °K after cooling (Curve *b*). The line width increases from ~ 400 to ~ 500 cm^{-1} on raising the temperature from 20 °K to 48 °K and the absorption maximum shifts to lower energies by 150 ± 60 cm^{-1}. These changes are quite reversible after initial annealing of the film. The line widths are of the same order as those reported for the $n = 2$ impurity Wannier state in naphthalene-rare gas matrices(2) and predicted by Rise and Jortner(3) for large radius impurity states in rare gas solids. The temperature dependence of the line profiles is greater than that observed in π^*–π transi-

TABLE 1 Transition Energies and Suggested Assignments in the Absorption Spectra of Benzene Doped Rare Gas Solids

Xenon matrix (20 °K)	Krypton matrix (20 °K)	Suggested assignments
53200 ± 30	53880 ± 30	$(0\text{–}0)_A\ E_{1u}\ A_{1g}$[a]
54150 ± 30	54800 ± 30	$(0\text{–}0)_A + 920\ (a_{1g}:\ \nu_2)$[b]
	55050 ± 50	" Site splitting "—250 cm^{-1}
55050 ± 30	55750 ± 30	$(0\text{–}0)_A + (920 \times 2)$
	56080 ± 50	" Site splitting "—330 cm^{-1}
55950 ± 30	56700 ± 30	$(0\text{–}0)_A + (920 \times 3)$
	57040 ± 50	" Site splitting "—340 cm^{-1}
56880 ± 30	57600 ± 30	$(0\text{–}0)_A + (920 \times 4)$
57470 ± 30	59130 ± 30	$(0\text{–}0)_B\ n = 2$ " Wannier "
57880 ± 30		$(0\text{–}0)_A + (920 \times 5)$
58200 ± 30		$(0\text{–}0)_B + 606\ (e_{2g}:\ \nu_{18})$[b]
58480 ± 30	60050 ± 100	$(0\text{–}0)_B + 920\ (a_{1g})$
59340 ± 30		$(0\text{–}0)_B + 920 \times 2\ (a_{1g})$

(*a*) This follows the assignment by Katz *et al.*(11)
(*b*) Ref. (12).

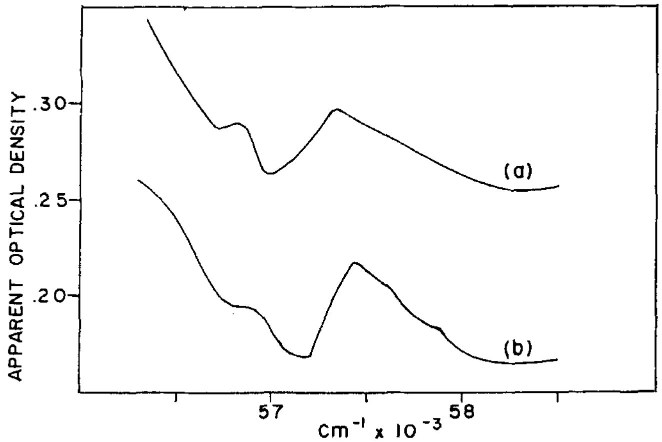

Figure 3. A section of the benzene-xenon absorption spectrum. Deposition temperature 40 ± 5 °K. Molar ratio (benzene-rare gas) 1 : 200. The apparent optical density is uncorrected for optical scattering. (*a*) Spectrum taken at 48 ± 2 °K after annealing at this temperature; (*b*) Spectrum taken at 20 °K after annealing at 40 ± 2 °K.

tions of the benzene molecule in a similar matrix. The electron atom scattering and the dielectric constant, properties which are critical in determining the line profile of large radius impurity states, will both depend upon the temperature of the matrix.

Finally, we note the existence of bands on the high energy side of the 57470 cm^{-1} impurity Wannier state. These bands are probably vibronic bands of the Wannier transition corresponding to a progression in the α_{1g} fundamental (920 cm^{-1}, 2×920 cm^{-1}) and a single e_{2g} mode (606 cm^{-1}). The presence of the latter mode could indicate$^{(1)}$ dynamic Jahn-Teller coupling as in the free molecule Rydberg state.

Acknowledgement

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